Introduction of LFP and Ternary Cathode Materials of Lithium Battery

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Abstract. In recent years, with rapid development of mobile devices and electric vehicles, lithium-ion battery as an efficient and clean battery technology has attracted wide attention. Cathode material of Li ion batteries (LIBs) is the core part that determines the battery performance. This paper aims to review the research status and latest progress of cathode materials for Li ion batteries, analyze their advantages and disadvantages, and discuss their application prospects in batteries. The review includes two kinds of cathode materials which are widely used and have the best performance in commercial uses for now: lithium iron phosphate (LFP) cathode material and ternary cathode material. The structure, properties, synthesis and modification methods are analyzed and summarized. Based on the analysis of the two materials respectively, the influence factors and countermeasures on the capacity, cycling life and safety of cathode materials for LIBs are emphatically discussed, and the future development is prospected, too.

Keywords: Cathode material, LFP, Ternary, Lithium battery.

1. Introduction

Under the multiple adverse conditions of environmental deterioration and insufficient energy supply, people begin to urgently seek cleaner way of production. In order to solve the problem of resource exhaustion which is very likely to happen in the future, the search for alternative and renewable energy sources has become an important task for people. Of course, people also need to find effective ways to store energy. As a secondary battery, Li-ion battery is widely used in mobile, power transportation and energy storage equipment because of its high specific energy density. Compared with traditional fossil fuels, the biggest disadvantage of battery storage is that its specific energy density is much lower than that of fossil fuels. How to improve its specific energy density is a major research topic in the field of battery energy nowadays. Since the specific energy storage density of the cathode is much less than that of the anode, how to improve specific energy density of cathode is quite urgent. In the present research and market, two kinds of cathode materials have good performance and wide application which are lithium iron phosphate (LFP) positive electrode material and ternary (mainly NCA and NCM) cathode material. Lithium iron phosphate materials are better than traditional lamellar materials and spinel materials in safety performance and cycling life, which are widely used in power and energy storage fields. The ternary cathode materials have a higher upper limit of specific energy density and can continuously improve its actual specific energy density by adjusting the proportion of elements (increasing the nickel content), which has become a hot topic of research and application. This paper gives a overview of these two kinds of cathode materials in aspects of the structure and properties, preparation technology (solid phase synthesis method, spray drying method, etc.) and modification methods (element doping modification, surface modification, material nano modification, surface coating modification, etc.).

2. Lithium Iron Phosphate

2.1. Structure and Properties

$LiFePO_4$ cathode has many advantages like smooth discharge plateau, high energy density (170 mAh/g), excellent cycling/thermal stability, low cost of raw materials, etc. It is acknowledged as one of the best cathode materials for LIB [1-2]. The crystal structure is shown in Figure1 [3].

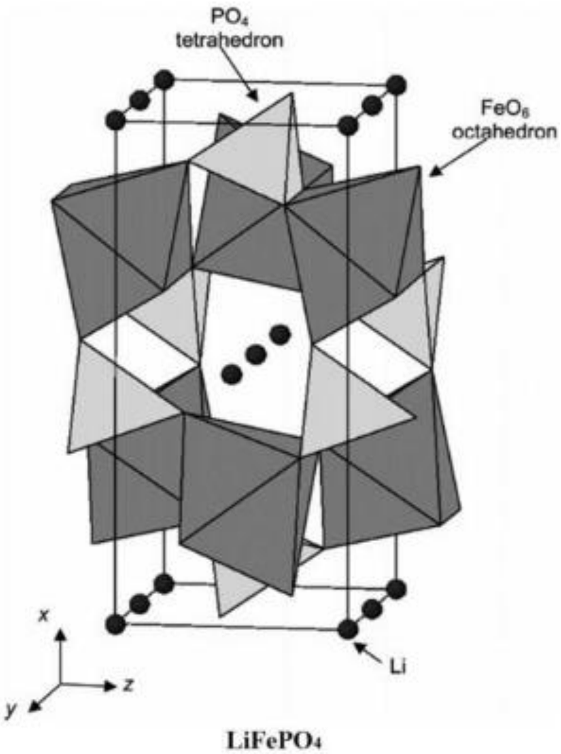

Figure 1. Structure of LFP [3].

$LiFePO_4$ has olivine type structure. In its structure, phospho-oxygen tetrahedron, ferri-oxygen octahedron and Li-oxygen octahedron are formed around P, Fe and Li, respectively. Since the P and PO_4 in O tetrahedra are interconnected by strong covalent bonds, the oxygen atoms are avoided to be oxidized, which makes the oxygen atoms always in a stable state during charging and discharging, making $LiFePO_4$ perform much better than other materials in the aspects of safety and cycling endurance. However, because FeO_6 octahedra in its structure are separated by the anion PO_4^{3-}, a continuous FeO_6 network structure cannot be formed and only the LiO_6 octahedra form long chains in the [010] direction in the form of co-edges which leads to a quite low electronic conductivity (10^{-9}~10^{-10} S/cm) and diffusion coefficient (DLi<10^{-14} cm^2/S for LFP), which makes it inferior to other cathode materials in terms of multiplier performance [4-7]. This is one of the reasons why $LiFePO_4$ as cathode material for Li^+ batteries are hard to be used on a widely use in the field of power batteries.

2.2. Preparation Method

2.2.1. Solid phase synthesis method

Mixing various phosphates, iron salts and lithium salts in certain proportions and then calcined them under inert atmosphere and high temperature conditions. If adding moderate carbon containing organic substances in raw materials, carbon will coat on the surface of material which can effectively prevent oxidation of material.

DONG et al. used $NH_4H_2PO_4$, FeC_2O_4 and LiF as raw materials [7]. Mixing and ball-milling them in acetone for 7 h, holding them at 350 °C for 10 h in N_2 environment, and then calcining them at 650 °C for 1 h in a mixture of Ar:H_2 with a volume ratio of 95:5. Obtaining $LiFePO_4$/C cathode composite material. The specific capacity of initial discharge of the material reached 157 mAh/g at 0.1 C and 151 mAh/g after 50 cycles, with a loss rate of only 3.5%.

The advantage of solid-phase synthesis method is simple, convenient and easy to operate. But the influencing factors in the reaction process include the mixing method of raw materials, mixing uniformity, mixing time, calcination temperature, calcination atmosphere and calcination time all directly affect electrochemical properties of $LiFePO_4$ cathode materials.

2.2.2. Sol-gel method

The method is to mix phosphate, metal organic salts and other raw materials homogeneously. Then the mixture is formed into a sol by hydrolytic polymerization/condensation process, followed by sedimentation and evaporation condensation to form a gel. And the gel is finally dried and high temperature calcined to obtain the product $LiFePO_4$, which can ensure that the lithium and metal ions are uniformly mixed at atomic level, thus reducing activation energy required for ion migration during lattice reorganization. This process could ensure homogeneous mixing of lithium ions and metal ions at atomic level, thus reducing activation energy required for ion migration during lattice reorganization, which is conducive to shortening reaction time and lowering reaction temperature.

ROCE et al. prepared $LiFePO_4$ cathode material by sol-gel method by using Fe $(NO_3)_3$, LiOH and H3PO_4 as the source of Fe, Li and P element, respectively, and using 1% mass of Ag or Cu as the conductive agent [8]. The specific capacity of initial discharge reached to 140 mAh/g.

The process of sol-gel method is complex and costly, and difficult to realize industrial production.

2.2.3. Spray drying method

The method starts with dissolving reactants in water or alcohol-containing media. After spray treatment, the material will be dispersed in the hot air stream in the form of droplets and generate the precursors.

The spray drying method has many advantages, such as short synthesis cycle, easy industrial production, good batch stability, and easy preparation of spherical $LiFePO_4$ cathode materials. And the combination of ball milling and spray drying method can significantly improve performance of the material.

2.2.4. Hydrothermal method

Since the solubility of oxygen in water is extremely small, the hydrothermal system is an excellent inert environment. The hydrothermal synthesis method is able to obtain materials with good crystallization, high purity, homogeneous phases and tiny particle size. The raw materials are usually soluble ferrous salts, lithium salts and phosphoric acid. For example, FATHOLLAH et al. chose $FeSO_4$-7H_2O as the Fe source, H_3PO_4 as P source, and LiOH as Li source and produced rhombic, homogeneous nanoscale $LiFePO_4$ by hydrothermal method, which has a specific capacity of 157 mAh/g at 0.2 C and about 114 mAh/g at 5 C [9].

Although the hydrothermal synthesis method can obtain $LiFePO_4$ materials with good crystallization, uniform phase and small particle size, the preparation process requires a high-temperature/pressure-large reactor, which is difficult and costly to manufacture and not economic for large-scale industrial production.

2.3. Modification

2.3.1. Elemental doping modification

1) Single element doping modification

The doping of metal ions in lattice of LFP is a method to enhance its electrical conductivity. Using the high-temperature solid-phase method, Huang Xiaopeng selected Mg, Ti, Mn, Co, and Ni to dope the iron sites of $LiFePO_4$ cathode material [10]. The diffraction peaks of different element doped $LiFePO_4$ cathode materials matched with the standard $LiFePO_4$. The characteristic diffraction peaks were sharp and well crystallized and there were no other impurity peaks. The SEM patterns of undoped and element-doped $LiFePO_4$ showed that the undoped $LiFePO_4$ samples had obvious agglomerated structure and the Mg-doped material had uniform distribution and a smaller particle size. In addition, the doping of Ti and Mn had a small effect on the particle morphology, while Co/Ni-doped material had a larger particle size and nano-spherical structure which can promote the LiFePO4 nucleation process and the formation of regular spherical particles.

2) Elemental co-doping modification

HUANG et al. used Li_2CO_3, $FeC_2O_4.2H_2O$, $NH_4H_2PO_4$, Mg $(CH_2COO)_2$ and TiO_2 as raw materials, ethanol as dispersant and sucrose as capping agent to form $LiFe_{1-x-y}Mg_xTi_yPO_4$ (x = 1.32-4.68, y = 1.32-4.68) cathode materials [11]. After Mg-Ti co-doping, the cell volume of $LiFePO_4$ was reduced. The Mg atoms had a great influence on the lattice constant of the material. The band gap of $LiFePO_4$ was reduced from 3.62 eV to 0.65 eV after co-doping, which helped to strengthen the material's electrical conductivity.

Shu et al. used high temperature solid phase method to form $Li_{1-x}Na_xFe_{1-x}Ti_xPO_4$ composite material [12]. The co-doped material still maintained the olivine structure of LiFePO4 but reduced particle morphology and lowered charge transfer resistance. And it exhibited best rate performance and cycling-stability at x=0.03. The capacity retention rate at 1 C could still reach 99.3% after around one hundred cycles, and the discharge capacity at high multiplicity of 20 C was still 97.3 mAh/g.

2.3.2. Surface modification modification

Carbon coating and metal oxide coating of $LiFePO_4$ cathode materials are also effective methods to facilitate the properties of $LiFePO_4$ [13].

HINDSA et al. prepared $LiFePO_4$ graphene nanocomposites by the sol-gel method by mixing the dispersed ox graphene with $LiFePO_4$ precursors [14]. The capacity of complex cathode reached 160 mAh/g, which is near upper limit, at low current and charging rate of 3 C.

2.3.3. Material nanochemical modification

The purpose of morphology control is to increase the surface area by turning down the size of the material to the nm level to increase reaction surface and improve the electrochemical performance. When $LiFePO_4$ is carefully controlled to nanometer level, it can help to weaken the polarization effect of the battery, reduce the electrical resistance and improve the material to discharge the electric energy at a large rate.

When the $LiFePO_4$ material is finely controlled to the nanometer level, it helps to weaken the cell polarization, reduce the electrical resistance and improve the material's high-frequency discharge capacity. Alsamet synthesized $LiFePO_4$ in nanomorphic form using a continuum-based sol-gel method combined with a hydrothermal method. During the reaction, the material appeared to have a regular lattice structure, and the structure of the crystals had a plate-like geometry with nano-sized thickness according to SEM and XRD results. Its discharge capacity was 126 mAh/g at 0.2C and its capacity retention was 97.5% after 100 cycles at 0.5 C.

3. Ternary Cathode

3.1. Structure and Properties

Although lithium iron phosphate has many advantages, its biggest limitation is the low upper limit of energy density. In order to achieve higher energy density limitation, it is imperative to find new materials. The Ni-rich layered cathode material is derived from lithium nickelate structure ($LiNiO_2$) first discovered by Dyer et al. in the 1950s, which is considered as a promising cathode material with supernal energy density (200~250 $Mahg^{-1}$) and operating voltage (≈3.8 V vs Li^0/Li^+). But in fact, $LiNiO_2$, which has perfect layered structure, is difficult to synthesize because of the serious stoichiometric ratio deviation and Li/Ni exchange problems during its synthesis process. Replacing nickel in $LiNiO_2$ with other metals (Co, Fe, Zn, Mn, Mg) can not only alleviate the severe deviation of stoichiometric ratio, but also improve its specific capacity, cycling life and thermal stability. Among all elements, Co, Mn and Al substitution are the most favorable for bringing on properties of nickel-rich layered materials. Co helps to improve rate capacity and ease cationic mixing. Doping Mg is beneficial to bring on the structural stability of $LiNiO_2$. Aluminum's low cost and light atomic weight are also advantageous. Therefore, the two most common cathode materials are nickel-cobalt-manganese and nickel-cobalt-aluminum. Both are lamellar structures.

3.2. Preparation

3.2.1. High temperature solid phase method

The method involves grinding and mixing transition metal salt and lithium source in stoichiometric ratios to form a homogeneous mixture. The homogeneous mixture is first pre-sintered at low temperature and then calcined at high temperature to finally gain the target product. The method is simpler and more appropriate for industrial mass production. Saavedra et al. used LiO_2, NiO_2, Co_3O_4 and MnO_2 as raw materials and ball milled them in isopropyl alcohol solvent for 24 h and then dried at 60°C [15]. The obtained products were first sintered at 450 °C under air atmosphere for 4 h, followed by calcination at higher temperatures. The product is $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ with a layered structure. Its specific capacity of initial discharge is 132 mAh /g in condition of 3 to 5 V.

The experimental steps of this method are relatively simple, but the calcination temperature needs to be experimentally explored in order to obtain the best performing material. The higher the temperature the faster the efficiency of ion diffusion, but when the temperature is too high the material will crystallize and affect the properties. Moreover, the mixing of several compounds is difficult to achieve atomic-level mixing, which means the prepared materials has large differences in particle size and morphology, resulting in materials that do not have the desired electrochemical properties.

3.2.2. Sol-gel method

The method is synthetic which uses highly chemically active compounds as precursors. The raw materials and complexing agents are dissolved in a solvent to form a solvent. Then solution is evaporated or condensed to form a gel. Then the product is obtained by grounding and sintering. This method allows reactants to be mixed homogeneously at molecular scale to obtain accurate stoichiometric ratios. Lee et al. used lithium acetate, nickel acetate, manganese acetate and cobalt nitrate to be raw materials and citric acid as complexant to form gels [16]. Raw materials were sintered at 450 °C to remove impurities, and then calcined at high temperature to obtain products with good, layered structure, uniform particle size distribution and excellent electrochemical properties. The first discharge capacity of 1 C was 150 mAh/g in the range of 3~4.3 V, and 87% reversible capacity was maintained after 100 cycles.

This method can make up for the disadvantages of non-uniform element concentration in the high temperature solid-phase method. Then the obtained materials can be uniformly distributed at molecular level. Besides, reaction conditions are simple and easy to control, and the obtained materials have uniform size, high purity and good morphology. However, this method is inappropriate for large-scale industrial production because of its high environmental hazard and long production cycle.

3.2.3. Co-precipitation method

The process of this method is to dissolve a variety of cations such as nickel, cobalt and manganese uniformly in the solvent, adding ammonia water and cations to complex, causing solution precipitation to obtain a homogeneous ternary precursor, and then mixed with lithium source through high temperature calcination method to obtain ternary materials. Li et al. used $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ and $MnCl_2{\cdot}6H_2O$ as raw materials, and ammonia water as complexing agent to get $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ [17]. At 0.1 C current density, specific capacity of initial discharge was 192 mAh/g, and capacity retention rate was 91.56% at about 40 cycles.

3.2.4. Spray drying method

The process is to first ball mill the metal oxides into a slurry or dissolve the metal salts into a solution, and then use atomization equipment to introduce the solution or slurry into the reactor, where the slurry is rapidly dried after contact with hot air to form solid particles or powder precursors. Yue et al. took $CH_3COOLi{\cdot}2H_2O$, Ni $(CH_3COOH)_2{\cdot}4H_2O$, Mn $(CH_3COOH)_2{\cdot}4H_2O$ and Co $(CH_3COOH)_2{\cdot}4H_2O$ as raw materials and dissolved them in deionized water according to the stoichiometric ratio [18]. They set inlet temperature of spray dryer at 220°C and the outlet temperature at 110 °C. This solution was pumped into the reactor to produce the product. The specific capacity of initial discharge was 173.1 mAh g^{-1} at 0.1 C current density.

Spray drying method can be used in continuous production and has great prospect in industrial production of ternary cathode materials.

3.2.5. Hydrothermal method

The hydrothermal method is a method that uses a reaction kettle and a hydrothermal tank to create a high temperature and high-pressure environment to react the supersaturated liquid phase solution, and then filter, wash, dry and calcine to finally obtain the reaction products. The material particles synthesized by hydrothermal method have uniform morphology, and the morphology of the products could be further controlled by adjusting the conditions of PH value, reaction time and reaction temperature of the hydrothermal reaction, so the hydrothermal method is often used to synthesize different electrode materials. However, since the hydrothermal method cannot be used to produce electrode materials on a large scale, it is mostly performed in the laboratory.

3.3. Modification Method

3.3.1. Shape regulation

By adjusting the morphology as well as the size of the ternary material, the contact area between cathode material and electrolyte and deem bedding path of Li-ions can be controlled. When the contact area increases, the active sites for lithium-ion embedding are increased and the electrochemical reaction is more adequate, which effectively improves the electrochemical performance. When the size of ternary material is small, the migration path of lithium-ion de-embedding decreases, which reduces the resistance of Li+ diffusion and facilitates multiplicative performance of cathode material.

Zhen Wang et al. synthesized miniature flower-like $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ ternary material by hydrothermal method [19]. The cathode material had an exposed (010) active planar microstructure to promote the rapid de-embedding of Li^+ and reduce the degree of the mix of cation in the cathode material. In voltage range of 2.8-4.4 V, initial discharge capacity at 0.1 C current density reached 207 mAh/g with a coulombic efficiency of 87%. While initial discharge capacity and coulombic efficiency of the spherical NCA cathode material were 199 mAh/g and 84.3%, respectively, which were significantly improved in comparison. After calculation, the miniature flower-like material has a larger Li^+ diffusion coefficient.

3.3.2. Elemental doping

Elemental doping is a simple modification method which dopes appropriate amount of metal or scrap metal ions into the lattice of ternary cathode materials. Elemental doping method can facilitate the electrochemical stability of the cathode material mainly because: (1) introduction of inactive elements can effectively reduce the cation mixing in cathode material and make lattice structure of the material more stable. (2) Inhibit occurrence of irreversible phase change from lamellar to spinel during charging and discharging process of the batteries. (3) Elemental doping can make the lithium layer spacing of cathode material increase, and shuttle efficiency of Li-ions would be higher. (4) Ion doping can provide charge compensation when lithium ions are de-embedded, significantly enhancing the ion diffusion rate of the material as well as the electron conductivity.

3.3.3. Surface coating

Surface coating could form a stable compound 'protective film' on surface of the ternary cathode material. This electrochemical reaction in the charging and discharging process of Li^+ batteries mainly occur on contact surface of electrode material and electrolyte, and electrochemical performance of electrode material could be effectively promoted by changing nature of contact surface of electrode material. The cladding layer can inhibit volume change of the electrode material during charging and discharging and can effectively reduce erosion of electrolyte on cathode material and reduce dissolution of transition metal ions in cathode material, which can improve stability of electrode material. When the conductive material is used as the cladding layer, it can effectively enhance diffusion rate of lithium ions in cathode material, thus improving multiplicative performance of the cathode material.

4. Conclusion

In this paper, two categories of cathode materials for Li-battery are introduced: Li-iron phosphate cathode material and ternary cathode material. The structure, properties, preparation and modification methods of the two products were prepared and enumerated. Lithium iron phosphate cathode material has excellent stability property and long cycling life, but its biggest limitation is low upper limit of theoretical energy density. The upper limit of theoretical energy density of ternary cathode materials is much higher. Approaches of improving actual energy density of ternary cathode material by modification and different preparation methods are a hot research field nowadays. However, with the progress of science and technology and the increasing demand of people, its upper limit of theoretical energy density cannot meet people's needs. Therefore, the search for new cathode materials and structures with better performance has to be on the agenda. Such as solid-state batteries, lithium-ion air batteries and other batteries with higher theoretical energy density which still in the theoretical and experimental stage, will be able to enter the practical stage, replace fossil fuels and meet people's demand for high performance and clean energy batteries in the near future.

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