Advantages and Application of Nano LTO battery

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Abstract. In order to promote the development of new energy vehicles, it is very necessary to develop battery packs with high capacity and high safety performance. For achieving this goal, developing new negative electrode materials has proved to be an effective strategy. Among the many candidate materials, lithium titanate has received extensive attention due to its zero strain property. However, the size control of lithium titanate has become a very important factor to improve battery performance. By reducing the particle size, the growth of lithium dendrite can be suppressed and the ion utilization efficiency can be improved. Nanotechnology has been proved to be an effective way to create nano-scale $Li_4Ti_5O_{12}$. By optimizing the preparation process parameters, the size of lithium titanate can be controlled within the desired range In recent years, there are many reports about nano LTO technology. In order to have a comprehensive understanding of this field. This paper summarizes and analyzes the development status and future development direction of nanotechnology and lithium titanate battery, the application of nanotechnology in LTO such as sol-gel, molten salt, microwave, hydrothermal and solvothermal synthesis, including the latest synthesis method in recent years, and illustrated the structure-property relationship between $Li_4Ti_5O_{12}$ and LTO performance, which provides theoretical guidance for the development of the battery field.

Keywords: Nano LTO battery, Negative electrode material, Lithium titanate, Electric vehicle

1. Introduction

Given the widespread use of fossil fuels and worries about global warming, people have After extensive and in-depth research on low-carbon and environment-friendly electric vehicles [1]. Practice shows that for electric cars in particular, lithium ion batteries (LIB) with high energy density and extended cycle performance are ideal Automobile [2]. Lithium titanate battery is excellent in its stable structure, long cycle life and safety Characteristics have gradually become the focus of people's attention, showing excellent performance in the field of power energy storage The application prospect of this technology. And figure 1 illustrates the methods for the preparation of LTO battery with excellent efficiencies.

In order to further improve the practical application performance of lithium-ion batteries, it is very important to find advanced anode and cathode materials. $Li_4Ti_5O_{12}$ spinel is an excellent negative electrode material, which has excellent safety and good Cycling performance. However, it is found that the size of $Li_4Ti_5O_{12}$ has a significant impact on the battery performance. If the particle size is too large, it will reduce the ionic conductivity, and then affect the battery rate performance. Therefore, the development of $Li_4Ti_5O_{12}$ materials with small and uniform size has become the research hotspot of the negative electrode materials of LTO batteries. The emergence of nanotechnology has effectively solved this problem. By reducing the particle size of $Li_4Ti_5O_{12}$ to the nanometer level, the battery efficiency is greatly improved.

Relevant studies have proved that nano-sized $Li_4Ti_5O_{12}$ has a larger specific surface area and a higher ion utilization rate. In order to reduce the agglomeration effect of particles, it is possible to prepare excellent negative electrode materials for LTO batteries by compounding with other carbon materials. In recent years, there have been many preparation methods of nano-$Li_4Ti_5O_{12}$. Herein, the principle of nanotechnology is briefly analyzed, and the current preparation methods and application status of nano lithium titanate anode materials are summarized. The structure-activity relationship between nano lithium titanate and the performance of LTO battery was proposed, which provides a theoretical guidance for the preparation of advanced anode materials for LTO battery.

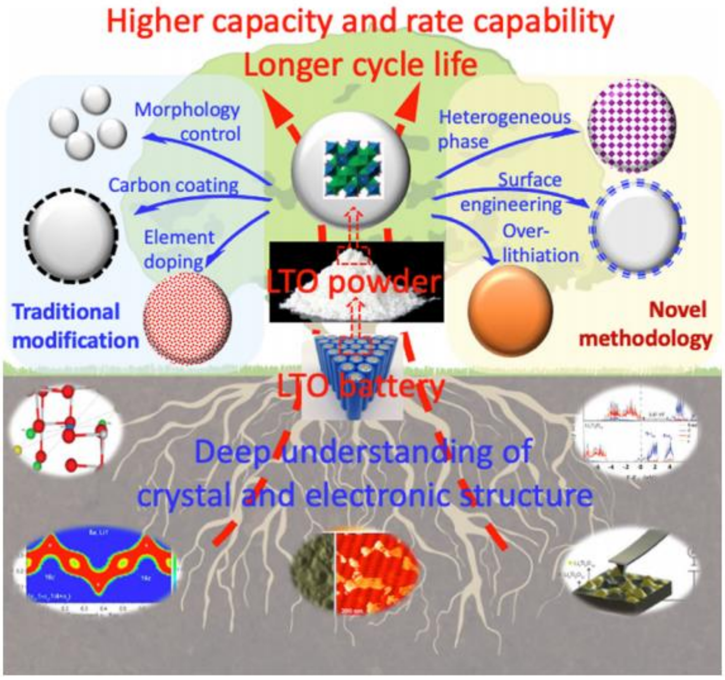

Figure 1. Relationship between $Li_4Ti_5O_{12}$ (LTO) anode's crystal/electronic characteristics, conventional and new modification techniques, and electrochemical energy storage properties is shown in a schematic.

2. Nanotechnology

Nanotechnology emerged in the middle and late 20 th century. In short, it is a technology that transforms nature within the nanometer size (10-10-10-7) and realizes material innovation by directly rearrangeing atoms and molecules. The main research object of nanotechnology is the material with a size of 1-100 nm. It focuses on observing the movement law and interaction of system composition and applies it to the treatment of practical problems, It has brought major breakthroughs to the research in many fields [3].
The fields of nano science and technology include nanosystem physics, nanochemistry, nanobiology, nanomaterials science, nanoelectronics, nanoprocessing science, and nanomechanics. As a field never involved in the past, nano technology is non macroscopic and non microscopic. This is not only a deeper understanding of the world, but also a milestone in the progress of people's natural transformation ability. On the basis of direct reduction to molecules and atoms, it will promote human science and technology into a new era.

2.1. Nanotechnology battery

The so-called nanotechnology battery is to use nanotechnology materials or manufacturing processes to produce battery products with particularly high performance in the manufacturing process of the battery. The small pore size effect and surface effect of nano materials are very related to the active materials in chemical power supply. After the active materials as electrodes are nano sized, the surface will increase, the current density will decrease, the polarization will decrease, and the capacitance will increase, thus having better electrochemical activity [4].

2.2. Classification of nanotechnology batteries

2.2.1. Nano activated carbon fiber battery

The use of carbon fibers maintains excellent mechanical strength while reducing the weight of the battery. In addition, the carbon fiber has strong corrosion resistance, ensuring that the battery will not be eroded during use, and improving the safety protection registration. This battery is mainly used in electric vehicles, electric motorcycles and electric mopeds. The battery can be recharged for 1000 times and can be used continuously for about 10 years. It only takes about 20 minutes to charge once, with a flat road journey of 400 km and a weight of 128 kg.

2.2.2. Nano solar cell

Compared with traditional solar cells, dye-sensitized solar cells have high efficiency, require less materials in the production process, resulting in low cost, and the source of materials is very rich. The process required in the production process is also very simple, and the performance is very stable. Organic polymer solar cells have good flexibility, light weight and rich material sources. The efficiency of solar light absorption can be improved by chemical modification or doping. Among them, MEH-PPV and fullerene materials have shown broad application prospects in solar cells. The third type is photovoltaic power generation solar cells. For example, doping rare earth metal elements into monocrystalline silicon can reduce the use of silicon and improve economic benefits. The fourth type is multi-component compound solar cell materials. Such materials belong to semiconductors with gradient band gaps, such as cadmium sulfide, gallium arsenide, aluminum phosphide, etc., which can expand the absorption range of solar energy spectrum.

2.2.3. Nano lithium ion battery materials

Lithium cobaltate with a layered structure is a common cathode material for lithium-ion batteries, lithium manganate and nickel cobalt manganese ternary materials, spinel structure lithium manganate and nickel manganate, and olivine structure lithium iron phosphate, lithium manganese phosphate and lithium vanadium phosphate. The use of nanomaterials in lithium-ion batteries' positive electrodes may effectively reduce the volume impact brought on by the intercalation and detachment of the batteries, shorten the lithium ions' transmission channel, and increase the rate performance and power density of batteries. Orthorhombic $LiMnO_2$ nanorod crystals were produced by Hongmeiji et al. [5] using a quick and easy temperature-controlled microwave hydrothermal process. The tiny diameter can raise the electrode power and enhance the material's electrochemical performance by reducing the time required for lithium ion and cathode material to diffuse into one another. One-dimensional porous nanotubes were created by electrospinning by Ding et al [6] for use as the cathode of lithium-ion batteries. This kind of electrode has good charge specific capacity, cycle stability and rate performance.

The application of nano materials in the negative electrode can better adjust the changes brought by the volume, and will not be powdered or destroyed after cycling. Secondly, the porous and hollow construction raises the active material's specific surface area and boosts utilisation rate. In addition, the incorporation of nanomaterials expands the negative electrode's contact area and the current collector, which can accelerate the conduction of ions and electrons, so that the battery has excellent cycle performance and rate performance.

As for membrane materials, electrospun nanofiber membranes have attracted wide attention due to their wide range of raw materials, wide working temperature range, high porosity, good liquid absorption and retention performance.

3. LTO battery

Lithium titanate is a kind of negative electrode material used in lithium-ion batteries. Lithium titanate can produce a 2.4V or 1.9V lithium-ion secondary battery when paired with positive electrode components such lithium manganate, ternary compounds, or lithium iron phosphate. It may also be used as a positive electrode to build a 1.5V lithium secondary battery with a lithium metal or lithium alloy negative electrode. Lithium titanate has the qualities of high safety, high stability, long life and environmental protection [7]. The supply market of lithium titanate battery mainly includes electric vehicles (including buses, rail transit, etc.), energy storage market (mainly including wind farms, power grid quality control and frequency control, etc.), industrial applications (including forklifts and port machinery and equipment, etc.). Altay has formed a unique core technology in the manufacture of lithium titanate batteries, which is in a leading position in the world [8]. Moreover, it has basically solved the most prominent problem affecting the application of lithium titanate batteries - gas inflation. The fourth generation 65 Ah single lithium titanate battery produced by the company has been applied in the energy storage system. After tens of thousands of cycles, its capacity has no obvious attenuation. In terms of system application, the protera hybrid electric bus produced by the company for California has been running for more than 10 years, and the overall application is in good condition. The fuel economy index of the bus is 106.4 kg/L, which is far higher than the 23.8 kg/L of the traditional diesel generator. In addition, the company has also supplied 1MW storage system to the wind power plant in Hawaii to realize grid connection with the local power grid. The lithium titanate energy storage system is mainly used to regulate the corresponding voltage fluctuation of renewable energy, so that the load change rate of the unit is controlled within 1MW/min. For AES, the energy enterprise, Austria titanium has provided two sets of storage systems for grid frequency modulation energy, which have been running for nearly 10 years. The 1MW energy storage unit produced by Aoti is the only lithium titanate battery product that has been used for more than five years in the United States power grid. The energy storage system has gone through more than one million cycles, the system capacity loss is about 3%, and the power does not show obvious attenuation.

3.1. Advantages of LTO battery

3.1.1. Good safety and stability

Due to the high intercalation potential of lithium titanate negative electrode material, the generation and precipitation of metal lithium are avoided during the charging process, and because its equilibrium potential is higher than the reduction potential of most electrolyte solvents, it does not react with the electrolyte and does not form a solid-liquid interface passivation film, which avoids many side reactions and greatly improves the safety. Like electric vehicles, the safety and stability of energy storage power stations are the most important indicators [9].

3.1.2. Excellent fast charging performance

Too long charging time has always been an obstacle difficult to overcome in the development of electric vehicles. Generally, slow charging pure electric buses are used, and the charging time is at least 4 hours. Many pure electric passenger vehicles have a charging time of up to 8 hours. The lithium titanate battery can be fully charged in about ten minutes, which is a qualitative leap over the traditional battery.

3.1.3. Long cycle life

Lithium titanate, $Li_4Ti_5O_{12}$, face centered cubic spinel structure. The intercalation and deintercalation of lithium ions during charging and discharging have little effect on the structure of lithium titanate material, because the crystal structure of lithium titanate has hardly changed, and the value only increases from 0.836 nm to 0.837 nm. Therefore, lithium titanate is also called "zero strain material". This attribute is crucial for the electrode material because it prevents structural changes brought on by the expansion and contraction of the material throughout the charge and discharge process. This enhances the huge attenuation of the electrode's capacity and lengthens the battery's useful life.

3.1.4. Good temperature resistance

Lithium titanate has a chemical diffusion coefficient that is orders of magnitude greater than carbon negative electrode materials. High diffusion coefficient means that lithium titanate has faster and more cycle charge and discharge times than other carbon negative electrode materials. Lithium itself cannot provide a lithium source, so it can only be matched with electrode materials containing lithium. The only permitted negative electrode materials when using lithium titanate as the positive electrode are metal lithium or a lithium alloy. The battery's voltage right now is around 1.5V. A battery with a voltage of roughly 3V may be created using lithium titanate as the negative electrode and a positive electrode material like lithium cobalt oxide. Although both a negative and a positive electrode may be made using lithium titanate, the potential relative to Li^+/Li is 1.5V, so there are not many studies and applications as a positive electrode material. Spinel structure has a unique three-dimensional lithium ion diffusion channel, so lithium titanate is also excellent in high and low temperature performance.

3.2. Application of LTO battery

$Li_4Ti_5O_{12}$ spinel has a cubic structure and belongs to the space group FD3m. Li atoms are present in every tetrahedral 8a site and one-sixth of the octahedral 16d sites in this structure. Ti atoms occupy the remaining five-sixths of the 16d position, while oxygen atoms are found at the 32e sites. $Li_4Ti_5O_{12}$ cells have a theoretical capacity of 175 mAh/G because each cell may support three Li ions in the two-phase Faraday process with regard to Li / Li^+ at a flat potential of roughly 1.55V. This reaction results in a topological change from spinel $Li_4Ti_5O_{12}$ to rock salt type $Li_7Ti_5O_{12}$ when the three inserted lithium ions and tetrahedrally coordinated lithium ions relocate to occupy the nearby 16C octahedral positions (Figure 2.). Compared with other anode materials, one of the greatest advantages of$Li_4Ti_5O_{12}$ is that during the lithiation process.

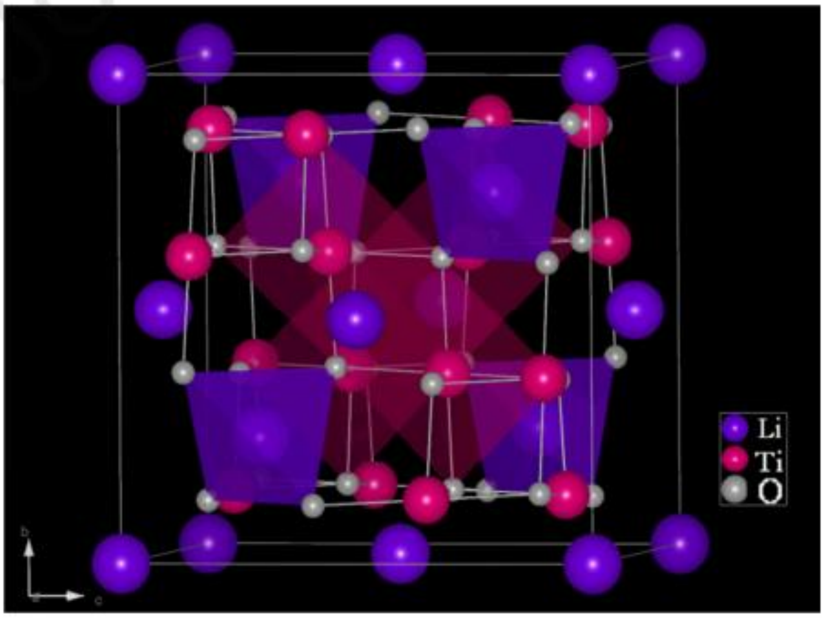

Figure 2. Crystal structure diagram of $Li_4Ti_5O_{12}$ [10].

$Li_4Ti_5O_{12}$ nanoparticles have been synthesised using a variety of techniques up to this point, including sol-gel, molten salt, microwave, hydrothermal, and solvothermal synthesis. These techniques may produce nanoparticles with a restricted size distribution and have strong stoichiometric control, a reduced calcination temperature, and a comparatively quick processing time. $Li_4Ti_5O_{12}$ nanoparticles with different morphology can be prepared by controlling the parameters in the preparation process. Such as zero dimensional nanoparticles, nanowires and nanosheets. Dual-phase lithium titanate nanowires are easily synthesised as anode materials for lithium-ion batteries by Jie et al. To enhance the lithium storage capabilities, Tian et al. [11] created $Li_4Ti_5O_{12}$ anodes using an easy two-phase production technique and a nanostructure engineering method. By using crystallised water of lithium hydroxide to hydrolyze tetrabutyl titanate under high temperature and pressure conditions, Zhang et al. [12] created dual-phase $Li_4Ti_5O_{12}/TiO_2$ (LTO/TO). According to Tran et al, we used LiOH and $Ti(OBu)_4$ as precursors in a solution method to synthesis the nanoscale spinel $Li_4Ti_5O_{12}$.

3.3. Challenges faced by LTO

The application of nano electrode materials in batteries has shown superior performance, making the performance of traditional batteries reach a new high. Now, both pure nano materials and nano composite electrode materials can effectively improve the battery capacity or electrical cycle performance. At the same time, nano electrode materials have unfavorable factors such as uneven particle size, agglomeration, and high manufacturing cost, which are the problems to be solved in the future. However, we believe that the development of this technology will certainly drive the rapid development of the power supply market, and at the same time, it will greatly promote the market demand for new batteries with large capacity and high performance in the future.

4. Conclusion

The appearance of LTO battery technology has greatly promoted the development of new energy vehicles. The development of safe and efficient LTO battery devices has become the main direction of future development in this field. Lithium titanate is a commonly used negative electrode material in LTO. Its zero strain characteristic gives the battery a very slow capacity decay rate. In order to improve the recycling stability of the negative electrode materials and reduce the growth of lithium dendrites, the development of lithium titanate negative electrode materials with nanometer size has become a research hotspot. Researchers have developed many methods to prepare nanoscale lithium titanate, which dose not include traditional sol-gel, molten salt, microwave, hydrothermal and solvothermal method, but the newly developed dual-phase et al.Although the emergence of nanotechnology provides a new idea for the development of LTO technology. But there are still some challenges:

(i)It is very challenging to realize the transition from the laboratory research and development stage to the industrial and practical stage in the synthesis of nanoparticles.

(ii)The high surface energy, interface energy and defect formation energy of nanomaterials may lead to side reactions with electrolyte

(iii)In general, the density of materials composed of nano powders is lower than that of materials composed of microns, and the increase of the volume of material electrodes with the same quality reduces the volume energy density.

It has been proved by many researchers that there is a consensus on the improvement of discharge specific capacity by the nanoization of electrode materials. However, in the microstructure of nanomaterials, such as: particle size, morphology and lithium intercalation position versus capacity and electrode process. In terms of the impact of the battery cycle life, it needs further research.

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