Advances in Lithium Iron Phosphate Cathode Materials for Lithium-Ion Batteries

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Abstract. $LiFePO_4$ has become very prospective cathode materials for lithium-ion batteries because of its stable charge/discharge performance, high specific capacity and high safety. At present, the main challenges facing lithium iron phosphate cathode materials is the poor conductivity and low energy density, which urgently need to be optimized. This paper summarizes the mainstream modification strategies for lithium iron phosphate cathode materials by exploring the relevant literature in recent years. In detail, the crystal structure and the reaction mechanism of $LiFePO_4$ cathode materials during the charging and discharging process were investigated and reviewed. Based on the disadvantages of $LiFePO_4$ cathode, the three targeted modification methods including carbon coating, metal ion doping and nanosizing are also analyzed. By strengthening the research on the above improvement strategies, the ideal $LiFePO_4$ with excellent performance is expected.

Keywords: $LiFePO_4$, modification, carbon coating, Metal ion doping, nanosizing.

1. Introduction

Today, energy demand is growing with the acceleration of the globalization process. However, the large-scale exploitation and use of traditional fossil energy sources have caused serious environmental pollution and ecological crises. The need to develop renewable energy sources is imminent. Therefore, exploring and developing rechargeable battery technologies, especially lithium-ion batteries, has become a hot topic in the global research and industrial communities. Lithium-ion batteries have demonstrated great application potential in electric vehicles, portable electronic devices, and energy storage power stations because of their advantages of high energy density, long cycle life, high safety coefficient. Cathode materials, where electron and ion migration occurs, are one of the important factors affecting the battery performance of Li-ion batteries [1]. At present, lithium-containing cathode materials in Li-ion batteries are mainly divided into the following types: (1) Spinel-structured $LiMn_2O_4$ and $LiNiMnO_4$ materials, etc. which have three-dimensional lithium-ion diffusion channels; (2) Layered-structured $LiNiO_2$, $LiCoO_2$, ternary materials, and high-capacity lithium-rich materials, etc. which have two-dimensional lithium-ion diffusion channels; (3) The polyanionic compounds $LiFePO_4$, $Li_3V_2(PO_4)_3$, $LiVPO_4F$ materials, etc. with the one-dimensional lithium-ion diffusion channels of [2]. Among the above cathode materials, $LiFePO_4$ is the first commercially produced and most widely used cathode material for Li-ion batteries [3]. However, $LiFePO_4$ batteries face challenges such as low energy density and insufficient conductivity.

2. Charge-discharge reaction mechanism of $LiFePO_4$

The charging and discharging process of $LiFePO_4$-based batteries can be understood as a first-order phase transition between $LiFePO_4$ and $FePO_4$. As shown in Fig. 1, the internal structure of the $LiFePO_4$-based battery demonstrates its working principle. During the charging process, Li^+ in the cathode detach from the $LiFePO_4$ lattice and move to the anode across the electrolyte, while the charge transfers from the cathode to the anode through the external circuit so that Fe^{2+} (in $LiFePO_4$) is oxidized to Fe^{3+} (in $FePO_4$) to maintain the charge balance. This delithiation process of cathode results in an increase of its potential, which absorbs energy input from an external power source. On the anode side, lithium ions pass through the electrolyte membrane into the graphite materials, where they are embedded to form a lithium-carbon compound. In this process, the anode accepts electrons

from the cathode, completing the charge transfer and balance, causing the anode potential to decrease, thus realizing the chemical storage of electrical energy [3]. When the battery is discharged, the above process is reversed. Li^+ migrate from the carbon material of the anode to the cathode through the electrolytes and then re-embedded in the lithium-free cathode lattice to form $LiFePO_4$. At the same time, the electrons released from the anode flow to the cathode through the external circuit to provide electrical energy to the external device. This process reduces the potential difference between the cathode and anode of the battery and releases the stored chemical energy [3]. The reaction equations during charging and discharging process are shown in Eq. (1) and Eq. (2) [3].

$$\text{Charging reaction: } LiFePO_4 \rightarrow xFePO_4 + (1-x)\,LiFePO_4 + xLi^+ + xe^- \quad (1)$$

$$\text{Discharge reaction: } FePO_4 + Li^+ + e^- \rightarrow LiFePO_4 \quad (2)$$

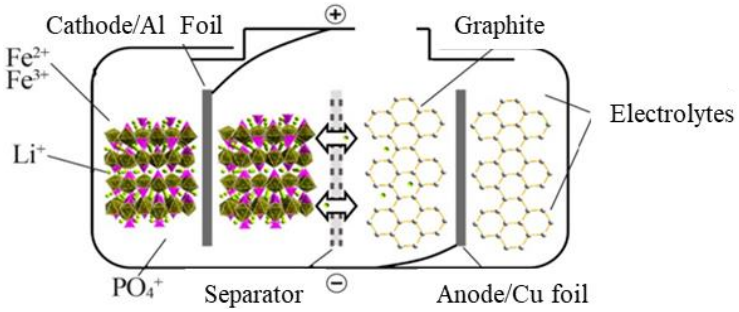


Figure 1. Internal structure of $LiFePO_4$ battery [4]

3. Basic Structure of Lithium Iron Phosphate Crystals

According to Fig. 2, the $LiFePO_4$ material has an orthorhombic crystal structure of olivine type. The $LiFePO_4$ crystal consists of PO_4 tetrahedra, LiO_6 octahedra, and FeO_6 octahedra [5]. In this case, the oxygen atoms show a twisted hexagonal dense stacking arrangement, and the phosphorus atoms are located in the center of the tetrahedra, forming a strengthened P-O chemical bond from which the oxygen atoms are difficult to detach, thus endowing the structure with very high thermodynamic and kinetic stability. On the other hand, this structure restricts the variation of the cell volume due to the absence of the continuous co-edge FeO_6 octahedral network and PO_4 tetrahedra between the octahedra in the $LiFePO_4$ cell [5]. This leads to the obstruction of electron and Li^+ transport processes, giving $LiFePO_4$ materials the disadvantage of low electronic conductivity and slow ion diffusion rate.

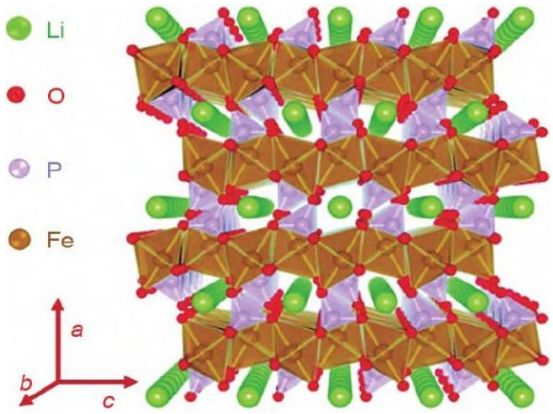


Figure 2. Lithium iron phosphate crystal structure in view of Li+ one-dimensional diffusion channels [6]

4. Modification of $LiFePO_4$

Lithium iron phosphate batteries currently face several challenges. This is because the O in the PO_4 tetrahedra separates the FeO_6 octahedra and produces non-co-edged FeO_6 octahedra, resulting in

the inability to form a network of continuous transition metal layers in the crystal cell. As a result, the $LiFePO_4$ material has low electronic conductivity. Meanwhile, the ion diffusivity in $LiFePO_4$ is low due to the limited variation of cell volume, which is fundamentally attributed to the stable structure of PO_4 tetrahedral structure and the strong covalent bonds between the octahedra [2]. The main means to improve the battery performance of $LiFePO_4$ include carbon capping, metal ion doping, and material nanosizing. Carbon capping technology involves covering the surface of $LiFePO_4$ particles with a layer of conductive material (e.g., a carbon layer) to form an electron-conducting network, thereby significantly improving the inter-particle electronic conductivity and reducing the electrochemical polarization phenomenon. Metal ion doping by introducing other elements into its crystal structure, on the other side, can regulate the electronic and crystal lattice structure, which can improve the electrochemical properties of $LiFePO_4$ materials. Material nanosizing, in another aspect, significantly increases the specific area of the material by synthesizing the nanoparticles or grinding the lithium iron phosphate particles to the nanometer level, thereby shortening the transmission distance of electrons and ions and then promoting electron and ion conductivity during the electrochemical reaction.

4.1. Carbon coating

Traditional inorganic carbon materials, including graphene and carbon nanotubes, have good electrical conductivity, low cost and readily availability. Coating carbon materials on the surface of $LiFePO_4$ is an effective means to improve the electrical conductivity. Graphene has attracted much attention in the application field of battery electrode materials due to its unique two-dimensional structure, high specific area and excellent electron transport ability. Therefore, graphene can be used as the coating layer of $LiFePO_4$ particles, the synthetic composite cathode exhibits better electrochemical performance compared with traditional inorganic carbon-capped materials, especially the rate performance which is attributed to the great electroconductibility of the graphene [7].

Carbon cladding can not only improve the conductivity of lithium iron phosphate particles but also provide migration channels for lithium ions, resulting in the improved rate performance of the Li-ion battery. In addition, the surface cladding shows the potential to protects the $LiFePO_4$ particles from the erosion of the electrolyte and improves the cycling stability of the $LiFePO_4$-based Li-ion battery.

Qiao et al. successfully prepared carbon nanotube-coated $LiFePO_4$ nanocomposites by using commercial carbon nanotubes and polyvinylpyrrolidone (PVP) as the precursor. The carbon nanotubes constructed a 3D network structure, which improved the electroconductibility and lithium-ion diffusion coefficient of $LiFePO_4$ materials, resulting in the composite cathode material exhibiting excellent multiplicity performance and ultra-long cycle life. After 1,000 cycles of charge/discharge at 10C current density, the discharge specific capacity of $LiFePO_4$ cathode was still about 123mAh/g, which only lost about 1.6% of the discharge specific capacity compared the first cycle. Moreover, the specific capacity was still maintained at about 100mAh/g after 3,400 cycles at the same high current density, which indicates a high capacity retention of 80% relative to the initial capacity [8]. Overall, the modified cathodes by carbon nanotube coating exhibit significantly improved electrochemical performance.

Guan et al. prepared a composite cathode material based on $LiFePO_4$ and commercial graphene, in the other hand, coating the $LiFePO_4$ particle with the activated carbon and graphene. The modified cathode exhibits the enhanced battery performance. The discharge specific capacity reached 66mAh/g at a current density of 100 C, while the capacity retention remained at 82% after 3,000 cycles even with a not changed structure [9].

From the above analysis, the improvement method of $LiFePO_4$ cathode by using carbon coating technology is effective in strength the battery performance, which is worthy of further in-depth study.

4.2. Metal ion doping

The introduction of metal ions into the $LiFePO_4$ crystal lattice, replacing atoms such as lithium, iron and phosphorus, may disrupt the original lattice structure and generate lattice defects, which demonstrate the potential to improve the diffusion path of Li^+ and enhance the electroconductibility if designed properly. It is shown that Na element doped can effectively suppress the generation of the undesirable $Li_4P_2O_7$ phase, although it will increase the formation of Li_3PO_4. This suggests that a moderate amount of Na elements doping helps to inhibit the generation of heterogeneous phases, thus optimizing the electrochemical performance of $LiFePO_4$ materials. Under the optimized experimental conditions of 1% Na^+ doping, the discharge specific capacity of the modified cathode decayed by only 1.3% after 200 cycles and remained at 142mAh/g [10]. Meanwhile, it was found that Na^+ and K^+ co-doped $LiFePO_4$ also significantly increased the discharge specific capacity [11]. In addition, the $LiFePO_4$/C samples after doping of Ni and V elements not only showed improved discharge specific capacity at room temperature but also decreased charge/discharge voltage plateau spacing, indicating that the doping reduced the polarization effect of the $LiFePO_4$ material. Figure 3 shows that 1% vanadium ion doping into $LiFePO_4$ resulted in an increase in the first discharge specific capacity to 124.9mAh/g from 111.3 mAh/g, while the initial discharge specific capacity of the modified $LiFePO_4$ with 1% nickel ion doping was 113.5mAh/g [12].

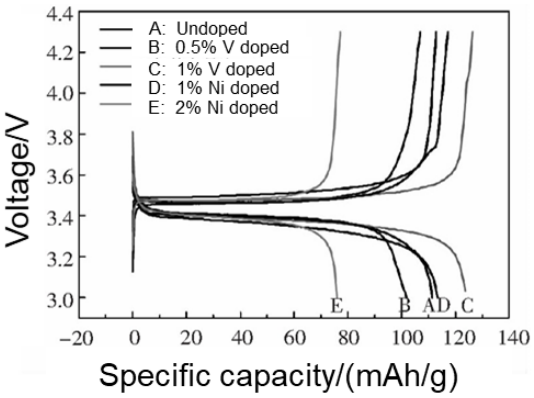


Figure 3. First charge/discharge curves of $LiFePO_4$/C samples at room temperature [12]

In addition, the doping of vanadium and nickel ions can still significantly enhance the discharge specific capacity of $LiFePO_4$ cathode at extreme temperature environments, as shown in Fig. 4, an increased specific capacity can be realized by such doping.

Therefore, these doping strategies are important for the optimization of $LiFePO_4$ material in terms of the temperature-dependent performance [12].

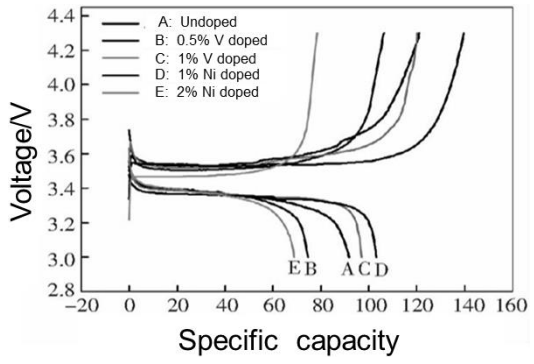


Figure 4. First charge/discharge curve of $LiFePO_4$ samples with or without V/Ni dopping at 0°C [12]

Huang et al. doped and modified lithium iron phosphate cathode materials using titanium elements. It was found that the first discharge specific capacity of titanium-doped $LiFePO_4$ material was increased to 140.6mAh/g at 0.1C from 132.4mAh/g of undoped $LiFePO_4$ cathode. Meanwhile, the first discharge specific capacity of titanium-doped $LiFePO_4$ material was also increased from

108.5mAh/g to 117.9mAh/g after 400 cycles. The capacity decay rate of Ti-doped $LiFePO_4$ material was only 0.0196% after 400 cycles. This indicates that Ti doping can not only improve the high-current discharge performance of $LiFePO_4$ cathode but also improve the cycling stability of the material [13].

Gu et al. studied lithium iron phosphate materials with Mg doping. The results showed that the discharge specific capacity of the Mg^{2+} doped $LiFePO_4$ material was 160.1mAh/g at 0.1C and the discharge specific capacity of the material was still 77.2mAh/g at a discharge current density of 20C, whereas the discharge specific capacity of the un-doped $LiFePO_4$ material was only 29.4mAh/g under the same circumstances. This shows that the Mg^{2+} doped $LiFePO_4$ material has an excellent discharge specific capacity and excellent rate performance [14].

In summary, the doping sites, doping element types, and doping amounts have important effects on the $LiFePO_4$ materials in terms of electrochemical performance. Future studies should further explore the material reaction mechanisms under different doping conditions in order to optimize and design new high-performance $LiFePO_4$ cathode materials.

4.3. Nanosizing

Nanoparticles show the short diffusion path of Li^+ in the lattice thereby providing a high ion diffusion rate. At the same time, the large specific area of nanoparticles increases the active sites, which is conducive to the efficient electrochemical reaction. Cao et al. utilized LiOH, Fe $(NO_3)_3$ and H_3PO_4 as the raw materials with 10% PVP/DMF as the carbon source, the (010)-$LiFePO_4$/carbon nanofiber cathode was successfully prepared by electrostatic spinning technique. In this structure, lithium iron phosphate is attached to the fiber surface in the form of flake particles, and its discharge capacity reaches 152mAh/g with 98.2% capacity retention after 500 cycles of 0.5 C. The discharge capacity is still 108.6mAh/g at a high discharge rate of 5 C. These excellent performances are attributed to the well-designed three-dimensional conductive network, the fast lithium-ion diffusion path, and the porous structure of the permeable electrolyte [15]. On the other hand, Wang et al. prepared $LiFePO_4$/(F+C) nanocomposites using polyvinylidene fluoride (PVDF) as a fluorine source. The microstructure and electrochemical performance of the nanocomposites were investigated in detail by various characterization techniques, and it was found that fluorine and carbon were tightly attached to the surface of $LiFePO_4$ particles, forming a three-dimensional conductive network structure. This superior structure ensures good electrical contact between the particles, reduces the diffusion distance of lithium ions in the particle interface, and facilitates the rapid transport of ions and electrons, thus improving the electrochemical performance. The initial discharge specific capacity of the modified cathode can reach 174.3mAh/g at 0.1 C, which exceeds the theoretical discharge specific capacity [16]. The above analysis shows that the nanosized $LiFePO_4$ material exhibits an effectively improvement of electrochemical performance. However, there are still challenges such as nanomaterial agglomeration during the synthesis process and high preparation cost that need to be solved.

5. Conclusion

In this paper, we have reviewed the research progress of $LiFePO_4$ cathode materials in recent years and presented its lattice structural features, electrochemical reaction mechanisms, and various improvement measures of its electrochemical performance. Its electrochemical properties can be significantly improved by surface modification, doping and nanosizing. The comprehensive analysis shows that the battery performance of $LiFePO_4$ can be modified by carbon coating. Moreover, it is suggested that future research focuses on exploring the influence law of carbon materials on the battery performance of $LiFePO_4$, the morphology regulation of the carbon materials layer and the coating cost. In addition, reducing the preparation cost of the nanosizing process and optimizing the preparation steps is helpful to increase the application possibilities of $LiFePO_4$ cathode materials and expand its wide application scenarios. Overall, although the emerging modification strategies, mainly

coating, doping, and nanosizing, for the $LiFePO_4$ cathode demonstrated positive effects, the high cost, complicated processing process and unstable ununiformed material performance still need to be further studied and improved.

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