

Study on Preparation of Cathode Material of Lithium Iron Phosphate Battery by Self-Cranning Thermal Method

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Abstract: The cathode material of carbon-coated lithium iron phosphate (LiFePO₄/C) lithium-ion battery was synthesized by a self-winding thermal method. The material was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The electrochemical properties of LiFePO₄/C materials were measured by the constant current charge-discharge method and cyclic voltammetry. The results showed that the LiFePO₄/C material prepared by the self-propagating heat method has a typical olivine crystal structure, and the product had fine grains and good electrochemical properties. The optimal sintering temperature is 700 °C, the sintering time is 24 h, the particle size of the lithium iron phosphate material is about 300 nm, and the maximum discharge capacity is 121 mAh/g at 0.1 C rate.

Keywords: Battery; Cathode material; Lithium iron phosphate; Autocratic heat method

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1. Introduction

Lithium iron phosphate is a kind of peridot structure of lithium-ion battery cathode material, because of its excellent safety performance, long cycle life, and low price, especially for overcharge tolerance is very good, is recognized as the best electric vehicle lithium battery cathode material [1,2]. It is widely used as energy supply and storage material for new energy vehicles, smartphones, laptops, and other equipment [3,4]. The synthesis method of lithium iron phosphate is also various, usually using a high-temperature solid phase method, the hydrothermal method, the coprecipitation method, the microwave method, and the emulsion drying method to prepare high-purity and good quality products [5-8]. However, the above synthesis methods have the defects of large amounts of consumables and obvious pellet-like products. Coupled with the poor conductivity and low lithium-ion diffusion coefficient of lithium iron phosphate material itself, researchers have carried out modification studies on it, such as doping ions, carbon coating, nanomaterialization, and so on [2,4,10].

Self-propagating thermal method (also known as the self-propagating combustion method, referred to as self-propagating high-temperature synthesis (SHS)) is to ignite the reactant powder body with an external heat source and uses the heat released by the chemical reaction of the powder itself to maintain the synthesis process ^[11]. The synthesis process has the advantages of low energy consumption, short production cycle, high purity, simple production process, and large powder sintering activity ^[12]. Therefore, the carbon-coated lithium iron phosphate cathode material was prepared by the self-spreading combustion method, and the influence of sintering conditions on its electrochemical properties was studied.

2. Experiment

2.1. Preparation of materials

Using lithium carbonate (LiCO_3) as the lithium source, ferric oxide (Fe_2O_3) as the iron source, and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) as the phosphorus source, according to the molar ratio of 1.05:1:1 weighing a certain amount of raw material, using the addition of glucose is 20% as the carbon source, the composite material was synthesized by the self-propagating heat method ^[5]. The reaction raw material was put into the ball milling tank, and the appropriate amount of absolute ethanol was added as the dispersing agent in the ball milling process. The ball milling speed was 400 r/min, and the ball milling was performed for eight hours. The ground powder was ignited by ignition in an oxygen atmosphere so that it fully reacted and decomposed by self-spreading combustion to obtain combustion products. The combustion product is put into the well furnace in the reactor, and heated to 300 °C under a high-purity nitrogen atmosphere for pre-decomposition. Then two groups of experiments were designed to study the effects of sintering temperature (600 °C, 700 °C, 800 °C roasting for 24 h) and sintering time (700 °C roasting for 16 h, 24 h, 30 h) on the electrochemical properties of the prepared lithium iron phosphate cathode materials.

2.2. Characterization of the material

The crystal structure was analyzed by a fully automatic X-ray diffractometer (XRD) D/max-III A of Rigaku Company. The Cu target $K_{\alpha 1}$, $\lambda = 1.54056 \text{ \AA}$ was used as the radiation source, the tube voltage was 30 kV, the tube current was 30 mA, the scanning rate was 3°/min, and the scanning range was $2\theta = 15^\circ$ to 65° . The microscopic morphology of the samples was confirmed by a field emission electron scanning electron microscope (FESEM).

2.3. Assembly and testing of the battery

2.3.1. Prepare test electrodes and simulated batteries

The corresponding amount of active substances and acetylene black were weighed with an electronic balance according to the mass ratio of 85.0:10.0, and the mixture was evenly mixed and ground for more than 20 minutes until the material was evenly ground, then 5% polytetrafluorethylene emulsion was added, and the mixture was fully stirred into a paste. After drying, placed in stainless steel mesh, plus a certain pressure pressed into a thickness of 0.08 mm to 0.1 mm, weighing 8 mg to 13 mg positive film. Finally, the positive electrode film was dried at 120 °C for 12 h in vacuum. The dried positive membrane was placed on the pole column of the working electrode in the experimental battery and pressed as the working electrode. The negative electrode was lithium metal sheet (99.9%), and a microporous polyethylene membrane (Celgard 2400 diaphragm) was used as the diaphragm of the battery, and a certain amount of 1 mol/L electrolyte [LipF/EC +

DMC (1:1, volume ratio)] was injected into the battery. Finally, the simulated battery for the test was obtained by sealing the simulated battery.

2.3.2. Experimental battery electrical performance test

After assembling the experimental battery, the Xinwei battery tester was used to charge and discharge the test at room temperature, and the charge and discharge potential range was set to 4.2 V to 2.7 V. The composite material was assembled into a simulated battery, and the lithium metal was used as the auxiliary electrode and the reference electrode. The cyclic voltammetry test was carried out with the CHI660B electrochemical workstation produced by Shanghai Chenhua Company. The scanning rate was 0.1 mVs^{-1} , and the scanning potential range was 2.5 V to 4.2 V.

3. Results and discussion

3.1. Effect of sintering conditions on the phase of lithium iron phosphate materials

From the XRD diffraction pattern of LiFePO_4/C with sintering temperatures 600 °C, 700 °C, 800 °C and roasting time 24 h, it can be seen that with the increase of temperature, the peak intensity of each diffraction peak increases, and the peak width gradually narrows, which can show that the increase of temperature is conducive to the growth of crystals in the process of material synthesis. The higher the temperature, the more perfect the growth of crystals, and the larger the crystalline grain will be. Using jade software, compared with the JCPDS card, it can be determined that the main diffraction peaks in the three XRD patterns are lithium iron phosphate, indicating that the main products are lithium iron phosphate. However, in the XRD analysis pattern of lithium iron phosphate prepared at 700 °C, the iron phosphide (Fe_2P) impurity phase appears, which is because at higher temperatures, the phosphate is reduced by carbon to produce a certain amount of Fe_2P impurity.

XRD diffraction patterns of LiFePO_4/C at a sintering temperature of 700 °C and sintering time of 16, 24 and 30 hours respectively. The trend of the curves is roughly the same, the peak shape is sharp, and the main diffraction peak intensity is high, indicating that the formed crystals are relatively perfect and the crystallization ability is strong. Using jade software, compared with the JCPDS card, we can know that the main diffraction peaks are lithium iron phosphate, indicating that the generated products are mainly lithium iron phosphate composite materials. However, if the time is too short, there will be impurities lithium phosphate (Li_3PO_4), and the lithium iron phosphate material sintered for 24 hours has the least impurities. With the growth of sintering time, the Fe_2P impurity phase is more obvious. The origin of Fe_2P is mainly because phosphate is generated by carbon reduction, so the growth of time will lead to more phosphate reduction in the process of synthetic materials ^[2,4].

3.2. Influence of sintering conditions on the morphology of lithium iron phosphate materials

The LiFePO_4/C composites synthesized by sintering for 24 h at 600 °C, 700 °C, and 800 °C were tested by scanning electron microscopy (SEM). The particles of the material prepared at 600 °C ranged from 300 nm to 1 μm , most of the particles were fine, and a small amount of them were connected into blocks, which may be related to insufficient reaction. However, the material prepared at 700 °C had finer particles and a more uniform particle size of about 300 nm. The agglomeration of the material prepared at 800 °C is very serious,

resulting in coarse particles with a particle size greater than 1 μ m. It can be seen that with the increase in calcination temperature, the particle size of the obtained composite will become larger. The increase in particle size will increase the transmission path of Li⁺ ions in the active particles, increasing the impedance of the electrochemical reaction, and the active substances in the center of the particles are difficult to participate in the reaction so that the electrochemical performance of the material becomes worse^[10,14]. Therefore, the particles of LiFePO₄/C composite synthesized at 700 °C are fine and uniform, and its electrochemical performance is also the best.

The LiFePO₄/C materials sintered at 700 °C for 16 h, 24 h and 30 h were tested by scanning electron microscopy (SEM). It was found that the material with a calcination time of 16 h had fine particles, but there were individual agglomerations with insufficient reaction. When the calcination time was extended to 24 h, the particles of the material were fine and evenly distributed. However, if the calcination time continued to extend, the particles of the material appeared serious agglomeration, resulting in larger particles. As mentioned above, the crystallization integrity and particle size of lithium iron phosphate materials are directly related to their electrochemical performance. Therefore, the calcination time for 24 hours of composite material, fine particles, perfect crystallization, and its electrical properties should also be better.

3.3. Effect of sintering conditions on electrochemical properties of lithium iron phosphate

The charge and discharge curve of LiFePO₄/C was obtained by using the constant current charge and discharge method at the charge and discharge rate of 0.1 C and the charge and discharge voltage range of 4.2 V to 2.7 V. LiFePO₄/C charge and discharge tests were prepared at temperatures of 800 °C, 600 °C, and 700 °C for 16 hours, 30 hours, and 24 hours, respectively. The lithium iron phosphate material prepared at 700°C has the largest discharge specific capacity, the smallest charge and discharge platform difference, and the optimal discharge specific capacity and platform rate at the platform. The lithium iron phosphate material prepared at 600 °C is the second, and the lithium iron phosphate material prepared at 800 °C has the worst charging and discharging performance. With the increase in temperature, the charging and discharging properties of the material first become better until a certain point and then become worse. In the XRD analysis, we found that with the increase in temperature, the crystallization property of the material is also gradually improved, the crystal growth is more perfect, and the grain is larger. The larger the particles are, the longer the diffusion path of lithium-ion in the material will be, thus reducing its migration rate, resulting in poor charging and discharging performance of the material prepared at too high a temperature. At the same time, higher temperatures will lead to the generation of more Fe₂P, which is generated by the consumption of electrochemically active substance lithium iron phosphate (LiFePO₄), which will lead to the reduction of the specific charge and discharge capacity of the material. At lower temperatures, the crystallinity is low, and the lithium iron phosphate material does not generate more perfect particles, so its charging and discharging performance is worse than that of the lithium iron phosphate material prepared at 700°C^[15].

At 0.1 C charge/discharge rate, the trend of the three curves is about the same, and the discharge voltage platform tends to be between 3.31 V to 3.39 V. The discharge-specific capacities of 16 h, 30 h, and 24 h sintered lithium iron phosphate composites were 117 mAh/g, 113 mAh/g, and 121 mAh/g, respectively. The discharge-specific capacity of the composite prepared at 24 h has the best electrochemical performance, while the products prepared at 16 h and 30 h have little difference, and the discharge-specific capacity of the lithium iron phosphate prepared at 16 h is higher than that at 30 h. If the temperature is too low, the crystallization ability of

the crystal is poor, the generated grains are not perfect, and the discharge performance of the material is poor. However, too high a temperature will make the grain size in the material too large. Larger grains will lead to lithium-ion migration path longer, resulting in a reduced lithium-ion migration rate, and at higher temperatures, will generate more Fe_2P non-electrochemical active substances, resulting in a reduction in the discharge capacity. Too much Fe_2P may also lead to a decrease in the diffusivity of lithium ions.

The cyclic voltammetry curve of LiFePO_4/C composite prepared at $700\text{ }^\circ\text{C}$ for 24 h shows that the REDOX peak of the lithium-ion cyclic voltammetry test curve of lithium iron phosphate composite prepared at $700\text{ }^\circ\text{C}$ for 24 h is a sharp, symmetrical, smooth and stable potential difference. Therefore, the lithium-ion deintercalation performance of LiFePO_4/C composite prepared under the best conditions is stronger, and the electrochemical performance is better.

4. Conclusion

LiFePO_4/C was prepared with 20% glucose as a carbon source by the self-tensing method under different sintering temperatures and sintering times. The results showed that the sintering temperature and sintering time had a great influence on the properties of lithium iron phosphate. Higher temperatures and longer time will lead to more Fe_2P impurity phase in the final product, and the grain size of the final product will be larger, which will lead to a decrease in the electrical properties of lithium iron phosphate. Lower temperatures and shorter time will lead to imperfect crystal growth, poor crystallization ability, and lower electrical properties of the composite material. The optimal sintering temperature and sintering time are $700\text{ }^\circ\text{C}$ and 24 h, respectively. The maximum discharge capacity of lithium iron phosphate material is 121 mAh/g at 0.1 C rate.

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Disclosure statement

The authors declare no conflict of interest.

References

- [1] Feng Z, Xiao Y, Zou L, 2019, Research Progress on Preparation of Lithium Iron Phosphate. Jiangxi Chemical Industry, 2019(01): 42–46.
- [2] Pan M, Zhou Z, 2012, Electrochemical Performance of LiFePO_4/C Doped with F Synthesized by Carbothermal Reduction Method Using NH_4F as Dopant. Journal of Solid State Electrochemistry, 16(4): 1615–1621.
- [3] Ai Z, Tian J, Wu J, et al., 2024, Research Progress of Lithium Iron Phosphate Cathode Materials for High Temperature Solid Phase Repair. Chinese Journal of Power Technology, 48(1): 9–25.
- [4] Pan M, Zhou Z, 2011, Carbon-rich Grain Surface of LiFePO_4 Enhancing its rate Capability. Material Letter, 65(7): 1131.

- [5] Ni JF, Zhou HH, Chen JT, 2006, Molten Salt Synthesis and Electrochemical Properties of Spherical LiFePO₄ Particles. *J Power Sources*, 2006(159): 307–311.
- [6] Guo J, Jia S, 2020, Synthesis and Properties of Lithium Iron Phosphate by Hydrothermal Method. *Inorganic Chemicals Industry*, 52(06): 36–40.
- [7] Wang H, Chen F, Gong W, 2019, Research on Heat Treatment Process of Preparation of Lithium Iron Phosphate by Co-Precipitation. *Nonferrous Metals (Smelting Part)*, 2019(11): 75–80.
- [8] Park KS, Son JT, Chung HT, et al., 2003, Synthesis of LiFePO₄ by Co-Precipitation and Microwave Heating. *Electrochemistry Communications*, 5(10): 839–842.
- [9] Yang MR, Teng TH, Wu SH, 2006, LiFePO₄/carbon Cathode Materials Prepared by Ultrasonic Spray Pyrolysis. *Journal of Power Sources*, 159(1): 307–311.
- [10] Zhang Y, Zhang R, Xu F, et al., 2019, Surface Structures, Crystal Orientation, and Electrochemical Behavior of Modified LiFePO₄ by Novel Strategies. *Energy Technology*, 7(10): 1900385, 1–8. <https://doi.org/10.1002/ente.201900385>
- [11] Cao C, Zhou T, Li W, et al., 2017, Synthesis of AlN Whiskers by Self-Propagating Combustion and its Growth Mechanism. *Journal of Jiangxi Science and Technology Normal University*, 2017(06): 13–16.
- [12] Li H, Chen X, Zhang P, 2018, Synthesis of LiFePO₄ Nanocathode Material by Self-Spreading Combustion. *Metal Functional Materials*, 25(05): 1–6.
- [13] Zhang R, Xiong Z, Li J, et al., 2019, Preparation and Properties of LiFePO₄/C Cathode Materials by High Temperature Solid Phase Method. *Journal of Guizhou University (Natural Science Edition)*, 36(03): 57–61.
- [14] Li L, Dong G, Li Z, et al., 2019, Effect of Solid-Phase Reaction Conditions on Electrochemical Performance of Lithium Iron Phosphate. *Powder Metallurgy Technology*, 37(05): 332–338.
- [15] Raj H, Rani S, Sil A, 2018, Antisite Defects in Sol-Gel-Synthesized LiFePO₄ at Higher Temperature: Effect on Lithium-Ion Diffusion. *ChemElectroChem*, 5: 3525–3532.

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