Research Progress of Lithium Iron Phosphate in the Cathode of Lithium-Ion Battery

Zihan Xia

St Catherine's School Bramley, Guildford, United Kingdom

Z-Xia18ST@stcatherines.info

Abstract. Lithium-ion batteries (LIBs) have been a new candidate for various industries. Unlike other types of lead-acid batteries, LIBs have a very high energy density, power density, and nominal voltage, making them a beneficial choice of battery for many electronic devices like electric vehicles. The role of cathode material in the battery is to start the electrochemical reaction, and the rate capacity is highly dependent on the ion-diffusion rate at the cathode. This makes the cathode the most critical component in the battery. Therefore, it is essential to have excellent cathode material to perform its function. Lithium iron phosphate has always been a desirable cathode material due to its stable structure, high safety, and low cost. By choosing the appropriate material, high capacity and performance can be achieved. By modifying the material through different strategies, LFP has the potential to exceed its theoretical capacity and be applied in the broader field of the electronics industry. First, this article focuses on a comparison of different cathode materials and explains why LFP is superior. Then, it will introduce the synthesis methods, including solid-state, hydrothermal, and sol-gel methods. Finally, it will discuss ways to modify LFP, including nanostructured LFP, carbon coating, and doping. This paper aims to serve as a guide and reference for research in the battery industry.

Keywords: Lithium iron phosphate, cathode, lithium-ion battery, synthesis.

1. Introduction

As human society advances, energy demand constantly rises, dramatically pushing modern technologies forward. Examples include smartphones, portable electronic devices, artificial intelligence, and electric vehicles. These inventions all require the exploitation of energy. Energy has been derived from various sources, and the most chosen ones are non-renewable, such as burning fossil fuels. The main issue associated with this is global warming. Based on the annual report from NOAA's Global Monitoring Lab, the increase in global mean surface concentration of CO_2 in 2023 was 2.8 ppm, one of the many years that the rise in atmospheric CO_2 level exceeded 2 ppm during the 65-year tracking record [1]. This has encouraged many industries, such as the automotive industry, to search for and work on potential alternatives to internal combustion engines like electric vehicles. In the context of electronic devices, batteries play a universally important role. Among many batteries, the most promising candidate is undoubtedly LIBs. It has a very high energy density, promoting the performance of many electronic devices in everyday life. Lithium is a very reactive metal but highly stable in its oxide form. When a lithium atom is separated from its oxide, it will spontaneously form a lithium-ion and an electron due to the unstable nature of lithium atoms when they are detached from the oxide. If the ion and the electron are placed beside the lithium oxide, they would flow into the oxide structure and combine again to form part. This induces a flow of current, which provides electricity, which is the fundamental principle behind the battery. Lithium-ion batteries are mainly composed of an anode, a cathode, a separator, an electrolyte, and two current collectors, which are oppositely charged. The working process that is taking place inside the battery is simple. When a power source is connected, the electrons are attracted to the anode from the lithium oxide by flowing through the wire that is connected to the external circuit and deposit in the graphitic anode; the Li ions drift through the electrolyte and deposit into the space between the layers in graphite. This charges the battery, and the system is in an unstable situation. When a load is added in place of the power supply, the lithium ions then move back to the cathode through the electrolyte and convert back into the oxide form. The electrons go back to the cathode through the wire, which powers up the

load due to the flow of current through it [2, 3]. Therefore, it can be deduced that the choice of the cathode material is vitally important because it facilitates the functioning of the battery; it not only controls the rate of diffusion of lithium-ions but also determines the material's conductivity, which decides how well the battery functions. Among the traditionally used materials for cathodes of LIBs, LFP shows very advantageous performance due to its inexpensive nature and superior rate performance compared with other materials like lithium nickel manganese cobalt oxide (NMC) and lithium manganese oxide (LMO). Therefore, this paper will mainly focus on the application of LFP in the cathode of lithium-ion batteries, and it serves as a reference for relevant industries and research in the field of automation and batteries.

2. The characteristics of LFP

Traditionally, the material that makes up the cathode includes different types of metal oxides like NMC, LMO, and LFP. Each material has a unique energy density and structural stability, producing distinctive cathode performance. Table 1 demonstrates the theoretical specific capacity, the range of particular energies in the experimental and commercialized cells, and the attributes of different cathode materials, including NMC, LMO, and LFP. It is evident from the table that the greater the specific capacity, the higher the cost because of the type of precious metal being applied; this can sometimes weaken the rate performance and introduce cycling problems like short service life. As a result, nanotechnology has become a potential solution to these issues.

Table 1. Theoretical specific capacity, range of particular energies in the experimental and commercialized cell, attributes of NMC, LMO, and LFP cathodes

Cathode Material	Theoretical Capacity ($mAhg^{-1}$)	Capacity ($mAhg^{-1}$)	Voltage (V)	Advantage	Limitation
NMC	275	147~200	3.0~4.2	High capacity, high structural stability	Weak rate performance, high cost, cycling issue
LMO	148	90~135	4.0	Low cost, abundant, high energy, density	Cycling issue, weak rate performance
LFP	170	116~162	3.2~3.65	Low cost, low toxicity, high-rate performance	Low electronic conductivity at room temperature, low, poor electrochemical performance at low-temperature levels

LFP has a crystal structure that is olivine in shape, as shown in Figure 1 [3]. Each iron atom is covalently bonded to six oxygen atoms, which form an octahedron, with the Fe ion being the central metal ion. The PO_4 forms a tetrahedron, in which each phosphorous atom is bonded to four oxygen atoms. Lithium ions sit in the structure along the four edges parallel to the 010 direction, and they are constrained by the phosphate tetrahedra, meaning that they can only migrate in a single direction in the structure. Therefore, unlike other cathode materials such as the ones with layered structure material and spinel structured material like $LiMn_2O_4$, which have two-dimensional and three-dimensional lithium-ion diffusion pathways, LFP only has one-dimensional diffusion, making the process insufficient and vulnerable to defects [2]. During charging processes, lithium ions are removed with the oxidation of Fe: $LiFePO_4 \rightarrow FePO_4 + Li^+ + e^-$, the electrons released travel to the anode through the external wire, and the lithium ions de-intercalate from the cathode concurrently and move toward the anode as well through the electrolyte to complete the circuit. Regarding the benefits of utilizing LFP, it has low toxicity, high stability, and good electrochemical performances, and it is also economically viable. However, at room temperature, it exhibits low electronic

conductivity. This is because the FeO_6 octahedra in the structure are spatially disconnected by the PO_4 tetrahedra, interrupting the electron conduction by continuous FeO_6 frameworks [4]. This leads to poor electronic conductivity from a structural perspective.

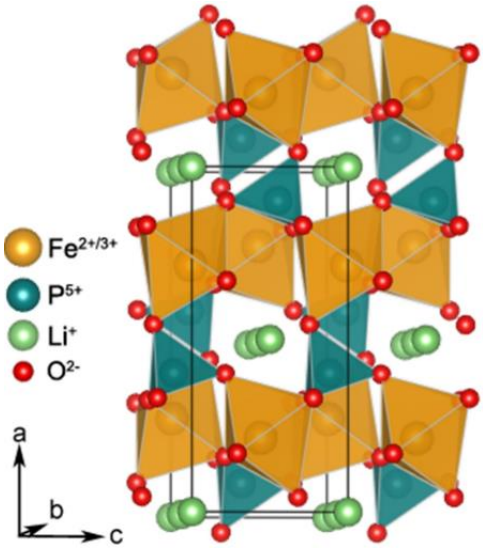

Figure 1. The crystal structure of olivine $LiFePO_4$ [3]

3. Preparation of LFP

3.1. Solid-state Synthesis Method

Traditionally, LFP is manufactured through the solid-state synthesis route. Generally, this approach is also referred to as a calcination process, which requires iron salt, lithium compound, and a source of phosphate source as precursors to be mixed in a particular proportion (since phosphorus is quickly released as NH_3 at high temperatures, phosphorus nitrogen compounds are recommended as phosphorus sources). The choice of the precursors significantly impacts the electrochemical properties of the LFP produced. The materials are then submitted to various heating stages with temperatures ranging from 400°C to 800°C, and the time taken for the calcination process is often between 10 to 24h [5]. To prevent Fe^{2+} from oxidizing, conventional solid-state synthesis of LFP also needs a reductive atmosphere (by adding more hydrogen) or inert gas (nitrogen or argon). Julien et al. [6] obtained a sample of pure LFP with the use of $FePO_4(H_2O)_2$ and Li_2CO_3 in stoichiometric amounts mixed in isopropanol; following drying, the mixture was then heated at 700°C for 8h under reduced pressure. As mentioned previously, LFP has a low electronic conductivity due to its structural limitations; carbon-coating outside the cathode is useful in increasing the material's conductivity without interfering with the electrochemical reactions. By performing the solid-state reaction method, this can be achieved by a one-step process simply instead of the two-step process where LFP is first synthesised and then coated with a carbon layer, in which a carbon precursor is added into the precursors of $LiFePO_4$ mentioned above [6]. This modified LFP was then found to be useful in lithium-ion batteries due to improved electrochemical properties.

3.2. Hydrothermal/Solvothermal Synthesis Method

Solid-state synthesis can produce materials with decent electrochemical qualities, but it is energy-expensive due to the high temperatures and lengthy heating times involved. Hydrothermal synthesis can result in significant energy savings because the precursors are exposed to lower temperatures (around 200°C) for 5–18 h [7]. Hydrothermal synthesis usually involves the following raw materials: Lithium hydroxide monohydrate, iron sulfate heptahydrate, and phosphoric acid. To create the $LiFePO_4$ precursor, those reactants were dissolved in deionized water by the stoichiometric proportions of $LiFePO_4$ and agitated for a few minutes at room temperature [8]. Specifically, the

procedure was conducted in an Ar atmosphere. The resulting precursor solution was put in an autoclave and heated for ten hours to 140, 160, 180, and 200 degrees centigrade. After that, the solution was separated and repeatedly purified with deionized water. The filtered powders were ground in an agate mortar after being warmed in an oven at 80°C [8]. It was then filled with Ar gas and heated to 650°C for six hours [8]. This produces the LFP powders, and the procedure is carried out with a different hydrothermal reaction temperature chosen and set for various reaction times of 6h, 8h, 10h, 12h, and 15h [8]. Heat transfer efficiency is enhanced when the hydrothermal methodology is combined with microwave heating, primarily because heat exchange occurs at the molecular level due to the direct interaction between reactants and microwave radiation, which shortens the synthesis time [7]. For example, Gao et al. [9] successfully synthesised a sample of LFP nanoplates with a single-mode microwave hydrothermal system, with ascorbic acid added to the precursors as a reducing agent.

3.3. Sol-Gel Synthesis Method

Besides the solid-state and hydrothermal synthesis methods, the sol-gel method is also a popular and successful way to obtain LFP. This procedure is more chemically based compared to the previous two methods, in which it creates a variety of nanostructures, especially nanoparticles made of metal oxides [10]. The molecular precursor is dissolved in water or alcoholic solution and transformed into a gel by warming and agitating via hydrolysis/alcoholysis. The damp gel formed from the previous step should then be dried using appropriate techniques according to the desired application of the gel [10]. Li et al. [11] obtained a sample of LFP synthesised by the sol-gel method. They used $FeCI_2 \cdot 4H_2O$, H_3PO_4, and Li_2CO_3 as the starting materials, and the molar ratio of Li: Fe: P were weighed as 1.3: 1: 1. The Fe, Li, and P sources of equivalent masses were then added to the alcoholic and acidic solvent. The mixture was well agitated until the reaction was finished. The attained sol was converted to a gel. The next part was to dry the gel appropriately and sufficiently, as mentioned previously, and it was placed in an oven at 60^{o}C for 12h. Finally, the sample was prevented from oxidation by introducing a protective atmosphere of nitrogen gas, and it was heated constantly at 350^{o}C for 6h, then increased and kept the temperature at 650~750^{o}C for 12h. The final product was at last obtained. After mixing the conductive carbon black and polyvinylidene fluoride and coating onto the copper current collectors in preparation of the electrode, the galvanostatic discharge-charge and cycling performance of the synthesised LFP electrode was tested and reported, the following conclusions are being made: A LFP cathode material with improved electrochemical performance was produced through the sol-gel synthesis method; distinctive cathode materials with varying grain sizes and characteristics were generated by altering the temperature at which the precursor was calcined; by adding the carbon layer, in addition to having strong conductivity, the material facilitates the incorporation and removal of lithium ions. Structural optimization has led to improved performance using the sol-gel method, and this material has the potential to be a viable cathode for commercial lithium-ion batteries [11].

4. Modification of LFP in LIBs

4.1. Nanostructure

Although there is an inherent property in LFP cathodes that challenges the utilization of LIBs, like the poor electronic conductivity and insufficient rate of ion diffusion along the one-dimensional b-axis of the structure, extensive research has still been done, and numerous solutions come out; one of these is to manufacture nanostructured LFP particles. By nanosizing the LFP particles, the distance of the diffusion pathway of Li^+ can be minimized, which assists the movement of the ions and further improves the battery's electrochemical performance. Because the controlled exposure of a particular crystal structure of $LiFePO_4$ is inevitably challenging, the synthesis pathway of (010)-oriented $LiFePO_4$ is generally limited to wet chemical techniques, namely "crystal engineering" or "orientation" of materials. Cao et al. [12] synthesised a free-standing $LiFePO_4$ carbon nanofiber

hybrid electrode of this type made in situ by a one-pot electrospinning technique. This means creating electrically charged jets from viscoelastic polymer solutions, which involves the application of electrostatic force. Eventually, the solvent evaporates, and nano-micro structures are produced when the process is finished. This allows electrodes with 3D structural properties whose layer thickness and porosity can be altered to be well produced. After preparing the material, they used it directly as an electrode of a lithium-ion battery without adding extra conductive agents and binders and made some valuable discoveries. The formation of (010)-face-oriented $LiFePO_4$ crystals is somewhat regulated by poly (vinylpyrrolidone) (PVP). As a perfect material, the best performing $LiFePO_4$/carbon nanofibers cathode with an ideal (010) manifest shows outstanding rate performance and discharge capacity. Apart from producing LFP/carbon nanofiber hybrid cathode, another material, hierarchically porous MXene decorated carbon coated LFP, was synthesised by Zhang et al. [13], which applied the electrostatic self-assembly method. MXene is a novel carbonitride or transition metal carbide with a two-dimensional structure akin to graphene. $M_{n+1}X_nT_z$ is its general chemical formula, where X stands for carbon or nitrogen, T could be an active functional group, and M is an early transition metal [14]. Figure 2 displays the experimental process of producing the LFP@C by Zhang et al. Due to their 2D and graphene-like nature, they exhibited excellent properties such as large surface area and good electronic conductivities, enhancing the increase in electronic conductivity and the rate of lithium-ion diffusion when incorporated into the construction of hierarchical porous LFP composites [13]. Their results proved that this material is a favourable cathode material for use in LIBs.

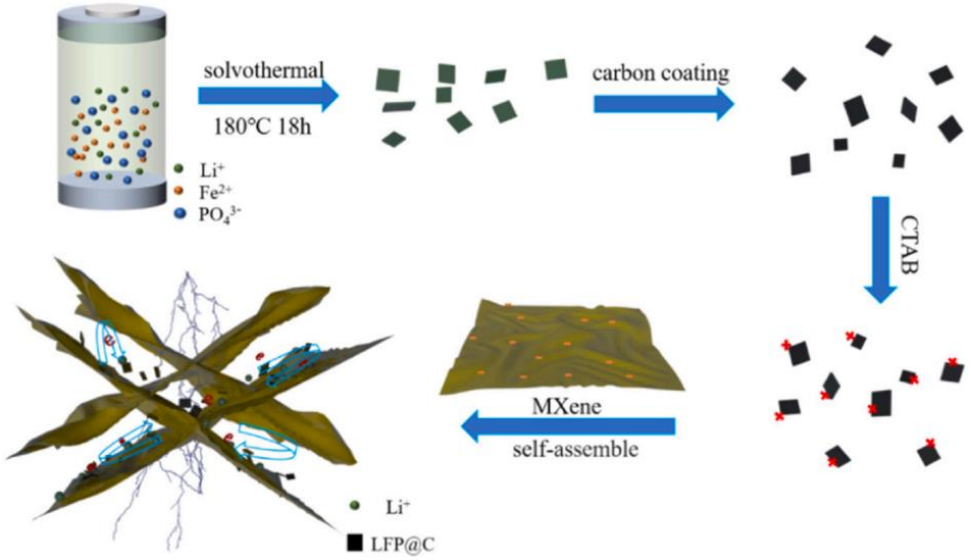

Figure 2. The production process of the LFP@C/MXene composites [13]

4.2. Carbon coating

Another technique to modify LFP cathodes in LIBs is through carbon coating. This means applying a sheet of carbon material onto the surface of the electrode, covering the LFP particles evenly. This aims to promote the flow of electrons to raise the electronic conductivity of the cathode material. This is because $LiFePO_4$ has poor surface conductivity, as mentioned previously; therefore, adding a highly conductive layer of carbon onto the electrode not only overcomes this challenge but also prevents the degradation of the electrode, avoiding the intervention of active particles in the electrochemical reactions by segregating them from the electrolyte. Carbon is mainly chosen because of its high electronic conductivity, structural stability, and economic viability [2]. Additionally, including carbon may function as a nucleating agent in the LFP cathode material to inhibit the formation of LFP grains. This narrows the diffusion channel of Li^+, leading to an improvement in ionic conductivity. Generally, the carbon precursors are mixed into the battery material and heated at very high temperatures. Raj et al. [15] synthesised samples of LFP cathode material with a carbon

coating, in which citric acid was used as both a source of carbon material and the chelating agent. The molar ratio of metal ions to citric acid was 1:0.5, 1:1, and 1:2 to prepare three samples with unique proportions of carbon. In the synthesised samples, they found that the thickness of carbon coating on the material is proportional to the concentration of citric acid used in the synthesis process. It is shown in Figure 3 that four samples of the cathode materials were investigated: the top left picture shows a LFP sample with no carbon coating found, the thicknesses of carbon coatings on LFP/C (1:0.5), LFP/C (1:1), and LFP/C (1:2) particles were found as 2, 4.2, and 14 nm, respectively. However, although the LFP/C (1:2) sample had the most significant carbon coating, this did not improve electrochemical performance since the dense carbon coating's pores lost their ability to pass electrolyte solution through them, slowing the diffusion of Li^+ ions. The LFP/C (1:1) sample showed the best electrochemical properties among them because the thickness of the carbon layer is in the optimum range, as research by scholars has shown. High graphitic carbon at the ideal thickness on $LiFePO_4$ nanoparticles is required for the highest electrochemical performance.

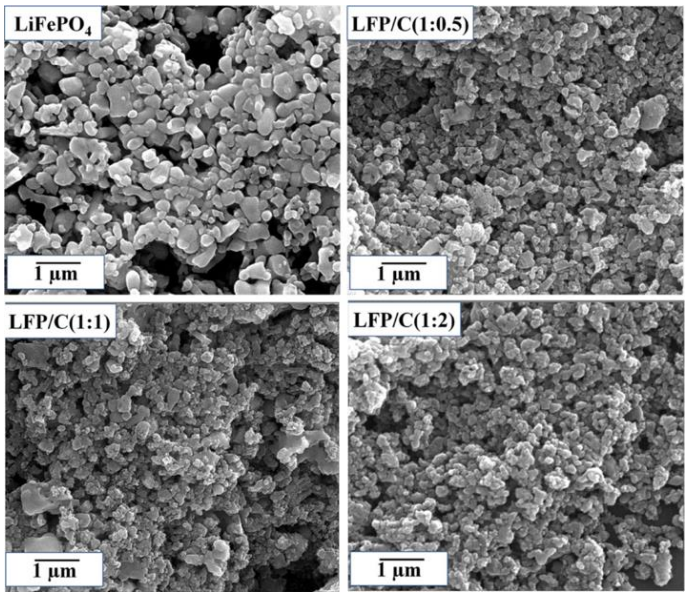

Figure 3. The FESEM images of LFP and LFP/C powders [15]

4.3. Doping modification

Besides the two previously mentioned strategies in modifying the LFP cathode, the doping technique is another promising solution to structural defects of $LiFePO_4$. This means improving the material's properties by incorporating additional materials into the desired product. This contributes to improving the particle's internal conductivity and the rate of diffusion of lithium ions, fundamentally resolving the issue of low conductivity and enhancing the electrochemical performance [16]. For example, it has been demonstrated that doping LFP with Mo, Nb, Mn, and Co increases its electronic conductivity [17]. There are often two choices of doping: doping in the Li site and doping in the Fe site, and the choice of the metal ion for this technique is highly dependent on its ionic radius. The smaller the difference between the radius of the doping element and the element being doped, the more effective it is at creating holes in the crystalline structure, encouraging the electronic conductivity and ion diffusion rate [16]. Gao et al. [18] calculated the structure of $LiFe_{1-x}Ru_xPO_4/C$ doped with Ru in the Fe site and investigated the properties this produced, as shown in Figure 4. The results revealed that Ru doping exchanging iron sites results in a considerably increased coefficient of lithium diffusion and conductivity, drastically enhancing the electrochemical performance [18].

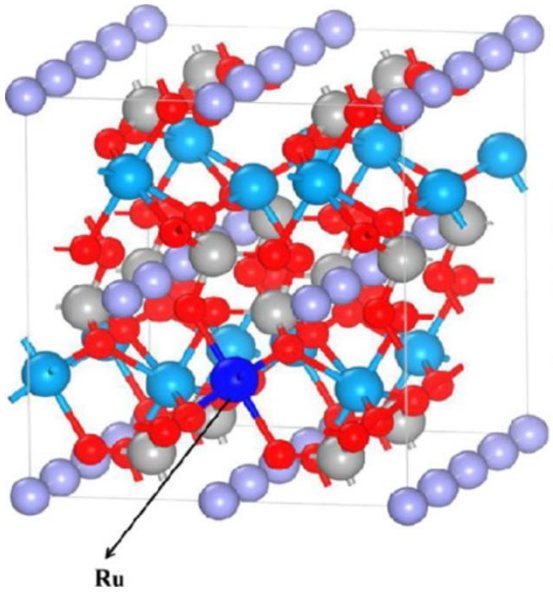

Figure 4. Structure of Ru-doped $LiFePO_4$ [18]

5. Conclusion

LIBs are widely used in various fields due to their advantages of high energy density, long cycle life, low self-discharge rate, no memory effect environmental performance, etc. The performance of cathode materials in LIBs has a direct impact on the overall performance of the battery. Therefore, this paper compares and analyses three common cathode materials: $LiNiMnCoO_2$, $LiMn_2O_4$, and $LiFePO_4$. LFP shows several advantages in LIBs, such as high thermal stability and safety, long cycle life, high energy density and capacity, environmental protection, fast charging, low self-discharge rate, and efficient charge/discharge performance. Three different routes for LFP preparation are also summarised in this paper. Solid-state synthesis is the most valuable and mature production method among these methods. In addition, three strategies for modifying LFP cathodes are given, all of which require the application of nanotechnology to improve the ion diffusivity and electronic conductivity of LFPs by altering their structure or adding other materials.

However, several challenges need to be addressed to maximise the potential of LFP. For example, the cost of manufacturing LFP can be significantly higher due to applying the technologies mentioned earlier. Another issue is the low vibrational and compaction densities of LFP, which results in a lower cell energy density. This means larger-sized LFP particles are needed to achieve the same capacity as other materials. Furthermore, LFP has a low-efficiency discharge rate, which may prevent LIBs from achieving fast discharges when high-power applications are required. Therefore, there is still much room for improvement of LFP materials. In the future, we can consider optimizing the microstructure of LFP by increasing the crystallinity of the electrode particles and the crystal surface's porosity to improve the material's electron and ion transport properties. Attempts can also be made to improve the performance of LIBs by doping other elements, modulating their lattice constants, and changing the electronic structure. Research should also focus more on coating methods, which can simultaneously improve electronic conductivity and prevent material degradation by electrolytes over time. The application of another oxide-based compound to coatings, such as aluminum oxides, could also be explored, which would be highly beneficial. From the perspective of lithium-ion batteries, nanotechnology is a very promising strategy for improving energy density and rate performance, as a great deal of research has already been carried out in this area; this applies not only to cathode materials for LIBs but also to anode materials, electrolytes, and structural components for electric vehicles to improve driving range and minimise vehicle weight.

References

[1] NOAA Research: No sign of greenhouse gas increases slowing in 2023, April 5, 2024.

[2] Ahsan Zishan, Ding Bo, Cai Zhenfei, et al. Recent progress in capacity enhancement of $LiFePO_4$ cathode for Li-ion batteries. Journal of Electrochemical Energy Conversion and Storage, 2020, 18: 1-54.

[3] Shruti Kaushik, Tushar Mehta, Prakash Chand, et al. Recent advancements in cathode materials for high-performance Li-ion batteries: progress and prospects. Journal of Energy Storage, 2024, 97: 112818.

[4] Chen Zhangxian. A review on cathode materials for advanced lithium-ion batteries: microstructure designs and performance regulations. Nanotechnology, 2020, 31, 012001.

[5] Gu Fei. A Streamlined Route to Synthesise $LiFePO_4$/C in an Unrestricted Environment, UC Riverside, 2020.

[6] Julien C.M., Mauger A., Zaghib K. Surface effects on electrochemical properties of nano-sized $LiFePO_4$. Journal of Materials Chemistry, 2011, 21: 9955-9968.

[7] Bezerra, C.A.G., Davoglio, R.A., Biaggio, S.R. et al. High-purity LiFePO4 prepared by a rapid one-step microwave-assisted hydrothermal synthesis. Journal of Materials Science, 2021, 56: 10018-10029.

[8] Liu Y., Luo G., Gu Y., et al. Study on the preparation of $LiFePO_4$ by hydrothermal method. Materials Science and Engineering, 2020, 761: 012004.

[9] Chao Gao, Jian Zhou, Liu Guizhen, et al. Microwave-assisted synthesis and surface decoration of $LiFePO_4$ hexagonal nanoplates for lithium-ion batteries with excellent electrochemical performance. Journal of Materials Science, 2017, 52: 1590-1602.

[10] Dmitry Bokov, Abduladheem Turki Jalil, Supat Chupradit, et al. Nanomaterial by sol-gel method: synthesis and application. Advances in Materials Science and Engineering, 2021, 5102014: 21.

[11] Li Zongfeng, Dong Guixia, Kang Jingrui, et al. Preparation and electrochemical properties of nanoparticle structural $LiFePO_4$/C by Sol-Gel method as cathode material for lithium-ion batteries. Journal of Materials Science: Materials in Electronics, 2019.

[12] Cao Zhaoxia, Sang Min, Chen Shengnan, et al. In situ constructed (010)-oriented $LiFePO_4$ nanocrystals/carbon nanofiber hybrid network: facile synthesis of free-standing cathodes for lithium-ion batteries. Electrochimica Acta, 2021, 333: 135538.

[13] Zhang Hongwei, Li Jiayi, Luo Linqu, et al. Hierarchically porous MXene decorated carbon coated $LiFePO_4$ as cathode material for high-performance lithium-ion batteries, Journal of Alloys and Compounds, 2021, 876: 160210.

[14] Zhang Jianfeng, Cao Huiyang, Wand Hongbing. Research progress of novel two-dimensional material mxene. Journal of Inorganic Materials, 2017, 32 (6): 561-570.

[15] Raj H., Sil A. Effect of carbon coating on electrochemical performance of $LiFePO_4$ cathode material for Li-ion battery. Ionics, 2018, 24: 2543–2553.

[16] Zhang Huanhuan, Zou Zhengguang, Zhang Shuchao, et al. A review of the doping modification of $LiFePO_4$ as a cathode material for lithium-ion batteries. International Journal of Electrochemical Science, 2020, 15 (12): 12041-12067.

[17] Zhang Bo, He Yufang, Gao Hongqiang, et al. Unraveling the doping mechanisms in lithium iron phosphate. Energy Mater, 2022, 2: 200013.

[18] Gao Yuan, Xiong Kun, Zhang Haidong, et al. Effect of Ru doping on the properties of $LiFePO_4$/C cathode materials for lithium-ion batteries. ACS Publications, 2021, 6 (22): 14122–14129.