The Improved Method to Fabricate Lifepo4 Positive Cathode Materials

Haoying An[1, *, †], Gengze Li[2, a, †]

[1] School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710000.China

[2] Research Institute of Powder Metallurgy, Central South University, Changsha 410023, China

* Corresponding Author Email: 18403224@masu.edu.cn, [a]754523751@qq.com

[†]These authors contributed equally.

Abstract. Lithium iron phosphate ($LiFePO_4$) is a widely used cathode material for lithium-ion battery on account of the well electrochemical performance, environmentally friendly, and wide application prospects. In this paper, we summarize the state-of-art preparation methods of lithium iron phosphate ($LiFePO_4$) cathode materials proposed from the perspectives of improved cold sintering process, microwave sintering and hydrothermal synthesis. On this basis, the advantages of these preparation methods are analysed, and the future research direction and application of lithium iron phosphate cathode materials are discussed. These results shed light on guiding future researches for the sake of improving preparation processes and pave a path for industrialization of these preparation processes.

Keywords: Li-ion batteries; Cathode material; Cold sintering process; Microwave sintering; Hydrothermal synthesis; Lattice parameters; Electrochemical performance.

1. Introduction

Lithium-ion battery possesses plenty of the advantages, e.g., large specific energy, high power density, long cycle life, small self-discharge, high performance and price ratio, and environmental friendliness, and has become the main choice of refundable power supply for portable products [1]. With the wider application and deeper research of batteries, scholars have persuaded more and more high-performance requirements of batteries, and the choice of cathode materials is more and more stringent. In theory, materials with layered structure and spinel structure can be used as cathode materials for lithium-ion batteries. At present, the popular cathode materials are cobalt, iron, nickel, manganese, vanadium oxides, common lithium cobalt oxide, lithium iron phosphate etc. The advantage of these materials is that the transition metal elements contained in them have a mixed valence state, which is difficult to undergo disambiguation reaction, which often have excellent electronic conductivity [2-4].

So far, the industrial synthesis method is a simple solid phase method. Compared with the solid phase method, the liquid phase method product shows better performance, but the more complex synthesis process and higher energy consumption require that there are greater limitations in practice. Therefore, it is necessary to consider simpler synthesis methods to prepare materials with excellent properties. With this in mind, this paper will introduce some improved methods to fabricate LiFePO4 positive cathode materials. The rest part of the paper is organized as follows. The Sec. 2 will discuss the improved solid-phase method. The Sec. 3 will demonstrate the hydrothermal synthesis of lithium iron phosphate. Eventually, a brief summary will be given in Sec. 4.

2. Improved solid-phase method

The high-temperature solid-phase method was the first method used for lithium iron phosphate synthesis, which was first proposed by John Goodenough. The traditional solid phase synthesis method usually uses lithium carbonate, ferrous oxalate, ammonium di-hydrogen phosphate as raw materials, and evenly mixed in a certain proportion of inert gas (e.g., Ar, N_2, etc.) after high temperature roasting to obtain lithium iron phosphate. This method is simple; however, the mixing time is long, the particle size of the product is not easy to control, uneven distribution, irregular shape. Besides, there may be partial sintering phenomena [5], and a large number of organic functional groups are pyrolyzed, leading to the decrease of product benefits and atomic economy [6]. Although the performance of lithium iron phosphate is excellent, it has the defects of low conductivity at room temperature.

In addition, other scholars have prepared a high-capacity binderless $LiFePO_4$ positive electrode using a cold sintering process (CSP) [7]. The CSP can compact the cathode structure, directly formed on the collector, and thus improve the $LiFePO_4$ base cathode volume energy density. This method makes unbonded $LiFePO_4$ positive poles with a density of ~ 2.42 g/cm^3 and can circulate even at a high current rate of 10C. The weight and volume capacity of cold sintering $LiFePO_4$ at 10℃ were ~102mAh/g and 247mAh/cm^3 [7], respectively. This method shows good prospects for industrial applications. The CSP process flow is shown in Fig. 1.

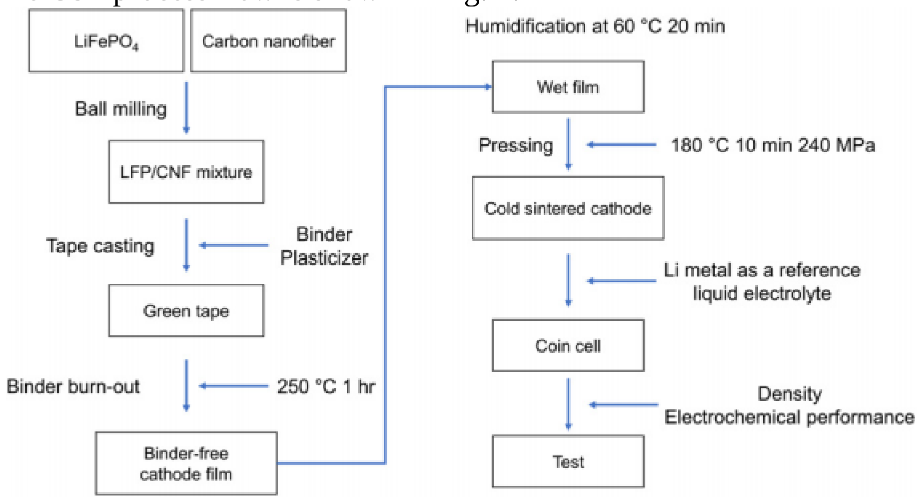

Fig. 1 A schematic diagram of the cold sintering process [7].

Hou et al. combined with microwave drying and microwave sintering process. In this method, the prepared $LiMn_{0.75}Fe_{0.25}PO_4$ precursor was mixed with sucrose solution at a weight ratio of 10:2, the resulting slurry was spray-dried, the spherical $LiMn_{0.75}Fe_{0.25}PO_4$/sucrose composite obtained by secondary granulation was heated to 350℃, and insulated in the N_2 box furnace. Later, the $LiMn_{0.75}Fe_{0.25}PO_4$/C nanoparticles were obtained by microwave sintering treatment. The results are shown in the Fig. 3, and the lattice parameters (a, b, c) of microwave sintering samples are smaller than those compared with those of conventional sintering samples. Transmission electron microscopy (TEM) showed that the microwave sintering sample grain is less than 50nm. Microwave sintering samples also have excellent electrochemical properties after 225 cycles with a discharge capacity of 143.5mAhg^{-1} and a capacity retention rate of 94.3% [8]. It shows that the sintering process has a strong influence on the structure and morphology of the prepared powder, and thus on the electrochemical properties of the product. This study proposes a preparation method combining liquid phase synthesis and traditional technology. According to the analysis, microwave sintering is an economical, energy-saving and time-saving synthesis method for preparing high-performance battery electrode materials, which has wide industrial applications.

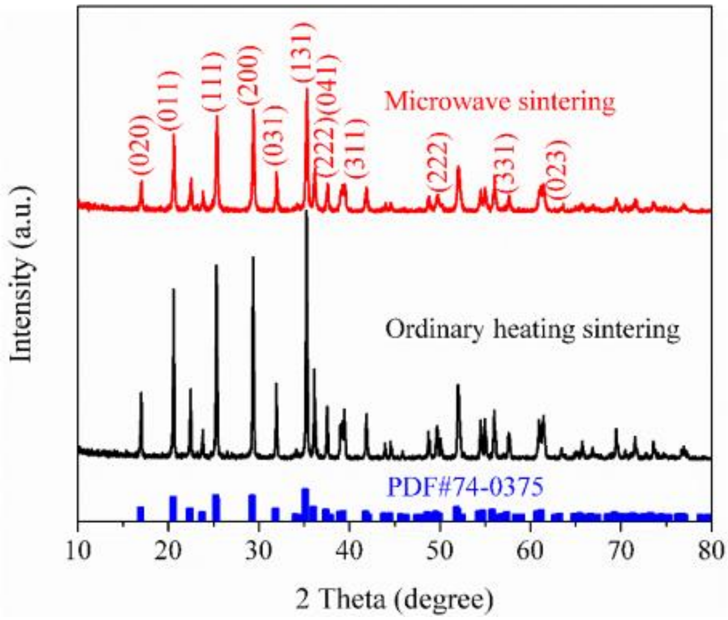

Fig. 2 Loading scene of specimens XRD patterns [8].

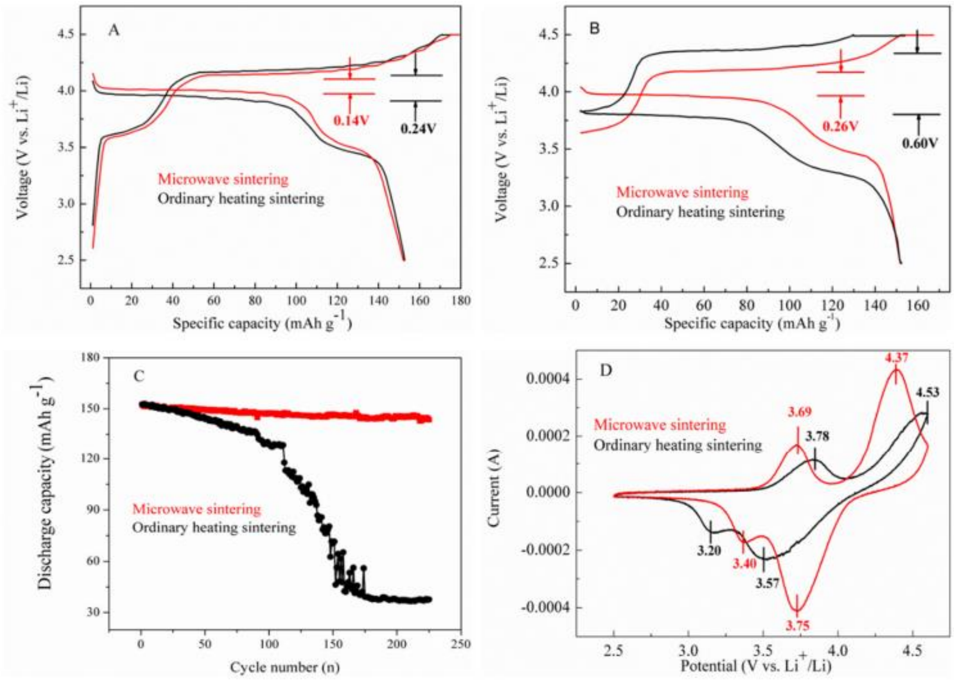

Fig. 3 Electrochemical properties of LiMn0.75Fe0.25PO4/C composites calcined by ordinary heating sintering and microwave sintering [8].

Contemporarily, most manufacturers apply the traditional high-temperature solid phase method for large-scale production of $LiFePO_4$ materials, but this method has issues that need to be further studied and addressed (e.g., high energy consumption, high cost and poor particle uniformity). At the same time, there are many relevant research results are still stay in the laboratory stage, for its industrialization out of the laboratory, popularization still needs further research and popularization. In conclusion, the grading technology is used to homogenize the raw materials, study the size and morphology relationship between the raw materials, precursors and the products to optimize the product performance, and improve the traditional preparation method with new technology may be a hot direction for future research.

3. Hydrothermal synthesis of lithium iron phosphate

Hydrothermal synthesis method is to make usually insoluble or insoluble substances dissolved and recrystallized synthesis of lithium iron phosphate. Specifically, it is based on soluble ferrous salt, lithium salt and phosphoric acid as raw materials, in a closed reactor (autoclave), using aqueous solution as the reaction medium, by heating the reactor, under high temperature and high-pressure conditions. The advantages of this method are that the crystal shape and particle size of the product are easy to control, the phase is uniform, the particle size of the powder is small, and the process is simple. Its disadvantage is: the need for high temperature and high-pressure equipment, industrial production is difficult. Li iron phosphate with average particle size of 3 microns was synthesized by hydrothermal method in a short time (5h) at 120℃. The capacity of the material is 100mAh/g when charging and discharging at the current density of 0.14mA/cm^2 [9].

The preparation process of hydrothermal method: a certain amount of ferrous sulphate, lithium hydroxide and phosphoric acid were weighed according to the molar ratio of 1:3:1. In order to avoid the formation of Fe (OH) and the final oxidation into $Fe(OH)_3$, H_3PO_4 and $FeSO_4{\cdot}7H_2O$ were first mixed, a small amount of distilled water was added, and the dissolved LiOH solution was slowly added into the mixed solution, and the mixture was stirred evenly. Then, the solution was moved to the high-pressure reaction kettle, and the temperature was kept at 220℃ for 1h, and then pumped and filtered. After repeated washing with distilled water, the product was dried at 40℃ for 2h in a vacuum drying oven.

There are two kinds of sources of lithium iron phosphate, one is the nature of lithium iron phosphate ore and the other is synthetic. Regarding to the former approach, the content of lithium iron phosphate is not high, there are many magazines, so its electrochemical performance is very poor. Nowadays, the lithium iron phosphate used is mostly synthesized artificially. There are many methods for the synthesis of lithium iron phosphate, among which the high-temperature solid-phase method is the most commonly used method, but the particle size of the product obtained by the solid-phase method is not uniform, which affects its further use. Hydrothermal synthesis method has attracted more and more attention from researchers for its advantages of low synthesis temperature, flexible and controllable conditions, uniform composition and structure of products, simple equipment and process [10].

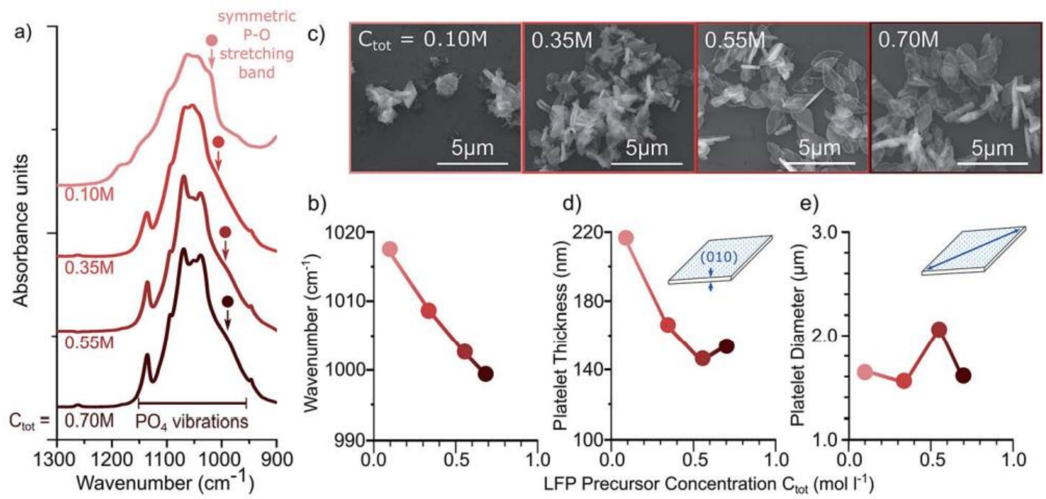

Fig. 4 (a) FTIR spectra (b) peak positions of symmetric P-O stretching bands of samples. (c) SEM images, (d) average particle thickness, (e) average particle diameter [11].

Fig. 4 presents the optimal conditions of lithium iron phosphate the SEM of the sample images. As illustrated in the diagram, the particle size of hydrothermal method is smaller, but there are still uneven distribution of particle size distribution, existing in the preparation of the particles with larger rod-shaped particles and the smaller stars particles, particle size distribution of non-uniform leads to low utilization rate of materials in the process of charging and discharging, Further affect the electrical properties of the material.

Fig. 5 exhibits the polarization curves of LFP samples prepared at different reaction times at C/10 rates. Apparently, a voltage platform can be seen on both the charging curve and the discharge curve, and the voltage platform is between 3.4 and 3.5V. The voltage platform of $LiFePO_4$/C material appears in the charging and discharging process because $LiFePO_4$ and $FePO_4$ two phases appear in the charging and discharging process of $LiFePO_4$. The electrode material of ion battery can really provide stable working voltage for electronic equipment is the voltage level at the voltage platform during discharge.

The ratio of the discharge capacity at the station to the full discharge capacity of the corresponding cycle really reflects the utilization rate of the material. The high platform capacity and utilization rate of the material can provide longer working time for the electronic equipment. As can be seen from Fig. 5, the $LiFePO_4$/C material prepared under the optimal conditions has a high discharge capacity of about 158 mAh/g, and the discharge capacity at the platform accounts for a high proportion of the entire discharge capacity, indicating that the utilization rate of this material is high.

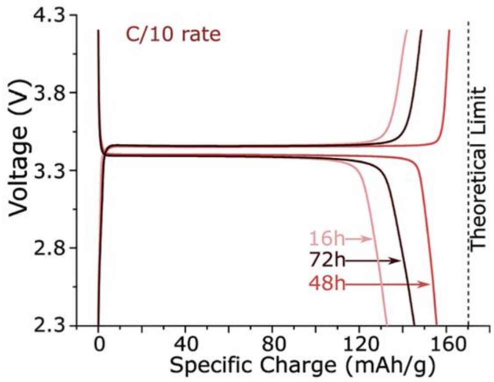

Fig. 5 Polarization curves at C/10 rate of LFP samples prepared with different reaction times [11].

4. Conclusion

In summary, this paper discusses two preparation methods of lithium iron phosphate anode material for lithium-ion battery based on information retrieval and literature analysis. Specifically, improved cold sintering process, microwave sintering and hydrothermal synthesis are detailed demonstrated based on previous research data. In addition, the future prospects of the state-of-art preparation methods are also proposed. Overall, these results offer a guideline for improvement of preparation method of lithium iron phosphate in future.

References

[1] Liu Heng, Sun Hong-gang, Zhou Da-li, Zhang Ping, Yin Guang-fu. (2004). Fine-particle Lithium Iron (II) Phospho-olivine Prepared by A Novel Modified Solid-state Reaction.Journal of Sichuan University: Engineering Science Edition, 36(4), 74-77.

[2] Xu Bin-shi. (2000). Amazing surface engineering (Vol. 11). Tsinghua University Press Co., Ltd.

[3] Berríos, J. A., Teer, D. G., Puchi-Cabrera, E. S. (2001). Fatigue properties of a 316L stainless steel coated with different TiNx deposits. Surface and Coatings Technology, 148(2-3), 179-190.

[4] Padilla, K., Velasquez, A., Berríos, J. A., Cabrera, E. P. (2002). Fatigue behavior of a 4140-steel coated with a NiMoAl deposit applied by HVOF thermal spray. Surface and Coatings Technology, 150(2-3), 151-162.

[5] Li Da-guang, Lai Gui-tang, Li Jun, Li Tie-hu, Huang Hui-min. (2008). Experimental study of LiFePO4 prepared by solid-state method and liquid-state method. New chemical materials, 36(11), 70-71.

[6] Hou Qin, Zhang Jing-sai. (2019). Patent technology analysis of the raw material preparation of lithium iron phosphate by high-temperature solid-phase method. Shanxi chemical industry.

[7] Seo, J. H., Verlinde, K., Guo, J., Heidary, D. S. B., Rajagopalan, R., Mallouk, T. E., Randall, C. A. (2018). Cold sintering approach to fabrication of high-rate performance binderless LiFePO4 cathode with high volumetric capacity. Scripta.

[8] Hou, C., Hou, J., Zhang, H., Ma, Y., He, X., Geng, W., Zhang, Q (2020). Facile synthesis of LiMn0. 75Fe0. 25PO4/C nanocomposite cathode materials of lithium-ion batteries through microwave sintering. Engineered Science, 11(4), 36-43.

[9] Yu Chenjie, Mo Xiangyin, Kang Cairong, Ni Cong Ding Yi (2011). Research progress in preparation and modification of lithium iron phosphate cathode materials for lithium ion batteries.Journal of materials science and engineering (03), 468-470+454. doi: 10.14136/j.cnki.issn1673-2812.2011.03.015.

[10] Yang, S. (2013). Preparation of lithium iron phosphate cathode material for lithium-ion battery by hydrothermal method (Master's thesis, Tianjin University).

[11] Benedek, P., Wenzler, N., Yarema, M., Wood, V. C. (2017). Low temperature hydrothermal synthesis of battery grade lithium iron phosphate. Rsc. Advances, 7(29), 17763-17767.