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Research Progress of $LiFePO_4$ Cathode for Lithium-ion Batteries

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Abstract

Lithium-ion batteries(LIBs), with their high energy density and desirable cycling performance, have become the dominant battery technology for everything from portable electronics to electric vehicles. In recent years, lithium iron phosphate ($LiFePO_4$) has been regarded as one of the most attractive cathode materials for lithium-ion batteries due to its good cycling stability, low price and excellent safety. However, the rapid development of $LiFePO_4$ is limited by key challenges such as low conductivity and low diffusion rate of Li^+. In order to improve these defects, many studies have been carried out to improve the electrochemical performance of $LiFePO_4$. In this paper, the basic structure, charge-discharge principle, preparation method and modification of lithium iron phosphate are reviewed, and the research on improving the electrochemical performance of lithium iron phosphate at home and abroad are reviewed, including surface coating, ion doping and material nanocrystallization. At last, the development trend of this field is prospected, and the direction of future research is suggested.

Keywords

Lithium-ion Battery; Lithium Iron Phosphate; Cathode Material.

1. Introduction

The performance and cost of lithium-ion batteries are largely determined by the cathode, which is the most significant component of lithium-ion batteries. Its electrochemical performance plays an important role in battery voltage, specific energy density, cycle life and safety performance. Researchers in related fields have tried to carry out various researches on cathode materials. Lithium battery cathode materials are usually layered $LiMO_2$(M=Co,Ni,Mn), $LiNi_{1-X-Y}Co_XMn_Y$, spinel $LiMn2O_4$ and $LiFePO_4$. Among them, olidine-structured $LiFePO_4$ was proposed by Padhi in 1997. Compared with spinel manganese $LiMn_2O_4$ and layered $LiMO_2$(M=Mn,Co,Ni), $LiFePO_4$ is superior with high development value,which has the advantages of thermal stability, high cycle performance, low price, high theoretical capacity of 170mA·h/g, high operating voltage of 3.4V and so on. The theoretical diffusion coefficient of $LiFePO_4$ is 108 Scm1, which is sufficient to deintercalate Li^+ in nanoparticles. However, many challenges such as poor ionic and electronic conductivity, low diffusion rate of Li^+, low temperature performance issues, low yield, and patent issues have hindered its widespread application.

In order to solve the difficult of $LiFePO_4$ being used as a positive electrode of LIBs, a large number of studies have been carried out to modify $LiFePO_4$ to meet the needs of utilization. The main factors affecting the electrochemical performance of $LiFePO_4$ include synthesis method, particle size, electrolyte environment, electrode structure, temperature and so on. Its performance can be optimized by means of structure blending, particle size reduction, surface modification and element doping. This paper mainly reviews three modification methods:

1)Surface modification, such as carbon coating to improve electrical conductivity;

2)Element doping, such as doping Ti^{4+}, Co^{2+}, Zn^{2+}, Mn^{2+} plasma to adjust its electrochemical performance;

3)Prepare $LiFePO_4$ into nanoscale or special morphology to improve its electrochemical performance.

2. Basic Performance of $LiFePO_4$

2.1. Basic Structure of $LiFePO_4$

$LiFePO_4$ has an ordered olivine type structure and a Pnma space group which belongs to the orthogonal crystal system. Four $LiFePO_4$ units occupy a cell, and the cell parameters are A=0.6008nm, B=1.0324nm, C=0.4694nm. In the crystal structure of $LiFePO_4$, O presents a slightly twisted hexagonal close packing, and the 4C position of O tetrahedron is occupied by P, forming PO_4 tetrahedron. Li^+ forms a colocal straight chain at the 4A site parallel to axis C, which enables Li^+ to achieve free nesting in the charging and discharging process. The strong P-O covalent bond forms a three-dimensional delocalized chemical bond, which has better thermodynamic and kinetic stability during charge and discharge.

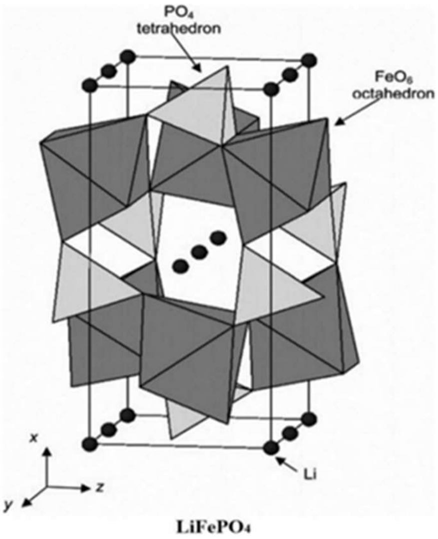

Figure 1. Structure diagram of olivine $LiFePO_4$

2.2. Charging and Discharging Principles of $LiFePO_4$

The charge-discharge principle of $LiFePO_4$ is significantly different from that of traditional cathode materials such as $LiMn_2O_4$ and $LiCoO_2$. In the battery, Li^+ is actually embedded and released back and forth between the positive and negative plates, which is called "rocking chair battery". When charging, Li^+ comes to the negative electrode from the positive electrode through the diaphragm and electrolyte, and the negative electrode is in a lithium rich state. The discharge process is the opposite. Its charge-discharge equation is shown in Equation (1) and Equation (2):

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

$$\text{Discharge reaction: } FePO_4+xLi^++xe^- \rightarrow xLiFePO_4+(1\text{-}x)FePO_4 \qquad (2)$$

2.3. Charge-discharge Reaction Model

When $LiFePO_4$ is charged and discharged, the PO_4 tetrahedron restricts the free space movement of Li^+, resulting in slow diffusion of Li^+ and low electron conductivity in $LiFePO_4$. Therefore, a large part of capacity will be lost when the charge and discharge rate is large. For Li^+'s' deembedding in $LiFePO_4$, there are three classic models of Padhi lithium ion radiation migration, Andersson radius and Mosaic model,which are widely accepted.

3. Preparation Methods

The preparation methods of $LiFePO_4$ mainly include coprecipitation, high temperature solid phase reaction, sol-gel synthesis, microwave heating and hydrothermal synthesis.

3.1. Chemical Coprecipitation Method

Chemical coprecipitation method can be divided into semi-liquid phase and full liquid phase. Fe salt and H_3PO_4 are fully mixed in aqueous solution in the former, and then ground with lithium source until uniform, inert protective gas is introduced, and the corresponding powder materials are calcined. The latter is to fully mix Li, Fe and P sources in an aqueous solution to prepare the precursor mixture at one time, and prepare $LiFePO_4$ by coprecipitation method. The process is relatively simple, but the different precipitation rates of each component may cause poor uniformity of products, and the final yield is low, which is not conducive to industrial production.

3.2. High Temperature Solid State Reaction Method

High temperature solid state reaction method is a method to calcinate $LiFePO_4$ at high temperature in inert atmosphere such as N_2 and Ar after mixing iron, lithium and phosphorus sources evenly according to stoichiometric ratio. The method is simple, easy to industrialization and easy to control. It is the most mature method for the synthesis of $LiFePO_4$ at present. The disadvantage is that it needs inert gas protection and has large diffiferent particle size and irregular morphology.

3.3. Sol-gel Method

Sol-gel method involves mixing the precursor Fe(III) with a certain proportion of lithium source, adding citric acid, and then adding the product to the P source. Adjust pH and temperature to get gel fully dried after high temperature sintering $LiFePO_4$. The advantages are that $LiFePO_4$ can be prepared with uniform molecular scale, high purity, regular morphology and fine particles, and the equipment is relatively simple. Using $FeC_2O_4\cdot H_2O$, $NH_4H_2PO_4$ and $LiOH\cdot H_2O$ as raw materials, citric acid as gel complexing agent, and sucrose as carbon source, Zhang et al. synthesized $LiFePO_4/C$ composite material, which showed good reversibility of ion intercalation and smaller polarization of anode and cathode peaks. Compared with $LiFePO_4$ in organic electrolyte, the electrochemical performance of $LiFePO_4/C$ in 1mol/L Li_2SO_4 aqueous solution has a greater application prospect.

3.4. Microwave Heating Method

Microwave heating is a heating process by absorbing electromagnetic energy and making the heated material obtain energy. Because the sample can absorb microwave directly, it can achieve uniform heating in a short time and shorten the reaction time. The method requires no inert gas and is simple. But the cost of equipment is high, so industrialization is not easy. Smecellato et al. synthesized $LiFePO_4$ through microwave-assisted solid phase reaction and systematically studied the products obtained at different microwave calcination times through a series of indicators. The results showed that when the microwave calcination time was 3 minutes the products performed best. This method can prepare nano-$LiFePO_4$ particles with high electrochemical activity.

3.5. Hydrothermal Synthesis Method

Hydrothermal synthesis method uses soluble Fe^{2+} salt, K^+ salt and H_3PO_4 as raw materials to directly synthesize $LiFePO_4$ under high temperature and high pressure in hydrothermal synthesis reaction kettle. The solubility of O_2 in hydrothermal system is very small, avoiding the oxidation of Fe^{2+} during the reaction, so there is no need to fill inert gas protection. The advantage of this method is good dispersibility and easy particle size control. But the reaction needs equipment to withstand high temperature and high pressure, adverse to industrialization. Martins et al. prepared $LiFePO_4$ in an autoclave using $LiNO_3$ instead of LiOH lithium source and $FeSO_4{\cdot}7H_2O$ as iron source under mild conditions for the first time.

4. $LiFePO_4$ Modified

Due to the structural defects of $LiFePO_4$ crystal, its rate performance is poor, and Li^+ diffusion rate and conductivity are not high. Modification methods include using carbon nanotubes, activated carbon, carbon fiber, graphene and other carbon materials to modify or cover the surface of the positive electrode; doping Ti^{4+}, Co^{2+}, Zn^{2+}, Mn^{2+}, N^{3+}, F^-plasma; making into nanomaterials, etc.

4.1. Surface Modification Through Carbon Materials

Coating the conductive material on the surface of the material can improve its conductivity, reduce the polarization of the battery, increase the specific surface area, and control the growth of the $LiFePO_4$ grain. Metal powder and carbon are often used as cladding materials. In recent years, through constantly trying new methods, many researchers have carried out a lot of research on the coating materials and created a lot of achivements.

Due to the excellent electrical conductivity of carbon materials, the preparation of composite positive materials by compounding activated carbon, mesoporous carbon, nano carbon fiber (CNF), multi-walled carbon nanotubes (MWCNTs), graphene and $LiFePO_4$ can effectively improve the electrochemical properties such as cycling rate. The electrochemical performance of $LiFePO_4$ can be improved by coating with activated carbon or nitrogen-doped activated carbon. Electrochemical performance is greatly improved compared to commercial $LiFePO_4$. In addition, graphene is often used in electrochemical modification of anode and cathode materials for lithium batteries due to its excellent properties. It has been reported that the cycling or rate performance of $LiFePO_4$ has been effectively improved by directly using graphene or nitrogen-doped graphene. The results show that the mass fraction of graphene has a great influence on the microstructure of the composite cathode material, and the effect is most obvious when the mass fraction is 10%. Graphene makes the particles of the composite material contact with each other more effectively, shortens the diffusion channel of lithium ion in the diffusion process, and improves the electronic conductivity. At 0.1c, the charge-discharge performance is the best, the first charge specific capacity can reach 169.07mAh/g, and discharge specific capacity is 114.12mAh/g. In addition, the charge-discharge performance is the best, the oxidation peak is 3.60V, the reduction peak is 3.32V, the peak spacing is 280 mV, the peak spacing is reduced by 300 mV, the battery polarization and battery internal resistance are reduced, and the performance of lithium ion battery is effectively improved. Last but not least, when the graphene mass fraction is different, the composite cathode materials prepared have complete crystal structure, which reflects the typical olivine structure of $LiFePO_4$. The discharge capacity increases firstly and then decreases with the increase of the graphene content in the composites.

The above analysis shows that it is effective to use carbon materials, especially graphene, to improve the electrochemical performance of $LiFePO_4$. However, the preparation process of carbon material is complicated, which will reduce the vibration density of the material to a certain extent. Further research is urgently needed.

4.2. Ion Doping Modification

Doping is mainly divided into lithium site and iron site doping, which refers to doping some metal ions or non-metallic elements with good conductivity into the $LiFePO_4$ lattice to change the grain size, form lattice defects, and improve the diffusion rate and conductivity of Li^+. It is a commonly used method to improve the electrochemical performance of $LiFePO_4$.

The addition of carbon can inhibit the oxidation of Fe^{2+} and increase the electrical conductivity of the material. Some ions with good conductivity are doped into the $LiFePO_4/C$ lattice covered with carbon layer to produce lattice defects, promote Li^+ diffusion and improve the internal conductivity of the crystal. The defects of $LiFePO_4/C$ mainly include lithium ion vacancy, iron deficiency, oxygen replacement and so on. According to the first principle proposed by S.Y.Chung et al., in $LiFePO_4/C$, if O is replaced by F, there will be the lowest bandgap width, followed by Mn replacing Fe or Na replacing Li. The reason is that during the charging and discharging process of the semiconductor $LiFePO_4/C$ battery, the coexistence of Fe^{3+}/Fe^{2+} mixing ratio will change, and the crystal will change between P type and N type. P type increases during charging and N type increases during discharge. The conductivity of Fe^{2+} or Fe^{3+} alone is poor. Metal ions can reduce the band gap between conduction band and valence band by introducing doped energy levels into the middle of the band gap of $LiFePO_4/C$, and cause the lattice defects of $LiFePO_4/C$, making the hole mobility greater than the electron mobility, and ultimately improving the conductivity and Li^+ diffusion rate.

Doping metal ions can also improve the properties of materials. Commonly used metal ions include Co^{2+}, Zn^{2+}, Mo^{6+}, Mn^{2+}, V^{3+}, Mg^{2+}, etc. S.y. Hung et al. doped $LiFePO_4$ with Mg^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Nb^{5+} and W^{6+} in 2002, which greatly improved the conductivity of $LiFePO_4$, exceeding $LiCoO_2$ and $LiMn_2O_4$, which were commonly used as cathode materials for lithium batteries, and attracted extensive attention from the scientific community. Since then, many scientists have made great efforts to improve the electrochemical performance of $LiFePO_4$ by doping. Although some progress has been made, various doping can improve the electrochemical performance of $LiFePO_4$ to varying degrees, but the effect of metal ion doping alone is not ideal. Metal ion doped modification and carbon coating are often both used, which results in an unclear mechanism for the change in the electrochemical performance of $LiFePO_4$. Therefore, it is necessary to conduct metal ion doping without carbon coating, and control grain size and particle dispersion, so as to obtain the specific law of metal ion doping on electrochemical performance.

4.3. Nanocrystallization of Synthetic Materials

According to Padhi et al., reducing particle size and increasing specific surface area can effectively improve the rate performance of $LiFePO_4$ materials. The size particularity of structural units of nanomaterials is quite different from that of conventional materials, which is reflected in four basic effects: surface and interface effect, small size effect, quantum size effect and macroscopic quantum tunneling effect. The nanoscale material has a great kinetic advantage when using high ratio charge because of the shorter diffusion path of Li^+ in the electrode. In addition, decreasing particle size is beneficial to improving ionic conductivity. Cai et al. prepared nano-$liFePO_4$ /C electrode with Ti_3SiC_2 by suspension mixing method, and the study showed that the particle size of $LiFePO_4$ was the determining factor of the rate. At a stable constant current, nano-composites containing 4% (mass fraction) Ti_3SiC_2 show excellent performance and excellent cycling speed, low charge transfer resistance and high Li^+ diffusion coefficient at low temperature. The advantages of preparing $LiFePO_4$ nanomaterials are as follows:

1) the large specific surface area increases reaction interface, providing more diffusion channels for Li^+;

2) More defects and micropores, higher theoretical lithium storage capacity, smaller particle size will reduce the path of Li^+ embedding and releasing, and accelerate the migration of Li^+;

3) The larger gap of nanoparticles can effectively relieve the stress of de-embedding Li^+ and ultimately improve the cycle life of the battery;

4) The creep of nanomaterials enables $LiFePO_4$ to have a strong volume change tolerance, which effectively alleviates the structural damage caused by material volume change in charge and discharge and improves the cycle stability of the battery.

Shell, lamellar, flower and other special microstructure are conducive to improving the specific surface area of materials, and can also improve the transmission rate of Li^+, which has attracted widespread attention. A large number of research results show that the electrochemical performance of $LiFePO_4$ with special morphology or nanometer level is significantly improved. However, the agglomeration of nanomaterials and high preparation cost are also brought about.

5. Conclusion

In this paper, the basic structure and properties of $LiFePO_4$, preparation methods, various modifications and recent research results are introduced. The cyclic ratio of lithium iron phosphate composite carbon material can be improved effectively. The electrochemical performance of $LiFePO_4$ can be improved by doping the $LiFePO_4$ bulk phase. Nanoscale $LiFePO_4$ material with mesoporous special morphology has large specific surface area and high Li^+ transmission rate. Based on the analysis of the existing experimental results, it is more practical to modify the $LiFePO_4$ surface coated carbon material. In the future, it is necessary to further study the law and cost of changing the electrochemical performance of $LiFePO_4$. If we can develop a simple preparation method of nanosized $LiFePO_4$ and $LiFePO_4$ material with special morphology, it is possible to solve the defects of $LiFePO_4$, and then the widespread use of $LiFePO_4$ can become a reality. Although a large number of studies have been carried out on surface modification, bulk phase doping and preparation of nano-$LiFePO_4$, there are still problems such as complex process and unstable performance, which need further research and exploration.

In general, the preparation process of $LiFePO_4$ has been relatively mature, and the focus of future research is to develop more effective modification methods, comprehensive modification based on traditional methods, and further study on the battery mechanism of $LiFePO_4$ as a cathode material.

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