

Progress in the Application of Nanotechnology in Lithium-ion Batteries

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Abstract. With the rapid development of electric vehicles in recent years, researchers are looking for more efficient electrode materials for lithium batteries. With the iteration of positive and negative electrode materials for lithium batteries, ordinary electrode materials have been unable to meet the market demand for battery performance. The emergence of nanometer electrode materials began to solve this problem gradually. Therefore, many nanomaterials have emerged in recent years. This paper describes the working principle of lithium-ion batteries (LIBs) and the application of nanotechnology and nanomaterials in lithium battery electrodes. This paper is divided into two aspects: the application of nanotechnology to positive electrode materials and the application to negative electrode materials. In the application of cathode materials, this paper focuses on introducing lithium manganese phosphate and lithium iron silicate and their nano-sized morphology. It includes the disadvantages of original materials and the advantages of nano-sized materials. At the same time, it also introduces ways of preparing nano-sized materials, such as the solid phase method and gel method. In the negative electrode application of nanomaterials, this paper presents the iteration of two traditional inorganic, nonmetallic materials used in electrodes in batteries and the preparation methods of nanization by comparing graphite with carbon nanotubes and silicon with nano-silicon wires, such as the arc discharge method.

Keywords: LIBs, nanotechnology, negative electrode.

1. Introduction

With the rapid development of electric vehicles in recent years, electric cars mainly rely on battery power supply as the main application field of new energy. Today's electric car batteries are mostly lithium batteries (terpolymer lithium batteries, used in Tesla Model S) and lead-acid batteries because lead-acid batteries have particular pollution to the environment and poor cycle performance, so researchers are looking for more efficient electrode materials for more environmentally friendly lithium batteries [1,2]. The structure of a lithium battery mainly includes the upper and lower cover of the battery, positive electrode plate (the active substance is lithium cobalt oxide), diaphragm (a particular composite film), negative electrode (the active substance is carbon), organic electrolyte, battery shell (which can be divided into steel shell and aluminum shell) and so on. With the continuous iteration of positive and negative electrode materials for lithium batteries, ordinary electrode materials such as elemental silicon and graphite have been unable to meet the market demand for high-performance batteries (high energy density, long service life, low cost). Due to the development of nanotechnology, the application of nanotechnology and nanomaterials in batteries has brought significant advantages, mainly including improving the energy density, electron transport capacity, and chemical stability of batteries, thereby improving battery performance and sustainability [3]. The application of nanotechnology in new energy batteries has been widely recognized and applied. Nanomaterials can improve the energy density of batteries and have excellent electron transport capacity and chemical stability, which makes nanomaterials an ideal choice for new energy batteries. For example, nanoscale metal oxides can be used as precious metal catalysts to improve the electrolyte efficiency of batteries. In addition, nanoscale carbon materials can also be used as negative electrode materials for batteries, enhancing their energy storage efficiency. These applications not only improve the battery performance but also contribute to the sustainable use of the battery. Specific to lithium-ion batteries, the application of nanotechnology is mainly focused on improving the performance of positive electrode materials. For example, by making positive electrode materials into

nanoparticles and coating them with conductive materials (such as carbon), conductive polymers, and metals, the electronic conductivity of the materials can be improved, thus improving the charge and discharge performance of the battery. It can be seen that the nanization of traditional materials has become the leading research direction of electrode materials. In this paper, the nanomaterials active in today's market and scientific research field are generally classified and summarized. It includes the advantages of various nanomaterials and compares them with the common electrode materials in the past. It also lists the different ways nanomaterials are prepared and their advantages and disadvantages.

2. LIBs' Operating Principle

Li-ion batteries mainly rely on lithium ions to move between the positive and negative electrodes. In the process of charging and discharging, Li^+ is embedded between the two electrodes. When charging, Li^+ is de-embedded from the positive electrode and embedded into the negative electrode through the electrolyte, and the negative electrode is in a lithium-rich state. The opposite is true for electrical discharge. The movement of lithium ions creates free electrons in the anode, which creates a charge at the positive current collector, as shown in Figure 1 [3]. The electrical current flows through the powered device and back to the negative current collector. In lithium batteries, different electrode materials have various specific capacities, which means different performances. It affects batteries' storage capacity, affecting how long they can power devices or electric vehicles.

While processing, there are challenges in various aspects, such as cost, energy density, and performance. In the market, the negative electrode of lithium batteries is mainly made of graphite. The graphite electrode in a lithium-ion battery typically has an energy density of around 160Wh/kg due to its specific capacity of approximately 372 mAh/g. However, graphite electrodes are costly; for example, the market price of UHP600 is 17140 CNY per ton. And graphite electrodes have a short service life of about 500-700 circles.

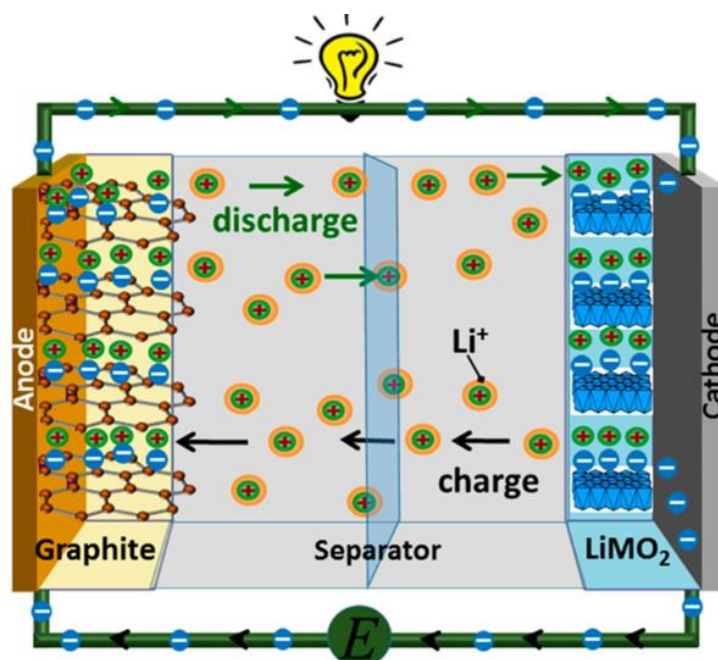


Figure 1. Operating principle of LIBs [3]

3. Nanotechnology Application in LIBs' Cathode Materials

3.1. Lithium Manganese Phosphate

Olivine-type lithium manganese phosphate is a hot research topic of cathode materials for lithium batteries. In addition to its advantages of low ownership cost, high energy density, and good cycling

performance, its electronic conductivity and lithium-ion diffusion ability are severely limited by its structure. At the same time, there are two voltage platforms for the charge and discharge of lithium manganese phosphate, which correspond to the REDOX of manganese and iron. Due to the different charging and discharging voltages of manganese and iron, there are two voltage platforms for charging and discharging lithium ferradenophosphate, which increases the difficulty of the battery management system. The Ginger haler effect of manganese ions leads to manganese dissolution, which reduces the battery's cycle life. Figure 2 shows the crystal structure of LiMnPO_4 .

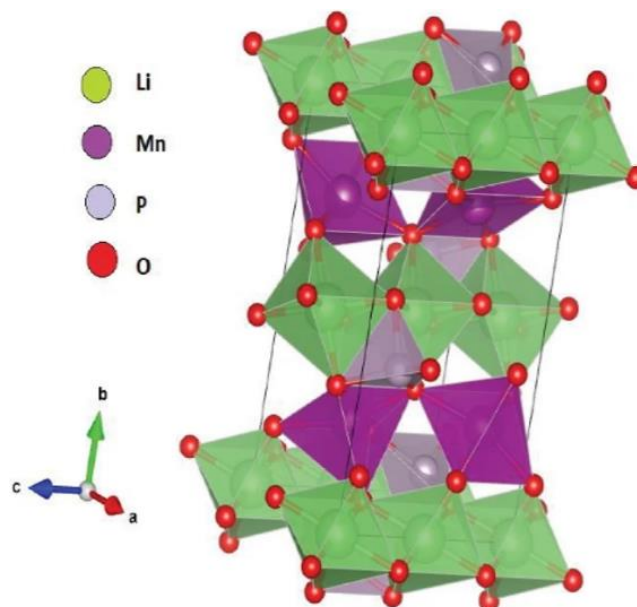


Figure 2. Crystal structure of LiMnPO_4 [4]

The size of the material particle has an essential effect on the activity of the electrode. Reducing the particle size can effectively shorten I. The diffusion distance of Li^+ reduces the adverse impact of the defect area on the diffusion of Li^+ , thus effectively improving the lithium manganese phosphate energy. Currently, liquid phase methods, such as the sol-gel and hydrothermal synthesis methods, are the main methods to prepare nano-sized lithium manganese phosphate particles. The size of the material particles can also be adjusted by changing the molar ratio of the raw materials lithium source, phosphorus source, and manganese source. After adding carbon coating, the material was divided into 156.9 mAh/g, 122.8 mAh/g, and 89.7 mAh/g at 0.05 C, 1C, and 10C conditions, and the volume retention rate after 200 cycles at 1C [5]. These methods, by controlling reaction conditions and introducing specific additives, realize the nanocrystallization and performance optimization of lithium manganese phosphate and provide an effective way to improve the performance of lithium-ion batteries.

The three main synthetic ways of lithium manganese phosphate (sol-gel method, solid-phase synthesis method, hydrothermal synthesis method) have advantages and disadvantages. The sol-gel method dissolves raw materials in water or ethanol through intense stirring to form a uniform sol of each component. The lemon method is to dissolve raw materials in water or ethyl solution and, through intense stirring to form a uniform sol for each element, with the help of citric acid, oxalic acid, and other chelating agents, increase the temperature to gelate the system, and finally sintering at high temperature to get the finished product. The product synthesized by this method is high, but the cost is too high, and the process is complicated. The solid phase synthesis method is relatively simple and suitable for mass production and industrial application. The common preparation process is to grind the raw material evenly first and then treat it at high temperature under the protection of inert gas to form lithium manganese phosphate product. In addition, the lithium manganese phosphate anode material prepared at a suitable calcination temperature has a lower dielectric constant, higher mass factor, and relative density. The hydrothermal synthesis method is one of the liquid phase preparation methods; the primary process is to put the raw material into the hydrothermal synthesis

reactor and directly generate lithium manganese phosphate cathode material under high temperature and high-pressure conditions. Because the product's shape can be controlled by preparation in this way, it is often used to prepare nanoscale cathode materials. However, hydrothermal synthesis is more complex, the synthesis conditions are more stringent, and the process often uses J-organic solvent as the reaction solvent, which will cause environmental pollution, so the industrialization process of this method is faced with specific difficulties.

3.2. Lithium-iron Silicate

$\text{Li}_2\text{FeSiO}_4$ has excellent thermal stability and safety, Si and Fe reserves are abundant in the crust, and the price is low. The above advantages make $\text{Li}_2\text{FeSiO}_4$ have potential application value in large-scale lithium-ion battery energy storage. The $\text{Li}_2\text{FeSiO}_4$ system still has some shortcomings, such as low conductivity and lithium-ion diffusivity, which are common in phosphate systems, limiting its further development [6]. The researchers used various methods, such as carbon coating and metal cation doping, to improve its electrochemical performance. In addition, there are studies on synthesizing lithium ferrous silicate/peanut shell carbon composite material to enhance further the material's electrical conductivity and lithium-ion diffusion coefficient and solve the problem of poor electrical conductivity and low lithium-ion diffusion coefficient. Figure 3 shows the crystal structure of $\text{Li}_2\text{FeSiO}_4$ [7].

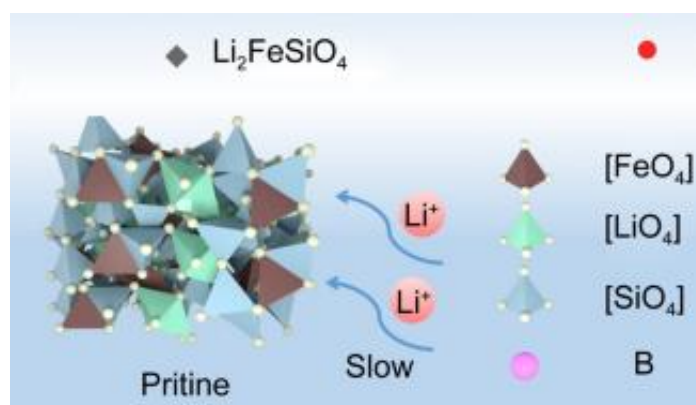


Figure 3. Crystal structure of $\text{Li}_2\text{FeSiO}_4$ [7]

At present, the modification research of $\text{Li}_2\text{FeSiO}_4$ mainly focuses on two aspects: experimental (surface coating, nano, and ion mixing) and theoretical simulation. In the nanization experiment, the researchers found that the nano $\text{Li}_2\text{FeSiO}_4$ electrode material has poor stability and low battery energy density. For this reason, the researchers actively explored the development of porous nano microstructure material $\text{Li}_2\text{FeSiO}_4/\text{C}$ to provide more lithium-ion expansion paths and improve the material performance [6]. However, lithium ferrous silicate still improves lithium-ion batteries' energy and power density through nanoization. Carbon surface coating, synthetic nanoparticles, and metal doping can improve the electrochemical properties of nano-sized lithium ferrous silicate. These methods can effectively improve the material's conductivity, reduce the energy loss during charging and discharging, and thus improve the battery's overall performance.

Lithium ferro silicate can be prepared by solid phase method, various soft chemical synthesis methods (hydrothermal/solvothermal method, sol-gel method, ultrasonic spray method), and some other methods (microwave/solvothermal method [8], high temperature and high-pressure supercritical drying method [9]). By hydrothermal method, Liu et al. prepared 4 nano-sized $\text{Li}_2\text{FeSiO}_4$ particles under different dynamic growth conditions. Arrhenius equation and Lifshits Slayozov Wagner (LSW) model were used to analyze the structural morphology of the products. The results show that the particle size distribution of the prepared $\text{Li}_2\text{FeSiO}_4$ material is broad, mainly due to the low nucleation activation energy, and the growth rate is primarily affected by the growth unit diffusion [10]. With the help of external physical means, the $\text{Li}_2\text{FeSiO}_4$ material with uniform composition and good electrochemical performance can be obtained by ultrasonic spray method. Using an ultrasonic spray, Zhuang Z Y prepared $\text{Li}_2\text{FeSiO}_4/\text{C}$ materials with complete structure and

high purity with different carbon coating amounts. The maximum charge-discharge ratio exceeded 166 mAh/g by circulating at 1.5 ~ 4.7 V with 0.1 C [11].

4. Application of Nanotechnology in LIBs Anode Materials

4.1. Carbon Nanotubes

As an allotrope of graphite, carbon nanotubes (CNT) are approved as suitable negative electrode materials for lithium batteries. The disadvantages of traditional graphite materials mainly include that they are expensive, difficult to produce, easy to pollute, low transparency, low density, and hardness, which lead to the poor performance of graphite products. Graphite is prone to acid corrosion at high temperatures and pressures, especially in a strong alkaline environment. In addition, the strength and hardness of graphite materials are relatively low and easily mechanically damaged, which limits them in some areas with high mechanical properties.

The cathode material of carbon nanotubes is characterized by large battery power and is not easy to crush. Their morphology makes them particularly suitable for replacing graphite as a negative electrode material for commercial lithium-ion batteries. As mentioned, CNT has ideal properties such as high strength, high conductivity, and relative inertia. Carbon nanotubes have a higher capacity than graphite and can also be used as a support substrate to form new carbon nanotubes and metal composites [12]. Carbon nanotubes, as the electrode material of lithium batteries, have a certain capacity for lithium insertion, which will not reduce the capacity of the negative electrode material. The uniform doping of carbon nanotubes can significantly improve the permeability of electrolytes in electrode materials. At the same time, it has good mechanical properties; the addition can make the electrode sheet with high toughness so that it can effectively inhibit the material in the charge and discharge process due to volume changes caused by spalling so that the active substance particles in the charge and discharge process can always maintain good electrical contact, thereby improving the cycle life of the electrode.

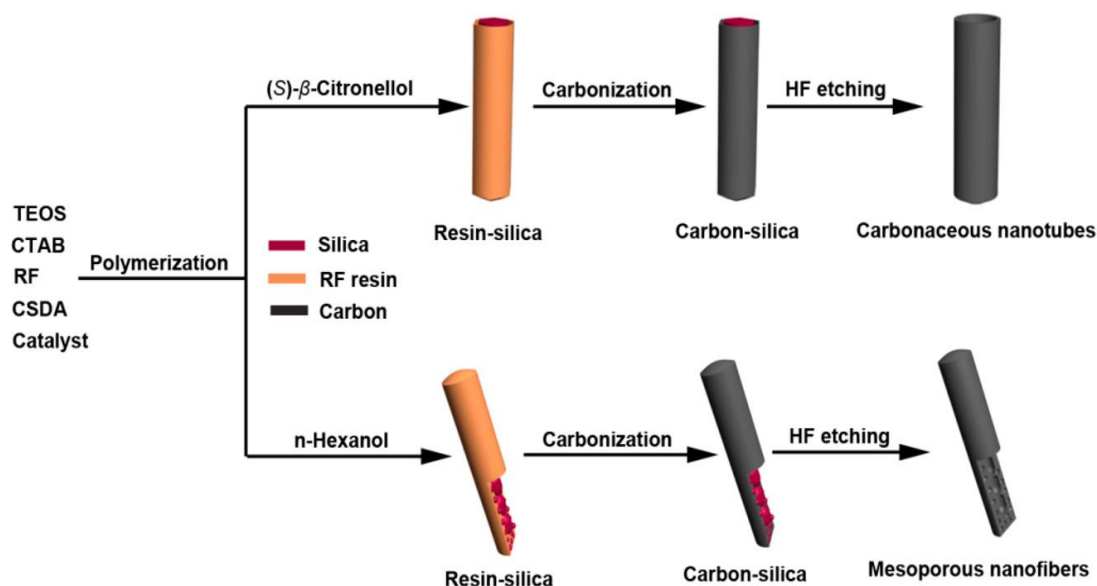


Figure 4. Synthesis route of CNT and CNF [13]

The preparation methods for carbon nanotubes mainly include chemical vapor deposition, catalytic cracking, arc discharge, and laser ablation. Figure 4 shows the preparation route of CNT and CNF [13]. Carbon nanotubes were first synthesized by arc discharge. Firstly, inert gas is introduced into the reactor, graphite rod is used as anode and cathode electrode, and after the direct current is introduced, the anode vaporizes to form carbon nanotubes, which are deposited on the cathode surface and around the cavity wall in the form of soot. In general, synthesizing multi-walled carbon nanotubes does not require the addition of catalysts [14]. Single-walled carbon nanotubes can be synthesized by

adding metal catalysts such as Fe, Co, and Ni into the anode. Smally et al. discovered the laser ablation method, which produces carbon nanotubes by vaporizing solid graphite with a high-energy laser in an inert atmosphere [15]. Compared with the arc discharge method, this method is more beneficial to the growth of single-walled carbon nanotubes and easy to analyze the growth mechanism.

4.2. Nanometre Silicon

As a negative electrode material for lithium batteries, silicon has the advantages of abundant reserves, low raw material cost, and high electrochemical lithium storage capacity. The charging and discharging voltage platform are low, and the safety is better than that of graphite material. Therefore, Si is considered a new type of high-capacity lithium-ion battery anode material with the most potential for development. However, in the electrochemical lithium storage process, the volume change of Si and lithium to form an alloy phase is as high as 400%. The vast volume effect will cause severe mechanical stress, resulting in the powder of silicon particles. At the same time, particle pulverization makes the Si anode material constantly expose a fresh surface, which reacts with electrolytes to form SEI film, reducing the alloy's intrinsic capacity and electrolyte loss [16].

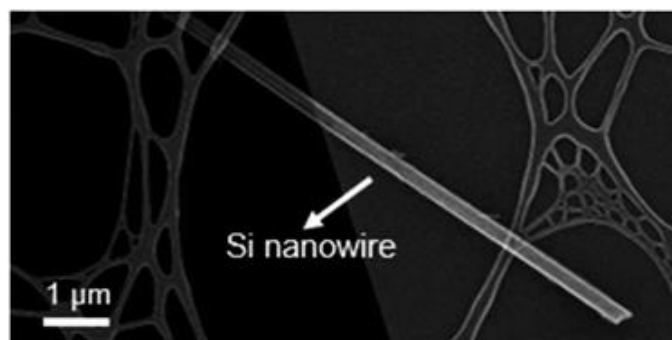


Figure 5. SEM image of silicon nanowires [17]

The way to solve this problem is to use tiny silicon nanowires. Each has a diameter of one-thousandth the thickness of a sheet of paper, as shown in Figure 5 [17]. It can soak up lithium and inflate to four times its normal size. Unlike other silicon shapes, they do not fracture. Compared with other granular silicon electrode materials, silicon nanowire electrode materials have a high tolerance to the change of electrode volume during the cycle and can avoid the damage of electrode structure to a greater extent. Its large specific surface area is conducive to the effective contact between electrolyte and electrode and shortens the charge and discharge time. At the same time, it can also assist in other functions, such as no fluid collection and self-support; silicon nanowires also have a high specific surface area and controllable structure, which make them have a wide range of potential applications in catalysis, sensing, and other fields. Its excellent electrical, mechanical, and optical properties show great potential in various fields.

5. Conclusion

This paper mainly describes the working principle of lithium batteries and the use of nanotechnology in the positive and negative electrodes of LIBs. Lithium manganese phosphate and lithium iron silicate are used in positive electrode materials, and carbon nanotubes and silicon nanowires are introduced in negative electrode materials. The preparation methods of lithium manganese phosphate, lithium ferrous silicate, and carbon nanotubes are listed, and the characteristics and advantages of each method are discussed. It can be seen from this that the performance of the nano-nanometer material is higher, and it has better structural characteristics than ordinary materials, which makes it show higher properties (higher energy density, better electrical conductivity, better mechanical properties, etc.).

However, preparing nanomaterials requires sophisticated processes and controls to ensure their stability and consistency. This results in high preparation costs and is a challenge for large-scale

commercial applications. The interfacial issue between electrodes and electrolytes in nanobatteries is a key challenge. On the nanoscale, interfacial effects can be more sensitive, which can easily lead to loss of performance and instability of the battery, affecting the cycle life of the battery. While nanomaterials can improve battery performance, they may also introduce new safety risks. For example, nanoparticles' easy agglomeration and high reactivity may lead to problems such as short-circuiting or thermal runaway inside the battery. With the continuous development and maturity of nanotechnology, it is expected that the preparation cost of nanomaterials will be reduced in the future by optimizing the preparation process and improving the production efficiency, making them more commercially competitive. At the same time, people should continue to study the interface problems in nano-batteries in depth and improve the interaction between electrodes and electrolytes by means of surface modification and interfacial engineering to enhance the stability and cycle life of the batteries. Through continuous research and innovation, it is believed that nanomaterials will bring more breakthroughs and progress to developing lithium-ion batteries in the future.

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