

Research Progress on the Modification of Lithium Titanate Anode Materials

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Abstract. Along with the advancement of the global "carbon neutrality" goal, the rising demand for lithium-ion batteries in electric vehicles, energy storage systems, and other fields, and the restrictions of traditional graphite anodes such as lithium dendrite growth, low rate performance and short cycle life, the research of new anode materials is unequivocally imperative. Lithium titanate (LTO) is a promising material with its "zero-strain" structure, high capacity of lithium insertion, wide temperature tolerance and extremely long cycle life. However, its low lithium-ion diffusion rate and electronic conductance have restricted its practical application. Scientists have developed several modification techniques to break this limitation. On the coating modification aspect, carbon coating can physically disperse LTO particles, suppress grain agglomeration and overgrowth, and reduce direct contact between the particles and the electrolyte, therefore lowering the side reaction frequency. Ion doping can adjust its electronic structure and crystal defects, in effect enhancing electronic conductivity and lithium-ion diffusion rate. Structural nanosizing may shorten the ion transportation route and increase the contact area between the electrode and electrolyte. This thesis summarizes the recent studies on LTO anode material modification in the expectation of offering a reference for future high-performance LTO material development.

1 Introduction

With the enhancement of international environmental protection awareness and the advancement of the global "carbon neutrality" goal, lithium-ion batteries, as the key clean energy storage devices, have witnessed a steady increase in demand in electric vehicles and mega-scale energy storage systems. The development of advanced-performance lithium-ion batteries is a significant means to reduce reliance on traditional fossil energy and promote the development of the energy industry [1].

Graphite is widely employed as the anode material in lithium-ion batteries at present. However, there are several drawbacks in this material while charging and discharging, for example, it develops lithium dendrites (with short circuit risk), exhibits poor rate capability (not able to satisfy the requirements of quick charging), and has limited cycle life (typically less than 1000 cycles) [2]. For the purpose of overcoming this bottleneck, the development

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of innovative high-safety, long-cycle-life, and high-rate-performance anode materials has emerged as a research focus and an urgent market need in the battery field.

Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) is a highly promising new anode material with a unique "zero-strain" crystal structure that whose volume change rate is as low as only about 0.2% during charging and discharging, which provides it with ideal cycling stability and an exceptionally long lifespan. However, its lithium-ion diffusion coefficient and electronic conductivity are extremely low, leading to severe capacity degradation at high current density. To solve these issues, scientists have developed a series of optimization techniques, including coating modification, ion doping, and nano-structural, which have been able to significantly improve the electrochemical performance of LTO [3]. For instance, Liu H et al. prepared a lithium titanate/reduced graphene oxide (LTO@rGO) composite, which showed outstanding cycling stability and rate performance [4]. Guo J et al. prepared F-doped LTO materials and found that F doping improved the charge transfer rate for charging and discharging, thereby lowering the degree of electrochemical polarization at high current densities [5]. This thesis summarizes the latest study progress on the modification of anode material for lithium titanate, with the aim of providing references for the subsequent development of high-performance LTO material.

2 The crystal structure and electrochemical properties of LTO

The crystal structure of LTO is spinel structure, which belongs to the family of face-centered cubic crystals. Its space group is $\text{Fd}\bar{3}\text{m}$, and the lattice constant is approximately 0.836 nm. Among them, oxygen atoms occupy 32e sites and are cubic close-packing. 3/4 of the lithium ions occupy tetrahedral 8a sites. Titanium ions and the remaining Li ions occupy octahedral 16d sites in a random way at an atomic ratio of 5:1. Such a structure forms a three-dimensional ionic channel for ion transport, allowing rapid insertion and extraction of lithium ions.

LTO's lithium-ion battery possesses relatively high lithium-intercalation potential, which can effectively inhibit the growth of lithium dendrites and reduce the risk of battery thermal runaway. Moreover, it also possesses superb low-temperature adaptability and can operate stably in a wide range of temperatures from -30°C to 60°C [1, 2, 6]. Under normal state operation, its cycle life is greater than 10,000 and can be even more than 50,000 in optimized systems, far greater than that of graphite anodes (commonly between 1,000 and 2,000). Lithium titanate as the perfect anode material, though with low theoretical capacity, its high reversibility ensures minimal capacity decay on overcharging and overdischarging of lithium titanate batteries. Therefore, the utilizable capacity of lithium titanate is practically in conformity with theoretical capacity [7].

3 LTO modification method

3.1 Coating Modification

3.1.1 Carbon coating

The basic process of carbon coating is the uniform mixing of LTO powder or precursor with a carbon source (such as glucose, asphalt and graphene) and then subjecting it to high-temperature heat treatment (typically from 400°C to 800°C). This triggers the formation of an uninterrupted carbon film on the surface of LTO particles. This carbon layer can physically isolate LTO particles, inhibit grain agglomeration and overgrowth, and reduce direct contact between the particles and electrolyte, thereby lowering the rate of occurrence

of side reactions (such as electrolyte decomposition). Amorphous carbon, graphene, and carbon nanotubes are the most commonly employed carbon-coated materials in present studies.

Liu H et al. used different mass concentrations of graphene oxide (GO) as the source of carbon [4], mixed it with LTO powder, and underwent high-temperature reduction to prepare a reduced graphene oxide-coated lithium titanate (LTO@rGO) composite material, and conducted performance testing on it. The data showed that rGO coating did not change the spinel structure of LTO. The composite material was mainly made up of C, O, and Ti elements. At GO mass concentration of 2 mg/mL, the electrochemical properties of the composite material were optimal - the initial specific capacity could reach a record maximum of 168 mAh·g⁻¹ at 1C, and the capacity retention rate after 50 cycles was as high as 98.3%; interfacial charge transfer impedance (R_{ct}) was much lower than that of pure LTO, with excellent cycling stability and rate performance. Graphene has a rich content of oxygen-containing functional groups, and with the combination of surface functional groups of LTO, it will be bonded to create a stable structure to improve the interface problem of LTO with the electrolyte but not just the performance of the material itself.

3.1.2 Oxide coating

The main function of oxide coating films (such as Al₂O₃, TiO₂ and LiNbO₃) are physically to protect LTO from the electrolyte, preventing the electrolyte from oxidative decomposition at elevated potentials. Simultaneously, it guides the formation of a thin and stable solid electrolyte interface (SEI) film and reduces impedance. For high-ionic-conductivity and electron-conductivity coating materials like LiNbO₃, it is able to construct "fast lithium-ion-electron transmission channels" on the surface of LTO to reduce charge transfer impedance and maintain its electrochemical performance at high-rate conditions.

Jeong E M et al. first prepared TiO₂-coated LTO (LTO@TiO₂) composite materials [8], then transformed the surface TiO₂ into a 1.6 nm thick partial lithiated titanium dioxide (Li_xTiO₂, x ≈ 0.5) coating layer. The specific capacity of LTO@Li_xTiO₂ was 174 mAh·g⁻¹ at 0.05C rate, approaching the theoretical specific capacity of LTO (175 mAh·g⁻¹). The capacity retention rate was 82.2% at 20C high rate. The capacity retention rate was 95.2% after 400 cycles at 1C rate, and it could also discharge steadily at -10°C in a low-temperature environment. Li_xTiO₂, an ion-electron mixed conductor, could realize simultaneous effective electron and lithium ion conduction, enabling LTO@Li_xTiO₂ to exhibit superior performance.

3.2 Ion doping

3.2.1 Metal ion doping

Metal ion doping (such as La³⁺, Mg²⁺ and Al³⁺) can improve the performance of LTO in two aspects - "lattice distortion regulation" and "carrier concentration enhancement". On the one hand, the substitution of Li⁺ or Ti⁴⁺ in the LTO lattice with divalent metal ions can form lattice defects and expand lithium ion transport channels. On the other hand, the outer electrons of the metal ions can increase the free electron concentration of LTO and thereby enhance electronic conductivity.

Gui F et al. utilized La³⁺ doped two-dimensional Li₄Ti₅O₁₂ nanosheets (La-LTO NSs) as inorganic fillers and introduced them into polyethylene oxide (PEO) based polymer electrolytes to obtain composite polymer electrolytes (CPEs) [9]. The study found that La doping made LTO NSs have high aspect ratios and oxygen vacancy characteristics, which not only significantly increased the amorphous fraction of the PEO matrix but also fixed

TFSI⁻ anions through oxygen vacancies. DFT calculation indicated that high charge density enrichment at the La element and oxygen vacancies, enhancing interfacial interaction between La-LTO NSs and PEO/TFSI⁻. This composite electrolyte constructed a number of lithium ion channels of "La-LTO NSs/PEO interface-PEO chain-La-LTO NSs" with fast lithium ion transmission and a reliable electrode-electrolyte interface.

3.2.2 Non-metallic ion doping

Non-metallic ion doping (such as F⁻, N⁻ and S²⁻) mainly focuses on the substitution of O²⁻ in the LTO lattice, modifying the electronegativity of the crystal as well as the interatomic distance. On the one hand, introducing non-metallic ions can increase lattice defects and provide additional transmission sites for lithium ions. On the other hand, the difference of electronegativity can regulate the electronic structure of LTO and enhance the electronic conductivity. Among them, F⁻ is the most widely researched non-metallic doping species due to its identical ion radius to O²⁻.

Guo J et al. prepared F⁻ doped LTO materials and studied the influence of F⁻ doping content on the performance of the material [5]. It was discovered that when the F⁻ doping content (atomic ratio) was 0.01, LTO performed optimally. At the rate of 1C, the initial specific capacity was 218.88 mAh·g⁻¹, which was superior to pure LTO (165 mAh·g⁻¹). Following 200 cycles, the capacity retention ratio was 93.27%, 7.87 percentage points greater than that of pure LTO. Following 500 cycles, the capacity retention ratio still amounted to 88.74%, while pure LTO was only 66.16%. With the increasing content of F doping, the electrochemical transfer impedance of the material rose gradually but remained lower than that of pure LTO. It implied that F doping accelerated the charge transfer rate of the material during charging and discharging, which could alleviate the electrochemical polarization degree under high current density.

3.3 Nanotechnology design

LTO's electron transfer efficiency and ion diffusion rate are significantly affected by the "transmission path length". By constructing nano-scale morphologies can realize the shortening of lithium ion transmission path, the enlargement of electrode-electrolyte contact area and the alleviation of volume stress. For one thing, the transmission path of the nanostructure is only 1/10 to 1/100 of that of micro-scale LTO, significantly reducing the diffusion resistance of lithium ions. For another, the high specific surface area can increase the contact points between conductive agents and LTO particles, reducing the electron transfer impedance. In addition, the nanoparticles can accommodate the minor volume stress during charging and discharging through elastic deformation and particle rearrangement, avoiding particle fragmentation and interface failure.

Yang W et al. prepared lithium titanate nanotubes with well-opened structures and good adhesion to the substrate via combining anodic oxidation and lithiation annealing [10]. They prepared well-shaped TiO₂ nanotube arrays through controlling the anodic oxidation voltage, oxidation time, and concentration of fluoride ions. Later on, they fabricated lithium-ion sieves via lithiation annealing and acid treatment. The experimental results showed that in an EG-based electrolyte with 0.5 wt% NH₄F, at the anodic oxidation voltage of 40V and oxidation time of 3h, a well-shaped and tightly adhered nanotube array could be obtained. Lithium titanate retained the nanotube shape after lithiation annealing treatment. In addition, after acid washing, the mean pore size grew from 50 nm to 65 nm.

4 Challenges and development

LTO has become a crucial choice of anode material in applications from electric vehicles to grid-scale energy storage due to its ultra-long cycle stability with the "zero strain" structure, high safety with the high lithium-ion insertion potential, and excellent low-temperature fitness. In the aspect of the intrinsic problem of poor intrinsic electron transportation efficiency of LTO, the subject field has progressed largely by way of coating modification, ion doping, and nanotechnology design, but numerous bottlenecks still exist in practical application.

In the process of carbon coating, volume variations of LTO particles will result in cracking of the carbon layer. In the case of long cycling times, the carbon layer has a tendency to be oxidized by the electrolyte, causing a gradual increase in interface impedance. For oxide coating, the insulating oxide coating layer will impede electron transmission, and uneven distribution of Li^+ is likely to occur in the production process, so that some areas lose transmission function and some areas experience lattice distortion. Doping modification also has many problems. If the doping dosage is over a specific value, the divalent metal ions will damage the "cubic symmetry" of the structure of the spinel. The "second phase" produced by agglomeration of the ions in the LTO lattice will block electron transmission. At low temperatures, the difference in electronegativity will increase the resistance to transmission of Li^+ , resulting in a low capacity retention rate. In addition, the surface energy of nano-LTO is extremely high, and in the process of drying, sintering, or electrode production processes, "secondary aggregates" will be formed, which will rather restore the Li^+ transmission channel to the micrometer level. High specific surface area will lead to an increase in the amount of Li^+ consumed for the formation of the SEI film, and the SEI film prefers being damaged by particle agglomeration and rupture, repeatedly regenerating and further consuming Li^+ , leading to capacity degradation. Loose stacking of nanoparticles and low bulk density lead to a loss of volumetric energy density of the electrode.

In the future, studies on LTO modification will use multi-strategy cooperative modification to form a "coating-doping-nanocrystallization" composite system, for instance, the structure "La³⁺ doped LTO nanosheets@rGO", with lattice control, surface conductivity and surface morphology optimization. Besides, the technology of continuous production can be optimized, for example, using radio frequency magnetron sputtering technology and rapid annealing treatment to prepare three-dimensional Sn-SnO₂/Li₄Ti₅O₁₂ composite film anode materials [11]. Apart from that, for high-rate, fast-charging applications, "carbon coating-nanoparticle LTO" can be designed to achieve a correct balance of performance and cost.

5 Conclusion

Lithium titanate is renowned as a "zero-strain" material due to its unique structural characteristics. It possesses better cycling performance in conventional anode materials and is appropriate for application in such high-growth technology applications like electric vehicles and energy storage systems. In order to improve the lithium-ion diffusion coefficient and electronic conductivity of lithium titanate batteries, scientific studies have made good advancements.

Currently, the most common methods of increasing the conductivity of lithium titanate are three in number. The first one is to modify the surface by coating with conductive material, thereby enhancing the electronic conductivity and the electronic connection between particles and the material conductivity. The second one is an ion-dopant, which basically strengthens the conductivity of Li^+ during charging and discharging and thus enhances the electrochemical performance of the material. The third one is nanomization, by using

different preparation routes to prepare nano-sized lithium titanate material, therefore shortening the path of transmission for lithium ions in lithium titanate.

Although these modification methods have significantly improved the electrochemical properties of LTO, their practical application in industry continues to be plagued by several challenges. The carbon coating layer, for instance, tends to crack, peel, and oxidize, which can hinder electron transmission and cause uneven distribution of Li^+ . The ions would tend to accumulate in the LTO lattice to form "second phases," and nano-LTO would be prone to the development of "secondary aggregates" upon drying, sintering, or electrode preparation processes.

Future research on the enhancement of LTO performance can be mainly focused on constructing multi-strategy collaborative modification systems to compensate for the shortage of a single modification strategy. Additionally, the continued optimization of continuous production technologies can render nano-LTO preparation less expensive and promote its large-scale production applications. With the constant breakthroughs in the modification technologies and the industrialization processes becoming mature, LTO will see widespread applications in mid-to-high-end energy storage and low-temperature electric vehicles, and become an important supplement to lithium-ion battery anode materials.

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