Promotion of Nanotechnology for Properties of Anode Materials in Li-ion Batteries

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Abstract: In recent years, the lithium-ion battery has been considered as one of the most potential energy storage technologies. At present, with the promotion of various electronic products (such as mobile phones, computers, cameras, etc.) and the popularity of electric vehicles, the requirements for battery performance have been further enhanced. In the research of enhancing battery performance, the improvement of electrode material is the most important aspect. For the traditional carbon anode materials, its performance cannot meet the needs of the next-generation lithium-ion batteries. Therefore, it is urgent to find new generation anode materials with a high specific capacity, high power, high safety, high cycle performance, and low cost. Among many improved methods of anode materials, nanotechnology is often considered. It has a significant effect on improving the cycle life, rate performance, and safety of batteries. This paper will mainly discuss three promising anode materials (silicon, lithium titanate, and transition metal oxides) and their improvement methods based on nanotechnology, including the current research progress, advantages, and disadvantages.

1. Introduction

Under the current situation, climate problems occur frequently, and environmental problems have also received extensive attention. To reduce extreme weather and deal with the energy crisis, many countries have made great efforts in energy transformation. Reducing the use of fossil energy and increasing new energy (such as wind and solar energy) has become a major trend. The storage of clean energy is also an important part of the research of new energy. In terms of energy storage, lithium battery is regarded as the most potential and the most researched battery at present.

Lithium batteries are mainly divided into two categories: lithium-ion batteries and lithium metal batteries. Lithium metal batteries usually cannot be charged and contain metallic lithium; Lithium-ion batteries can usually be charged, which does not contain metallic lithium. Due to the superior performance of lithium-ion batteries, lithium metal batteries are gradually eliminated. Lithium-ion batteries use lithium metal or lithium alloy materials as anodes or cathodes, and both electrode materials are required to be inserted and extracted lithium ions. In the charging process of the battery, the electrons in the cathode material will be transferred to the anode material through the external circuit, and the lithium ions in the cathode material will pass through the separator material in the electrolyte solution to reach the anode and insert; On the contrary, in the discharging process of the battery, the electrons in the anode material return to the cathode through the external circuit, and the lithium ions return to the cathode through the electrolyte and separator. At present, lithium-ion batteries are also widely used. In electronic products, they are used in laptop computers and mobile phones; In terms of transportation, they are mainly used in electric vehicles and city buses and are expected to be used in all-electric aircraft.
in the future. In addition, it also has superior performance in energy storage, military, and aerospace fields [1].

However, in the face of more demanding applications, such as electric vehicles and military applications, the combustible properties of traditional lithium-ion batteries have questioned their safety performance. In addition, some traditional lithium batteries also encounter bottlenecks in power density and energy density. With the development of nanotechnology, these problems have been solved to some extent. For example, the use of nanoparticles can improve the insertion and removal rate of lithium ions and electrons because it shortens the transmission distance [2]. And nanoelectrodes usually provide a larger contact area with an electrolyte solution to improve lithium-ion flux. Both these increase the rate of performance, which means the battery can have a higher power density. As an anode material preparation method, nanotechnology can also improve the cycle performance of the battery. For example, for high energy density anode material, silicon has a serious volume expansion effect in the process of use. The preparation of silicon nanowires as anode material can solve this problem [3]. In this paper, several potential nano anode materials will be discussed.

2. Improvement of Nanosized Anode Materials

2.1. Nanostructured Silicon

In the past many years, graphite has been the most commonly used anode material for lithium batteries. The advantages of graphite include low cost, light weight, easy preparation, et al. However, in recent years, graphite's relatively low specific capacity (372 mAh g⁻¹) cannot meet the higher requirements [4]. Researchers are looking for alternative materials with higher specific capacities. Silicon anode material is considered very competitive because it can provide a theoretical specific capacity of up to 4200 mAh g⁻¹, which is higher than a graphite anode [3]. However, silicon material has an obvious defect. In the process of lithium removal/intercalation, the volume change will exceed 300%, which means that the anode material will continue to shrink and expand, resulting in electrode damage. In addition, as an intrinsic semiconductor, silicon has poor electric conductivity, resulting in low power performance.

Many studies have shown that nanostructured silicon can improve the volume effect of silicon electrodes. Nanostructures can enhance the strain fracture resistance of the electrode and shorten the diffusion distance of ions and electrons, which provides the possibility of increasing the rate of performance [5]. At present, a variety of nanostructured silicon electrodes have been proposed, including nanoparticles, nanowires, nanotubes, and nanofilms.

The usual preparation methods of silicon nanoparticles include ball milling, chemical vapor deposition, and sol-gel method et al. The advantage of nanoparticles is that they can withstand large volume changes and prevent fracture. In addition, the preparation technology is relatively mature, and the cost is relatively low. The disadvantage is that a large specific surface area will promote the formation of solid electrolyte interphase (SEI) and side reactions. Xu et al. developed a novel but the simple process for synthesizing a nano silicon anode, which can be used in industrial production [6]. They used plasma-enhanced chemical deposition to directly deposit silicon nanoparticles on a porous carbon collector (Figure 1). The obtained electrodes can be directly used as anodes for lithium-ion batteries. In 2020, Zhang et al. tried to adjust the structure of the binder at the molecular level, which improve the stability of silicon nanoparticle anode in volume change [7]. In this study, they designed and prepared two optimized functional groups ("-OH" and "-COOH") as cross-linkable polymeric binders for nano silicon anodes of lithium batteries, which can effectively reduce the cracks generated by the anode during the cycle.

Fig.1 A schematic of electrode preparation process via direction deposition of Si nanoparticles [6]
Silicon nanowires or nanotubes can provide a continuous charge transport path and can grow directly on the collector during the preparation process, so there is no need for binders. The drawback is that the electrical contact with the current collector limits the electron injection, which will affect the rate performance. The common preparation methods of silicon nanowires include vapor-liquid-solid growth, laser ablation, and chemical etching and solution-phase synthesis et al. [8]. To explore the possibility of large-scale production of silicon nanotubes, Wen et al. synthesized silicon nanotubes from silica nanotubes by the magnesium thermal reduction method [4]. The obtained products have excellent rate performance and cycle life. Chen et al. prepared fast charge-discharge silicon nanowire anodes by one-step metal-assisted chemical etching, and this material has a high specific capacity and excellent cycle performance [9].

Silicon nanofilms have a uniform and thin structures, making them more stable in the insertion and removal of lithium ions. Still, the thickness of the films may limit their specific energy. Silicon nano films are generally prepared by physical vapor deposition or chemical vapor deposition. In the study of Chiu et al., they first synthesized micron carbon-fibers (MCFs) by thermal chemical vapor deposition, and silicon nano film anode was sputtered on the surface of MCFs [10]. The three-dimensional structure of the film can effectively reduce the stress in the process of charge and discharge to improve the stability in cycles.

Although these nanomaterials can improve the anode's cycle life and rate performance to a certain extent, the larger specific surface area will increase the side reactions on the electrode surface. To solve this problem, the most common solution is to prepare silicon nanocomposites or coat silicon nano anodes with other materials.

2.2. Nano Lithium Titanate

Lithium titanate (Li₄Ti₅O₁₂) is a potential material for anode material. Li₄Ti₅O₁₂ has a cubic-spinel structure, and its space group is Fd3m. Li₄Ti₅O₁₂ is called zero-strain anode material. During lithiation (Figure 2), there will be three lithium ions inserted into the spinel structure, and some of the original Li-ion positions will also change, resulting in the transformation of spinel structure (Li₄Ti₅O₁₂) into the rock-salt structure (Li₇Ti₅O₁₂). In this process, only 0.2% of the volume changes. The lattice parameter changes from 8.3596 to 8.3538Å [11]. This effectively avoids the battery capacity reduction caused by large strain. In addition, it provides a 1.5V high voltage platform as an electrode to avoid the formation of lithium dendrite, which significantly improves the safety of the battery [12].

However, Li₄Ti₅O₁₂ as anode material also has obvious limitations. Its electrical conductivity is low, making the battery unable to charge and discharge at a high rate [13]. And due to its limited capacity, it is not currently considered for high energy use. Thus, recently most of the research focuses on how to improve the power of the Li₄Ti₅O₁₂ battery. One of the most effective methods is researching nano-sized Li₄Ti₅O₁₂ to provide a larger electrode-electrolyte contact area and a shorter diffusion path for electrons and lithium ions [14].

Zhang et al. and Prakash et al. have prepared nanocrystalline Li₄Ti₅O₁₂ by sol-gel process and solution-combustion method and tested their performances, respectively, which proved that the nano size could improve the power density of battery [15, 16].
By using the sol-gel method to synthesize Li$_4$Ti$_5$O$_{12}$, high purity products can be obtained. In addition, this method has many advantages: it can mix the reactants evenly at the atomic or molecular level and has the characteristics of low temperature and short reaction time. The product size is very small, and the distribution is uniform. Although the sol-gel method has these advantages, it has high costs and complex processes, making it unsuitable for industrial production. Zhang et al. prepared Li$_4$Ti$_5$O$_{12}$ powder by sol-gel method [16]. Taking the bulk material as the control group, they measured the change of specific capacity of nano Li$_4$Ti$_5$O$_{12}$ at different charging rates and the change of discharge capacity after multiple cycles (more than 200 times). The first experimental results show that the specific capacity of nano Li$_4$Ti$_5$O$_{12}$ is much larger than that of bulk materials at the same rate. The second experimental result showed that only 3% of the power loss was found. These two results show that the rate capability and cycle performance of nano Li$_4$Ti$_5$O$_{12}$ are much better than the bulk materials.

![Fig. 3 The microstructure of nano Li$_4$Ti$_5$O$_{12}$ at different magnifications [15]](image)

Solution-Combustion is a well-known method for the preparation of nanocrystalline oxides. It involves a redox reaction between an oxidizer and a fuel. The features of this method are simple and cost-effective. A. S. Prakash prepared Li$_4$Ti$_5$O$_{12}$ nano-powders by solution-combustion synthesis [15]. Figure 3 shows the microstructure of Li$_4$Ti$_5$O$_{12}$ at different magnification. It is a porous structure. The reason for the high porosity should be that a large amount of gas is released by the combustion reaction during the preparation process. The pore size is generally in the range of nanometres and microns, and these pores will also have a certain impact on the conductivity of Li$_4$Ti$_5$O$_{12}$. They also conducted two tests to test nanomaterials’ rate capability and cycle performance and obtained very similar and positive results. The high rate of nano Li$_4$Ti$_5$O$_{12}$ also benefits from the large porosity so that the electrolyte can be filled, and the high flux of lithium-ion can be obtained. However, this large porosity also has defects, which will lead to lower bulk energy density.

According to the test results of nano Li$_4$Ti$_5$O$_{12}$ prepared by different methods, it is found that their rate performance and cycle capacity are greatly improved. Firstly, the nano-sized particles provide a larger contact area for the electrode and electrolyte and shorten the diffusion path of lithium ions and electrons. Secondly, because both samples have high crystallinity, the structural integrity of lithium ions can be maintained during intercalation and deintercalation processes, which speeds up the diffusion rate of lithium ions and electrons in solids. Generally, if nanoparticles are used, they may have some side effects with electrolytes, which will lead to safety problems of lithium batteries [14], thus limiting the service life. But for Li$_4$Ti$_5$O$_{12}$, there is no such problem. Compared with lithium, Li$_4$Ti$_5$O$_{12}$ has a high
enough potential to prevent forming a solid electrolyte interface, which greatly reduces the possibility of side reactions.

Currently, due to the low energy density of Li$_4$Ti$_5$O$_12$, it cannot be widely used in the mainstream direction. After the realization of nanotechnology, the rate performance of Li$_4$Ti$_5$O$_12$ is further improved to play an important role in many specific cases. It is currently used in some city buses, which can give full play to its fast-charging ability. In addition, in some places with low temperatures, the motor car has high requirements for low-temperature performance, safety, and battery service life. Lithium titanate battery is also used as the auxiliary power battery of the train, which can help the train start very well and can also be used as a standby power supply. In the future, considering the high safety and high power of Li$_4$Ti$_5$O$_12$, it has great potential for military application. Especially for some advanced weapons, Li$_4$Ti$_5$O$_12$ is a very good choice if it requires high power and superior safety performance in a short time.

2.3. Nanoscale Transition Metal Oxide

Transition metal oxide is also one of the most promising anode materials because of its high theoretical capacity and rich sources. But it also has some disadvantages, such as poor conductivity and obvious volume expansion in the process of charge and discharge. To solve these problems, improving the conductivity of transition metal oxide materials and to inhibit the pulverization and agglomeration of materials in the cycle process are effective. At present, the most common method is to prepare nanostructured materials with special morphology.

According to the lithium removal/intercalation mechanism in different materials, transition metal oxides can be divided into two categories. The first type of lithium intercalated oxides includes TiO$_2$, WO$_2$, MoO$_2$, Nb$_2$O$_5$, etc. structural changes in the lithiation process only accompany these transition metal oxides. Still, there is no formation of lithium oxide. These oxides have good lithium removal/intercalation reversibility and high capacity. Hao et al. studied the structure and electrochemical properties of different types of TiO$_2$ and designed a micro scale mesoporous yolk-shell microspheres with both anatase TiO$_2$ and TiO$_2$(B) phases [17]. The microspheres have a mesoporous core of anatase TiO$_2$ and are surrounded by a porous shell of TiO$_2$ (B) nanosheets, and the synthesis process is shown in Figure 4. Because the nanosheet shell provides an additional active area to stabilize the pseudo capacity, the open mesoporous structure also improves the diffusion of electrolyte on the electrode, which significantly improves the cycle performance and rate performance of the material. Cao et al. reported a novel composite, MnO$_2$ microspheres coated with a thin layer of TiO$_2$ (Nano-MnO$_2$@TiO$_2$) [18]. The synthesis method of this material is simple and cost-effective. Nanoparticles improve the rate performance, while the microsphere structure reduces the surface area of nanomaterials and ensures the battery’s energy density. In addition, the TiO$_2$ shell also provides good structural stability.

![Fig.4 Schematic representation of the synthesis of the mesoporous core-shell (CSM) and yolk-shell (YSM) anatase TiO$_2$/TiO$_2$(B) microspheres [17]](image-url)
The second type of transition metal oxide materials will form lithium oxide during lithium intercalation. During lithium removal, lithium oxide can remove lithium and regenerate transition metal oxide. The common second type of transition metal oxides is represented by MO (M = Co, Ni, Cu, and Fe). Thi et al. prepared undoped nano NiO anode and Co-doped nano NiO anode, respectively [19]. It is found that Co doping has no effect on the phase structure of NiO but has a great effect on its morphology, which can inhibit the agglomeration of nanoparticles and improve the specific surface area. In addition, Co can also replace Ni to produce holes and improve the conductivity of the material. Therefore, Co-doped nano NiO anode has a larger reversible capacity and stronger rate performance.

Transition metal oxide is a promising anode material for lithium-ion batteries because of its high theoretical capacity and abundant resources. At present, its main problem is poor conductivity and cycle stability. In addition to using nano technology, its properties can also be improved by composite materials and morphology control approaches. Although many related studies have improved the properties of these materials to a certain extent, they still cannot meet the standards of practical application.

3. Conclusion
Three kinds of anode materials are discussed in this paper, and the conclusions are obtained as below:

1. Silicon has an ultra-high specific capacity, but its application is limited due to the volume effect. The research of silicon nanostructures (nanoparticles, nanowires/nanotubes, and nano films) has solved this problem to a great extent, and the rate of performance has also been improved.

2. Lithium titanate has very high safety and cycling performance but poor conductivity. The nanostructure makes its electrode and electrolyte have a larger contact area, shortens the path of particle diffusion, and greatly improves the charge-discharge efficiency.

3. Transition metal oxides have a high theoretical capacity and have poor conductivity and poor cycle stability. The nanostructured materials with special morphology can effectively improve the conductivity and inhibit the pulverization/agglomeration phenomenon in the cycle process, obtaining anode materials with long cycle life and high-rate performance.

At present, there are a wide range of anode materials for lithium batteries, and their characteristics are also different. For different materials, there should be unique research and application in different fields. For nano silicon anode material, it is a very promising material. Currently some companies are using silicon nanowires in Li-ion batteries. One important aspect of future research is to improve the preparation technology of silicon nano materials, reduce manufacturing costs and realize large-scale mass production. For nano lithium titanate, the future research can focus on the application in the field of low temperature. Because of its low energy density, it is not easy to realize large-scale applications. However, its high rate and wide temperature characteristics make it have excellent applications in low-temperature areas and military fields. Although nanotechnology overcomes some defects of transition metal oxide anode materials, such as improving cycle life and stability. For future research, it is still necessary to composite with other materials or regulate the morphology of materials to further improve the electrochemical properties of materials.

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