A Comprehensive Study on the Performance Enhancement of Lithium Iron Phosphate Cathode Materials in Lithium-Ion Batteries: From Coating, Doping to Morphology Regulation

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Abstract. Under the backdrop of the accelerating transformation of the global energy structure and the deepening of the "carbon neutrality" goal, building an efficient, safe and sustainable large-scale electrochemical energy storage system has become a key direction that urgently needs to be broken through in the energy field. As well as, Lithium-ion batteries have stood out among numerous energy storage technologies due to their extremely high energy density, long cycle life, and excellent safety performance. As an important component of lithium-ion batteries, cathode materials have received extensive attention, among which lithium iron phosphate cathode material has been widely applied due to its outstanding safety performance and long cycle life. This research focuses on lithium iron phosphate cathode materials and analyzes three modification methods, namely surface coating, bulk doping, and morphology and structure regulation, to address the current limitations of poor conductivity and slow ion movement of lithium iron phosphate cathode materials.

1 Introduction

By the accelerated advancement of the global energy structure transformation and the proposal of the "carbon neutrality" goal, efficient, safe and sustainable large-scale electrochemical energy storage technologies have increasingly drawn attention. Lithium-ion batteries, with their advantages of high energy density, long cycle life and good safety, have become an important direction for current electrochemical energy storage technology routes and future development.

As a key component of lithium-ion batteries, the cathode material directly determines the energy density, safety, cost and cycle life of the battery. Among the numerous cathode materials, lithium iron phosphate (LiFePO4) stands out for its excellent safety performance, long cycle life, low cost and environmental friendliness, and has been widely used in the field of electric vehicles. However, LiFePO4 cathode materials still have some shortcomings, such as low electrical conductivity. In recent years, research has mainly focused on improving the electrical conductivity of LiFePO4 materials, with the most effective methods being carbon

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coating and metal ion doping. LiFePO4 has also become the preferred cathode material for medium-range electric vehicles and stationary energy storage systems. For instance, Zhang Wenwen and Liu Yanzhao have discussed the technical characteristics of new solid-state lithium batteries, the compatibility with existing electric vehicle systems, the current application bottlenecks and their optimization strategies. They have also proposed feasible development paths from the perspectives of material innovation and system integration, aiming to provide useful references for the optimization of solid-state lithium batteries in electric vehicles [1]. This study focuses on LiFePO4 cathode materials and aims to address the issues of poor electrical conductivity and slow ion movement by using three modification methods. The goal is to identify high-rate, long-life LiFePO4 materials and future development routes, to enhance their performance in power batteries and reduce production costs [2].

2 Overview of lithium iron phosphate

2.1 Crystal strcture

Lithium iron phosphate has high safety, long cycle life, abundant raw materials and low cost, and is the mainstream cathode material for power batteries. However, it has problems such as low electronic conductivity and lithium ion diffusion rate, and limited high-rate performance. Lithium iron phosphate (LiFePO4) has a typical olivine structure and belongs to the orthorhombic crystal system, with space groups of Pnma or Pmnb [3]. Lithium iron phosphate is a new type of cathode material for lithium-ion batteries developed in recent years [4]. Its structure is an olivine structure, with the Pmnb space group, and the unit lattice constants are a=6.008 Å, b=10.334 Å, c=4.693 Å, the volume of the unit cell is 291.43 Å. This structure endows the material with excellent thermal stability and safety, and helps achieve long cycle life; however, its intrinsic electronic conductivity and lithium ion diffusion coefficient are relatively low, and in practical applications, they often need to be enhanced through carbon coating, ion doping and other methods.

2.2 Reaction mechanism

The core electrochemical reaction of lithium iron phosphate is a two-phase topological transformation mechanism, which occurs during charging and discharging as an immediate conversion between the insulating LiFePO4 phase and the FePO4 phase, rather than a continuous change in the solid solution type. This mechanism endows the material with advantages such as stable voltage platforms, high cycle stability, and good safety. However, it also limits its electronic conductivity and ionic migration ability. Therefore, it is usually necessary to employ strategies such as carbon coating, nanosizing, and ion doping for collaborative modification to enhance its practical performance.

2.3 Electrochemical process

The electrochemical process of lithium iron phosphate is characterized by a typical two-phase reaction. As shown in Fig. 1, a reversible phase transition occurs between the LiFePO4 (rich lithium phase) and FePO4 (poor lithium phase), accompanied by the intercalation and deintercalation of lithium ions and the change in the oxidation state of iron ions (Fe^{2+}/Fe^{3+} redox) [5].

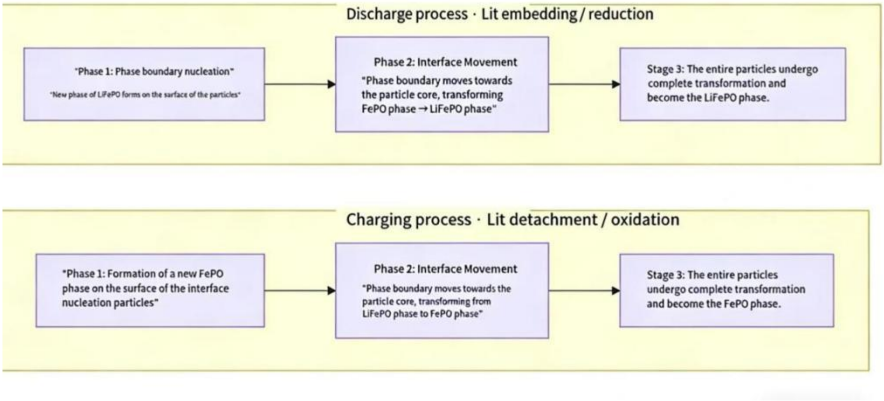

Fig. 1. Electrochemical two-phase reaction flowchart.

3 Method for modifying lithium iron phosphate

To address the issues of low intrinsic electrical conductivity and slow ion diffusion of lithium iron phosphate, systematic modifications were carried out from three aspects: surface coating, interphase doping, and morphological structure regulation, in order to synergistically enhance its electrochemical performance.

3.1 Surface coating

Surface coating is currently the most fundamental and crucial modification method. The coating methods can be classified as carbon coating, metal oxide coating, and conductive polymer coating. Carbon coating is the most mainstream and effective method. It involves adding organic carbon sources (such as glucose, sucrose, and asphalt) during the synthesis process or post-treatment, and then carbonizing at high temperatures to form an amorphous carbon layer on the surface of the particles. This method can effectively construct a conductive network and significantly reduce battery polarization. At the same time, it can improve the dispersion of the particles. It also prevents the oxidation of divalent iron ions during the high-temperature synthesis process. For example, Zhang Ning and Liu Yongchang et al. conducted research on carbon coating. They first selected appropriate carbon coating methods, such as in-situ carbon coating, non-in-situ carbon coating, sol-gel method, microwave-assisted solvent heat method, etc. Then, based on the selected method, they prepared LiFePO4/C composite materials. This step may include the selection of raw materials, the setting of reaction conditions (such as temperature, time, etc.), and the selection of carbon sources. Using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) methods, the structure and morphology of the prepared materials were characterized to understand the uniformity and thickness of the carbon coating layer. Through charge-discharge tests, cyclic voltammetry (CV), and alternating current impedance spectroscopy (EIS) methods, the electrochemical performance of the samples was evaluated, such as capacity, rate performance, and cycle stability. Based on the test results, the influence of carbon coating on the electrochemical performance of LiFePO4 was analyzed, and the influence mechanism of different carbon coating methods and carbon source types on the performance was discussed [6]. Their research focused on improving the electrochemical performance of LiFePO4 through different carbon coating methods, especially enhancing its conductivity and rate performance. By adjusting the carbon source type and carbon coating amount, the surface properties of LiFePO4 were optimized, thereby improving its overall electrochemical performance. According to their research results, carbon coating can significantly enhance the conductivity of LiFePO4, reduce the charge transfer impedance, and thereby improve its rate performance and cycle stability. Different carbon coating methods and carbon have varying degrees of influence on the electrochemical performance of LiFePO4. Among them, the in-situ carbon coating method is considered one of the most effective coating methods. However, an increase in the carbon coating amount may reduce the compactness and volumetric energy density of the electrode material. In summary, carbon coating technology shows great potential in improving the electrochemical performance of LiFePO4, but it also has some limitations that need to be further optimized [7].

3.2 Phase-diffusion doping

Phase-doping regulates the electronic structure and crystal environment of $LiFePO_4$ by introducing trace hetero-atoms into its lattice. It mainly includes two types: cation doping and anion doping. Cation doping usually involves the introduction of high-valent metal ions at the Li, Fe, or both positions; anion doping mainly occurs at the oxygen positions. Doping can effectively stabilize the crystal structure, broaden the lithium-ion transmission channels, and thereby enhance the ionic conductivity and structural stability of the material. From crystallographic knowledge, cations must stably exist in the octahedral gaps of anions, and their ionic radius must be large enough to prevent the anions from contacting each other. The ionic radius of O^{2-} is 140 pm, and for O^{2-} to occupy the octahedral gaps, the ionic radius of the cation must be greater than 58 pm; when 0.414 > r+/r > 0.225, cations can possibly occupy the tetrahedral gaps of anions, with the ionic radius of V5+ being 59.0 pm and that of Ce^{4+} being 92.0 pm, both greater than 58 pm. Therefore, V5+ and Ce^{4+} can enter the octahedral gaps to replace the Li or Fe positions. Thus, the relevant researchers chose V^{5+} and Ce^{4+} as doping ions and doped $LiFePO_4$ at the Fe and Li positions. Doping with Ce^{4+} increased the conductivity of $LiFePO_4$ by approximately 5 orders of magnitude; doping with V^{5+} increased the conductivity by 3 orders of magnitude. However, when the doping amount is excessive, impurity phases will appear in the product, resulting in a decrease in the electronic conductivity of the material [8]. Additionally, high-valent Sn^{4+} ions can also be introduced to systematically study the effects of different doping amounts (0-7 mol.%) on the physical, chemical, and electrochemical properties of nano-crystalline LiFePO4/C composite positive electrode materials, investigate the charge compensation mechanism of high-valent Sn4+ doping, and conclude that Sn doping belongs to mixed valence doping. Based on the differences in particle size and doping concentration, each sample exhibited different degrees of pseudocapacitive effect. Research shows that when the doping amount is 3 mol.%, the material has the best electrochemical performance, with a discharge specific capacity of 128 mAh/g at 10 C [9]. This doping can effectively improve the conductivity under strict control of the dosage, but further optimization is needed to reduce production costs to promote the practical application of this method.

3.3 Shape and structure regulationThe changes in modification methods

The core role of morphology and structure regulation lies in optimizing the lithium-ion transport path and reaction kinetics. This can be achieved by nanocrystallizing the materials and shortening the solid-state diffusion distance of lithium ions. The internal conductivity of LFP particles is related to the size and morphology of LFP particles. The electrochemical performance of nanized LFP will be significantly improved. The main reason is that the reduction in particle size shortens the transmission distance of Li+ and enhances the diffusion rate of Li+. Logan et al studied the influence of LFP particle size and specific surface area on the electrochemical performance of LFP/C materials [10]. The results showed that the LFP with the smallest particles had the highest capacity retention rate at high temperatures. Moreover, adding surface-active agents to control the morphology also affects the electrochemical performance of LFP.

4 Future expectations

4.1 The changes in modification methods

Current research on lithium iron phosphate has shifted from a single modification method to the simultaneous use of multiple strategies. In the future, it may combine carbon coating, ion doping, and shortening the ion transmission path to enhance the rate performance and cycle stability of the material. As research progresses, the optimization of material performance is shifting from the macroscopic scale to the microscopic structure. In the future, more attention will be paid to the precise control of microscopic features such as crystal plane orientation and pore structure. By reducing particle size to shorten the diffusion distance of lithium ions; by controlling the morphology to optimize the ion transmission path. In addition, the thickness and uniformity of the carbon coating layer will also be more precisely controlled, to improve conductivity while minimizing negative impacts, achieving a balance between conductivity and energy density. This multi-strategy collaborative approach will become the mainstream direction for breaking through the performance bottleneck of lithium iron phosphate.

4.2 Performance improvement in extreme scenarios

Although lithium iron phosphate is currently the mainstream cathode material in the lithium-ion battery field, its own performance still has significant shortcomings under extreme complex conditions such as low-temperature environments. In low-temperature conditions, the diffusion range of lithium ions in the lithium iron phosphate material significantly decreases, and electrode polarization significantly intensifies, resulting in rapid capacity degradation, low charging and discharging efficiency, and in high-altitude areas, it is prone to problems such as reduced range and charging difficulties. To address the performance deficiencies under such extreme conditions, future research and modification of lithium iron phosphate materials will focus on doping modification, introducing appropriate metal ions or non-metal ions to regulate the material's crystal lattice, optimizing the diffusion path of lithium ions, and fundamentally enhancing the ionic conductivity of the material in low-temperature environments, improving the low-temperature charging and discharging performance, and ensuring the capacity performance and cycle stability in low-temperature conditions. Through the above technical optimization and innovation, the performance shortcomings of lithium iron phosphate in extreme conditions can be filled, significantly expanding its application boundaries, promoting its stable performance in special scenarios such as new energy electric vehicles in high-altitude areas and energy storage power stations in extremely cold environments, further consolidating its mainstream position in the field of new energy storage and battery power, and facilitating the development of the new energy industry.

4.3 Cost control and green manufacturing

In the face of the global energy transformation wave under the "dual carbon" goal, the value of lithium iron phosphate materials lies not only in their high performance, but also in their potential to build a green closed-loop throughout the entire life cycle. In the future development, green manufacturing must be elevated to the strategic core. From three dimensions of source reduction, process control of consumption, and end-of-life recycling, a sustainable industrial system with low energy consumption, low emissions, and high recycling should be created, making it truly become the "green cornerstone" of green energy.

At the production source, we must completely abandon the traditional high-energy consumption and high-pollution approaches and fully develop low-carbon synthesis technologies. In the future, we should focus on researching and developing low-temperature solid-phase sintering and continuous production processes driven by clean energy, and utilize green electricity such as solar and wind power to replace fossil energy, significantly reducing the carbon footprint in the production process. At the same time, we should strengthen the construction of a green raw material system, explore the use of low-carbon raw materials such as industrial by-products of phosphorus and recycled iron sources as alternative supplies, reducing reliance on primary mineral resources, and maximizing resource utilization efficiency and minimizing environmental impact from the raw material end.

In the manufacturing process, the key lies in promoting refined and intelligent clean production. Through the digital twin system, production parameters are optimized, and the reaction temperature and time are precisely controlled to achieve the ultimate reduction of unit energy consumption. The promotion of waste-free process design is carried out, and the mother liquor and solvents in the production process are recycled in a closed loop, preventing direct discharge of wastewater and waste gas. An internal micro-circulation of "resources - products - recycled resources" is established to ensure that every production link complies with the strict standards of ecological and environmental protection.

At the industrial end, establishing a complete battery recycling and secondary utilization system is the key closed loop of green manufacturing. With the large-scale entry of power batteries into the retirement period, it is necessary to accelerate the development of efficient recovery technologies such as wet metallurgy and high-temperature metallurgy to achieve high-purity and high-value regeneration of lithium iron phosphate cathode materials and copper-aluminum current collectors, and reduce the demand for new resource extraction. At the same time, promoting secondary utilization technologies, using retired batteries for energy storage, backup power supply, etc., which have lower requirements for energy density, can extend the service life and create secondary value.

Through the comprehensive green transformation of the entire chain, the lithium iron phosphate industry will not only achieve continuous economic growth, but also achieve a positive cycle of environmental benefits. It will truly become a benchmark for high-quality development in the new energy field.

5 Conclusion

Lithium iron phosphate has become a key cathode material for power batteries and energy storage systems due to its stable olivine structure, flat working voltage, and excellent safety and cycle performance. Although the technical system is relatively mature, there is still room for continuous improvement in terms of higher energy density, faster charging and discharging rates, wider operating temperature range, and longer service life for extreme application requirements. Overall, the research on lithium iron phosphate is moving from macroscopic modification to a new stage of microstructure design and intelligent regulation. Through interdisciplinary integration and technological innovation, this material is expected to continue to play an important role in the energy storage system in the future, being safe, reliable, and economically viable.

References

1. W. Zhang, Y. Liu, Application research of new solid-state lithium batteries in electric vehicles. Automobile Electrical Parts **11**, 18-20 (2025).
2. D. Sun, J. Cui, X. Wang, T. Wang, N. An, H. Song, H. Jin, Research progress of lithium iron phosphate in lithium-ion batteries. Chinese Journal of Engineering **47**, 1055-1066 (2025).
3. Y. Zhang, Hydrothermal synthesis and modification study of lithium iron phosphate cathode material for lithium-ion batteries. Master Thesis, Hunan University (2012).
4. M. Tan, Electrochemical and thermal characteristics study of lithium iron phosphate battery during charge-discharge process. Master Thesis, South China University of Technology (2020).
5. C. Wang, W. Wu, J. Wang, H. Liu, J. Xu, L. Guo, Z. Peng, Application of advanced characterization techniques for lithium iron phosphate: Paving the way for an in-depth understanding of operation and fading mechanisms. The Journal of Physical Chemistry C **128**, 21627-21648 (2024).
6. Z. Yang, Y. Dai, S. Wang, J. Yu, How to make lithium iron phosphate better: a review exploring classical modification approaches in-depth and proposing future optimization methods. J. Mater. Chem. A **4**, 18210-18222 (2016).
7. N. Zhang, Y. Liu, C. Chen, et al., Research progress on carbon coating of lithium iron phosphate surface. Journal of Electrochemistry **21**, 201-210 (2015).
8. Q. Yi, Study on preparation of $LiFePO_4$ /C cathode material by melting method and doping modification. Master Thesis, Chengdu University of Technology (2012).
9. J. Ma, Preparation of nanostructured lithium iron phosphate cathode material and its doping and surface modification. Doctoral Thesis, Tsinghua University (2010).
10. E.R. Logan, A. Eldesoky, Y. Liu, et al., The effect of $LiFePO_4$ particle size and surface area on the performance of $LiFePO_4$ /graphite cells. J. Electrochem. Soc., **169**, 050524 (2022).