

Modification strategy of lithium iron phosphate anode materials in lithium-ion batteries

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Abstract. Because of the advantages of lithium-ion batteries, such as high energy density, long cycle life, and stable performance, they can dominate the market of electric cars, renewable energy systems, and even medical equipment. Choosing the suitable electrode material is an essential factor in determining the performance of lithium-ion batteries; this paper takes Lithium iron phosphate (LFP) cathode material as an example. The high safety, high-temperature stability, high theoretical capacity, and long life of LFP cathode material make it a promising cathode material. However, it has many disadvantages, such as low lithium-ion diffusion rate, poor battery life, and low electronic conductivity. This review first discusses its characteristics and shortcomings. Then, this paper describes three methods for preparing LFP cathode materials: the solid-state method, the hydrothermal synthesis method, and the Sol-gel method. Finally, three modification methods, namely nanostructure, element doping and surface coating, are emphasized in order to solve the problems existing in LFP and provide ideas for the development of LIBs.

Keywords: Lithium-ion batteries, cathode materials, LFP, modification method.

1. Introduction

The Earth's petroleum reserves are predicted to run out soon due to their rapid depletion. Furthermore, the need to avoid petroleum resources stems from their detrimental effects on the environment, including the air and water pollution that contributed to the difficulties associated with global warming. The urgent need to replace fossil fuels with alternative energy sources and reduce CO₂ emissions has sparked a great deal of recent academic interest in the development of renewables [1]. Globally speaking, renewable energy sources have a solid theoretical capacity to provide all of humanity's energy needs, and modernizing power storage systems is necessary for the growth of renewable energy, making lithium-ion batteries the best option due to their better performance. The anode and cathode, which are electrically insulated by an electrolyte, comprise the bulk of a lithium-ion battery. Electrons are sent to the external circuit by the anode and received by the cathode from the external circuit. The liquid or solid medium known as the electrolyte forces the electrons to flow through the external circuit by facilitating the movement of Li ions between the anode and cathode.

The performance characteristics of batteries are significantly shaped by the cathode materials used [2]. During the charge-discharge operations, these materials store and release positively charged ions, such as lithium. Many cathode materials, each with unique characteristics, are used in batteries. Generally speaking, the cathode material of a lithium-ion battery is its core, and three primary varieties are the most dominant: layered oxides, spinels, and the newcomer, olivines. This review will focus on the olivine LFP cathode material as it is inexpensive, has a high energy density, is environmentally friendly, and possesses good cycle and thermal stability. Its limited use has been caused by its low Li-ion diffusion coefficient and intrinsic weak electrical conductivity [3]. Due to structural constraints, LFP cathode materials have slower Li-ion and electron kinetics than most conventional cathode materials. LFP has a lower tap density and theoretical capacity than some other typical cathode materials. Therefore, this review discusses the modification methods of LFP cathode materials in LIBs, such as the solid phase method, hydrothermal synthesis method, and gel-sol method, which has a reference for modifying LFP lithium-ion batteries.

2. Characteristics of LFP

As a cathode material in lithium-ion batteries, lithium iron phosphate has been widely used since 1997 [4]. LiFePO_4 has a high theoretical capacity of 170 mAh/g and good safety properties [1]. It has a relatively smooth charge and discharge level station at moderate current and good cycle performance. The voltage of lithium metal is 3.5 volts, and it maintains its thermal stability even at high temperatures. It was demonstrated that two phases coexist when Li^+ is inserted and removed: LiFePO_4 and FePO_4 . For both stages, the space group (Pnma) remains the same. According to Padhi et al., the motion of the two-phase interface is connected to the insertion and extraction of Li^+ . They proposed the shrinkage core model, in which Li ions pass through the phase barrier and enter a particle from its surface. The interface's surface area shrinks during lithiation until it approaches a critical surface area, at which point the rate of Li insertion can no longer sustain the applied current. Therefore, this property makes LiFePO_4 a proper material for low-power applications.

However, due to imperfections in the crystal structure, LFP's magnifying capacity is inadequate [4]. One factor contributing to the poor lithium-ion diffusion rate of LFP is the tetrahedron $[\text{PO}_4]$ located in the LFP structure between the $[\text{LiO}_6]$ octahedron and the $[\text{FeO}_6]$ octahedron. During the charge and discharge process, the insertion and removal of Li^+ are influenced by the volume change of LFP, which is limited by this tetrahedron. However, Figure 1a, which depicts the anticipated crystal structure of LiFePO_4 in that direction, shows the Li^+ diffusion channels in the (010) direction [5]. The $[\text{FeO}_6]$ octahedrons are joined by sharing O corners to create a 2D network in the bc plane, whereas the $[\text{PO}_4]$ tetrahedrons are physically separated (Fig. 1b) to link adjunct $[\text{FeO}_4]$ planes (Fig. 1c). As a result, electron transport into and out of LiFePO_4 requires the $[\text{FeO}_6]$ 2D framework. This characteristic directly contributes to LFP's poor electronic conductivity.

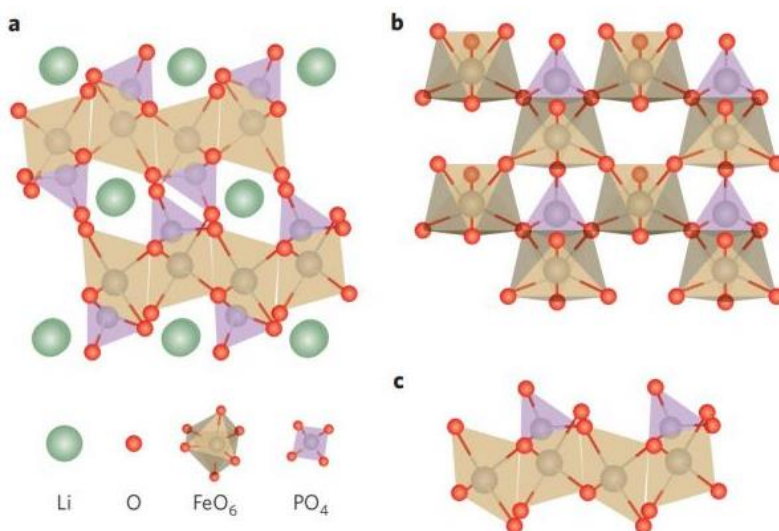


Figure 1 Projection of 3D model on (a) ab plane, (b) ac plane, and (c) theoretical prediction of blocked lithium ion 1D channels by anti-site defects [5]

3. Preparation of LFP

3.1. Solid-state method

Sources of iron include $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$, and $\text{FePO}_4(\text{H}_2\text{O})_2$; sources of phosphorus include $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. Sources of lithium include LiF , Li_2CO_3 , $\text{LiOH} \cdot 2\text{H}_2\text{O}$, and CH_3COOLi . Precursors are often mixed via ball milling or other techniques as the initial stage in the solid-state synthesis of LiFePO_4 powders [6]. Before calcining mixed precursors, they can be pelletized using a one-step heat treatment process. Two heat treatment procedures are usually used to prepare mixes. The first step, pre-calcination, is carried out at 250 and 350 °C to dissolve the precursors and release the gases. The ultimate calcination of the powders, which occurs at

temperatures between 400 and 800 °C, is the second phase. LiFePO₄ can also be made via an altered solid-state technique. LiFePO₄ was created by Ding et al. using deionized water, a combination of Fe₂O₃, NH₄H₂PO₄, LiOH, glucose, and oxalic acid [6]. The mixture produced fluffy powders heated in a crucible covered with carbon for three hours at 700 °C without using an inert gas flow.

3.2. Hydrothermal Synthesis

The benefits of hydrothermal synthesis include cheap cost, low complexity, improved electrochemical performance, and control over shape. Low yield is one of the method's common drawbacks, especially in laboratory settings. Notwithstanding this drawback, hydrothermal processes carried out at lower temperatures provide several advantages, one is the capacity to carefully regulate the size and form of the final LiFePO₄ particles. Lithium dihydrogen phosphate and iron (II) sulfate heptahydrate are dissolved in deionized water to create it [2]. To resist pressure, the solution was moved to an autoclave, and then this container was heated to 150°C for six hours in a vacuum oven. Filtration was used to extract the resultant material after heating. The material was then repeatedly cleaned to get rid of any contaminants. Lastly, the powder was dried for an entire night at 150 °C to remove any leftover solvent. As shown in Fig. 2, the dry powder was calcined at 700°C for 5 hours in an argon environment as the last stage.

Hydrothermal synthesis has several advantages, including low cost, low complexity, enhanced electrochemical performance, and shape control [7]. Low yield is one of the method's main shortcomings, particularly in laboratory settings. Despite this disadvantage, hydrothermal procedures conducted at lower temperatures provide several benefits, including the ability to precisely control the final LiFePO₄ particles' size and shape [2]. It dissolves iron (II) sulfate heptahydrate and lithium dihydrogen phosphate in deionized water. The solution was transferred to an autoclave to withstand pressure, and this container was then heated to 150°C for six hours in a vacuum oven. Filtration was used to extract the resultant material after heating. The material was then repeatedly cleaned to get rid of any contaminants. Lastly, the powder was dried for an entire night at 150 °C to remove any leftover solvent.

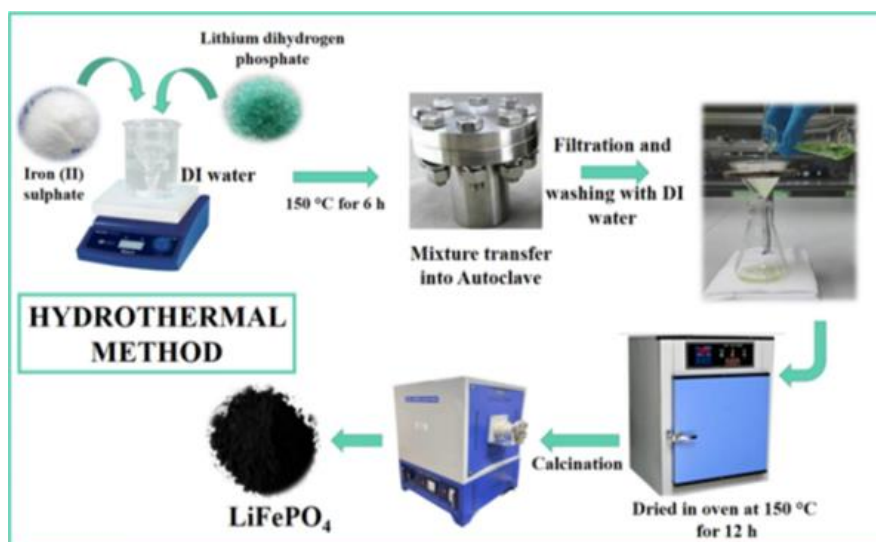


Figure 2. Hydrothermal method to synthesize LFP [2]

3.3. Sol-gel Process

The sol-gel technique, one of the synthesis methods, will be covered in this section. Due to its inherent advantages, sol-gel methods have emerged as one of the best choices for creating LiFePO₄ for lithium-ion batteries. These methods are better at creating exceptional materials because they accurately combine atoms to produce a very pure product with little impurities [2]. Moreover, this technique offers precise control over the size of the particles produced, which is critical for optimizing battery performance. The fact that sol-gel synthesis may accomplish these goals under less demanding

circumstances than other techniques may be its most alluring characteristic [4]. LiFePO_4 was initially produced by combining two precursors: lithium dihydrogen phosphate (LiH_2PO_4) and iron (III) citrate ($\text{C}_6\text{H}_5\text{FeO}_7$). These materials were dissolved in equimolar amounts in water, and then the mixture was heated to $60\text{ }^\circ\text{C}$ for ten minutes on a hotplate with a magnetic stirrer. The mixture was then dried at $70\text{ }^\circ\text{C}$ for a whole day, or twenty-four hours, to produce xerogel, a thick, jelly-like material. Next, as seen in Fig. 3, the xerogel is calcined to yield LiFePO_4 .

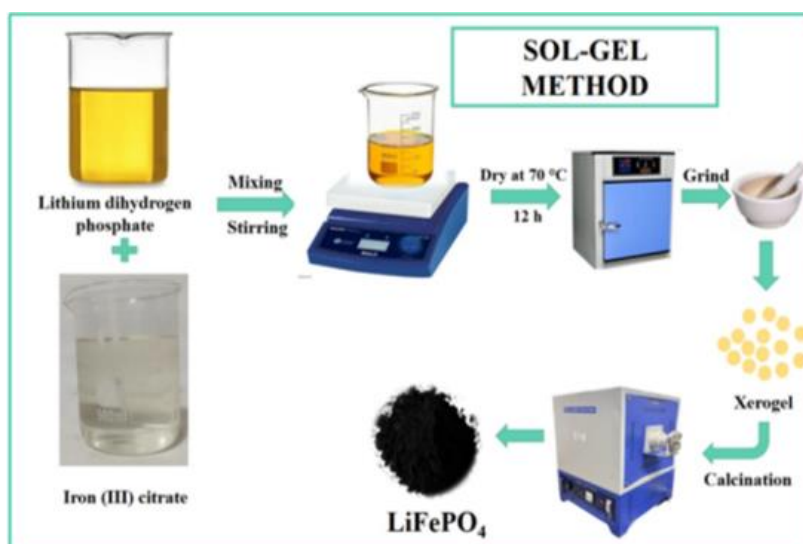


Figure 3. Sol-gel method of LFP synthesis [2]

4. Modification of LFP

4.1. Nanostructure

Enhancing electrical and ionic conductivity can be achieved most effectively by synthesizing nanoscale LFP [4]. According to Andersson et al., the "radial lithium-ion migration model" (radial model) may be deduced as follows: the smaller the particles, the greater the usage rate, and the smaller the irreversible capacity. In the meantime, the tiny particles maintain close touch with one another, minimize the depth of Li^+ insertion and removal, shorten the Li^+ 's diffusion route, and increase the diffusion rate [6]. Because there won't be any noticeable volume fluctuations, the ion embedding and unembedding process helps maintain the material's structure at small scales. Based on previous studies, Gabreski et al. believe that reducing the size of LFP particles is essential to improving the material's discharge capacity. The material's ratio performance improves with decreasing particle size [4]. Meethong et al.'s investigation on nano- LiFePO_4 revealed that when the particle count reaches a certain point, the immiscible zone of the LiFePO_4 two phases will disappear, and the discharge capacity will increase. This is because the immiscible zone contracts with particle size [6].

4.2. Element doping

The investigation conducted by Ding et al. revealed that Mn-composites could improve both ionic and electronic conductivity. This suggests that adding Mn to olivine LFP cathode materials might be a feasible way to increase conductivity and improve battery performance [8]. At a 1C rate, the Mn-doped LiFePO_4 has a discharge capacity of 149 mAh/g; after 500 cycles, this capacity decreases to 139 mAh/g with a 93% retention rate [8]. In contrast, pure LiFePO_4 can only maintain a discharge capacity of 119 mAh/g with an 82% capacity retention after 500 cycles, and it has a discharge capacity of 145 mAh/g at a 1C rate. Additionally, the Mn-doped LiFePO_4 has a more excellent rate capability than pure LiFePO_4 . The Mn-doped LiFePO_4 (Mn-LFP) was prepared via a wet chemical method. First, 10-3 mol/L of manganese acetate and 0.5 g of LiFePO_4 powder were mixed continuously in ethyl alcohol for an hour while the mixture was ultrasonically treated [8]. The solution progressively

evaporated at 60°C while forcefully agitated to get the dry mixture [8]. Ultimately, the Mn superficially doped LiFePO₄ sample was created by a 4-hour argon-simmered process at 500°C. Fig. 4 shows the atomic model of the Mn-olivine LFP olivine structure oriented along the [010] zone axis. Mn gets doped into the LFP surface when some Mn takes up the Fe spot on the surface [6]. A more stable LiMn_xFe_{1-x}PO₄ protective shell might be formed by Mn doping, which would effectively shield LiFePO₄ from electrolyte corrosion during electrochemical cycling [8].

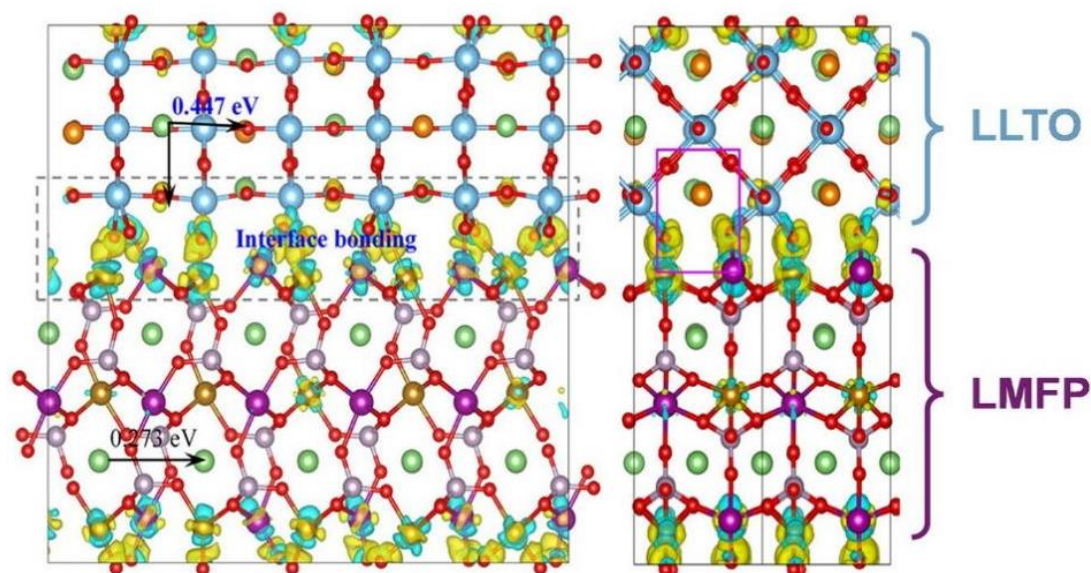


Figure 4. Atomic model for Mn-doped LFP (Mn-LFP) [8]

Because Mg²⁺ doping enhances cycle stability and graphene modification decreases crystallite size and provides active sites for nuclei, Wang et al. verified the improved rate of lithium storage. Whereas the inherent electrical and ionic transport of LFP crystals was improved by magnesium dioxide doping, the magnesium ions in magnesium-doped LFP preferred to occupy the Fe-sites. Sol-gel-assisted CTR syntheses were used to create LiFe_{0.96}Mg_{0.04}PO₄-C, which, according to Örnek and Efe, showed high discharge capacities of 103 and 92 mAh/g at discharge rates of 10 C and 20 C, respectively. Discharge capacity was maintained at over 97% after 300 cycles [3].

4.3. Surface Coating

The novel ZnAl₂O₄-coated LiFePO₄ (ZnAl₂O₄@LFP) electrode was made using the sol-gel technique with polypropylene glycol assistance [9]. Moreover, the ZnAl₂O₄@LFP electrode showed more excellent capabilities for charge and discharge, measuring around 122 and 95 mAh/g, respectively. The coulombic efficiency of ZnAl₂O₄@LFP electrodes showed exceptional stability throughout the following cycles, rising sharply from 80% in the first cycle to 99.8% in the eighth. Moreover, olivine phosphates coated with ZnAl₂O₄ provide more conduction channels for lithium-ion intercalation and de-intercalation. This makes the polypropylene glycol-assisted sol-gel procedure for producing well-dispersed LFP quite simple. During the synthesis process, stoichiometric quantities of LiNO₃ (98.9%), Fe (NH₄)₂(SO₄)₂·6H₂O (99.9%), and (NH₄)₂HPO₄ (98%) are dissolved in 100 milliliters of deionized water to generate a soluble salt solution with a Li: Fe: P molar ratio of around 1:1:1.

The main goal of applying a carbon coating layer is to coat the LFP particles uniformly so that electrons may travel more efficiently, increasing surface conductivity and allowing for high rates of active material utilization [3]. Carbon is the most often used material to cover LFP cathodes due to its low cost, good electrical conductivity, and stability. Moreover, using carbon can enhance ionic conductivity by shortening the Li⁺ diffusion path and functioning as a nucleating agent in the LFP cathode material to prevent the development of LFP grains. Conductive carbon coatings or additions can also function as reducing agents to prevent Fe²⁺ from oxidizing. With a discharge capacity of 160.7 mAh/g and a capacity retention rate of 82.1% after 100 cycles at 0.1 C, LFP/C with 15% carbon

content (LFP/C-15) demonstrated the most significant initial discharge specific capacity as well as the best capacity retention rate. Additionally, the discharge capacity already approaches the expected LiFePO_4 -specific capacity of 170 mAh/g. On the other hand, the electrochemical performance declines when the carbon concentration rises to 20%, suggesting that excess carbon content has the reverse effect of improving material performance [10].

5. Conclusion

LFP, as a cathode material that can dominate the electric vehicles market, certainly has its characteristics and advantages. Compared to ternary lithium batteries, the LFP battery has a much longer service life and reduces the frequency of battery replacement, which lowers the cost of use. It also performs better regarding safety and stability at high temperatures and is less prone to thermal out-of-control and other safety accidents. In addition, the materials utilized are more widely accessible and do not include hazardous heavy metals like nickel or cobalt. This makes LFP batteries more sustainable than other lithium-ion batteries. Why is it a suitable cathode material for lithium-ion batteries? In addition to describing the advantages and problems of LFP lithium-ion batteries, this review also covers the preparation method of LFP cathode materials and three kinds of modification methods, and through these methods to improve the performance of LFP batteries, such as increasing the electronic conductivity and lithium-ion diffusion rate. According to the characteristics of the three preparation methods, including the solid phase synthesis method, hydrothermal synthesis method, and gel-sol method, it can be judged that the solid phase synthesis method is the most commonly used preparation method in the factory because the solid phase method has a relatively simple synthesis process, low raw material cost, and stable product indicators. The other two processes also have their advantages, such as hydrothermal synthesis has a lower reaction temperature and good particle size and shape control, and the gel-sol method has a lower treatment temperature and can accept other elements doping.

Although many modification methods exist for LFP batteries, they also have some limitations. Firstly, nanotechnology costs more and leads to a higher overall self-discharge rate of LFP. Secondly, carbon coating may cause particle accumulation and growth of the modified material, affecting the battery's performance. To solve these challenges, some related technologies should be discovered in the future to optimize the preparation process and reduce the cost and operational difficulty of nanotechnology. Beyond that, though, people must also concentrate on the issues that must be resolved to have a sustainable and green future. What should happen to a lithium-ion battery when its life is over? Finding a method to recycle lithium-ion batteries or their components in the future will thus be essential to strike a balance between environmental preservation and battery performance.

References

- [1] Mohamed N, Allam NK. Recent advances in the design of cathode materials for Li-ion batteries. *RSC Advances*, 2020, 10 (37): 21662 - 21685.
- [2] Kaushik S, Mehta T, Chand P, et al. Recent advancements in cathode materials for high-performance Li-ion batteries: Progress and prospects. *Journal of Energy Storage*, 2024, 97: 112818.
- [3] Ahsan Z, Ding B, Cai Z, et al. Recent progress in capacity enhancement of LiFePO_4 cathode for Li-ion batteries. *Journal of Electrochemical Energy Conversion and Storage*, 2021, 18 (1): 010801.
- [4] Wang X, Feng Z, Zhang H, et al. Research process in rate performance of LiFePO_4 cathode materials. 2017.
- [5] Lu J, Chen Z, Ma Z, et al. The role of nanotechnology in the development of battery materials for electric vehicles. *Nature Nanotechnology*, 2016, 11 (12): 1031 - 1038.
- [6] Satyavani T, Kumar A, Rao PS. Methods of synthesis and performance improvement of lithium iron phosphate for high-rate Li-ion batteries: a review. *Engineering Science and Technology, an International Journal*, 2016, 19 (1): 178 - 188.

- [7] Qin X, Wang X, et al. Mechanism for hydrothermal synthesis of LiFePO_4 platelets as cathode material for lithium-ion batteries. *The Journal of Physical Chemistry C*, 2010, 114 (39): 16806 - 16812.
- [8] Jiang F, Qu K, Wang M, et al. atomic scale insight into the fundamental mechanism of Mn-doped LiFePO_4 . *Sustainable Energy & Fuels*, 2020, 4 (6): 2741 - 2751.
- [9] Moustafa MG, Sanad MM. Green fabrication of ZnAl_2O_4 -coated LiFePO_4 nanoparticles for enhanced electrochemical performance in Li-ion batteries. *Journal of Alloys and Compounds*, 2020, 903: 163910.
- [10] Liu X, Zhao R, Xia Y, et al. Improved electrochemical performance of LiFePO_4 /carbon cathode for lithium-ion batteries. *Ionics*, 2022, 28: 4579 - 4585.