# Spinel Lithium Manganese Oxide Modification Methods

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Abstract: Lithium-ion batteries (LIBs) are an excellent new generation of green, environmentally friendly, and renewable chemical energy sources. The positive electrode material is a crucial component in the production of LIBs. $LiMn_2O_4$ enjoys the benefit of being sourced from plentiful resources, high energy density, affordable pricing, zero emissions, and superior safety. Spinel lithium manganese oxide belongs to the cubic crystal system. Thanks to its three-dimensional tunnel structure, lithium ions can deintercalate within the spinel lattice without inducing structural collapse, allowing for reversible processes. This characteristic makes it one of the most promising positive electrode materials. $LiMn_2O_4$ stands out as a highly promising cathode material for lithium-ion batteries and finds extensive application in electric vehicles and energy storage devices. Additionally, the thermal stability and electrochemical performance of $LiMn_2O_4$ are excellent, enabling stable operation under high temperature and high current conditions. Its preparation process is relatively simple and cost-effective, making it easy to achieve large-scale production. As a highly promising LIBs cathode material, $LiMn_2O_4$ is commonly employed in electric vehicles and energy storage systems. It is expected to further promote the development and application of lithium-ion battery technology in the future, providing strong support for achieving greener and more sustainable energy solutions.

## 1 INTRODUCTION

### 1.1 Research Background

In the era of the low-carbon economy, LIBs are gradually most used batteries of the 21st century owing to their relatively high energy density. As a key component of LIBs, the efficiency of the positive electrode material significantly impacts the overall performance of the battery. Research on positive electrode materials for LIBs involves multiple disciplines such as chemistry, physics, materials science, energy, and electronics. The progress in this field has attracted great interest from the electrochemical and chemical power industries. With the continuous advancement in electrode material preparation methods, structure determination, performance improvement, and related theoretical research, it is expected that finding synthetic methods with easily controllable preparation conditions, simple operation, and feasible doping and composite approaches will strongly promote the research and application of LIBs. Modification can improve the electrochemical performance of $Mn_2O_4$, such as enhancing its electrical conductivity, lithium-ion diffusion rate, and stability, thereby increasing the battery's cycle life and energy density. Through modification, the structural stability of $Mn_2O_4$ can be enhanced, suppressing its volume expansion and structural damage during charge and discharge processes, thus improving the battery's cycle life and safety. Additionally, modification can control the crystal structure of $Mn_2O_4$, such as altering grain size, morphology, and crystallinity, optimizing its electrochemical performance, and enhancing the battery's performance stability and cycle life. Some modification methods can increase $Mn_2O_4$'s conductivity, such as conductive additive or composite materials, thereby reducing internal resistance and improving charge and discharge efficiency. Some modification methods can also reduce production costs, for example, by using inexpensive materials or simplifying production processes, making $Mn_2O_4$ positive electrode materials more competitive.

Traditional LIBs positive electrode materials, such as $LiCoO_2$, NCM, and NCA, though performing well in battery applications, also have some issues. The limited availability and high cost of metals such as cobalt and nickel in traditional positive electrode materials restrict large-scale commercial

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applications, leading to high battery costs. Moreover, safety concerns arise from the cobalt element present in positive electrode materials like lithium cobalt oxide, which can lead to thermal runaway reactions under high temperature or overcharging conditions, posing safety hazards. Traditional positive electrode materials also experience capacity decay during long-term charge and discharge cycles, mainly due to structural changes in the positive electrode material, electrolyte decomposition, and solid-liquid interface reactions. The cycle life of positive electrode materials is influenced by several factors，including the structural stability of the material and the stability of the electrolyte-electrode interface, which can result in decreased battery performance after prolonged cycling. Moreover, the specific capacity of traditional positive electrode materials is generally between 20-200 mAh/g, which cannot meet the requirements of high-energy-density batteries, limiting the potential for performance improvement.

The primary substance employed as a the positive material in LIBs is an intercalation compound formed by lithium and transition metal oxides，with spinel lithium manganese oxide being the most common. In the field of LIBs, spinel lithium manganese oxide is preferred due to its high energy density and extended cycle life, and relatively high electrochemical stability, finding widespread applications in portable electronic gadgets, electric automobiles, and energy storage grids, etc. Although commercial LIBs mainly use lithium cobalt oxide as the positive electrode material, the development and production of its utilized as a positive electrode material are of great significance for cost reduction and fully utilizing abundant, inexpensive natural resources.

Although spinel lithium manganese oxide has significant advantages in the realm of lithium-based batteries, its stability is somewhat lacking. Unmodified $Mn_2O_4$ positive electrode materials in lithium-ion batteries may encounter some issues: the relatively low electrical conductivity of pure $Mn_2O_4$ results in slow electron transfer rates, limiting the battery's powering up and draining rates and performance. The crystal structure of $Mn_2O_4$ may limit the diffusion rate of lithium ions within the material, resulting in slower reaction rates during charge and discharge processes, affecting the battery's power performance. During charge and discharge cycles, $Mn_2O_4$ materials undergo volume expansion and contraction, which may lead to structural damage and pulverization, thereby affecting the battery's cycle life and stability. $Mn_2O_4$ materials may experience capacity decay and structural damage during long-term cycling, leading to decreased battery performance and reduced cycle life. Additionally, the specific capacity of $Mn_2O_4$ is generally relatively low, unable to meet the requirements of certain high-energy-density batteries, limiting the performance development space of batteries. Therefore, improving its performance through doping and modification methods is a feasible direction. If these challenges can be successfully overcome, spinel lithium manganese oxide, as an excellent positive electrode material for LIBs, will demonstrate broad application prospects in renewable energy, intelligent gadgets, electric cars, energy storage solutions.

### 1.2 Energy Storage Principle

As a positive electrode material for LIBs, spinel lithium manganese oxide, its energy storage mechanism relies on the diffusion and migration of lithium ions between the positive and negative electrodes during the charge and discharge cycles of the battery. Throughout the charging phase，lithium ions migrate from the electrolyte to the spinel lithium manganese oxide lattice structure, leading to an increase in lithium ion count in the material and an increase in the battery voltage until it reaches full charge. During discharge, lithium ions deintercalate from the spinel lithium manganese oxide structure, leading to a gradual decrease in battery voltage, while releasing energy and converting it into electric current to provide power to the external circuit. When all lithium-ions are deintercalated from the positive electrode material, the battery is in an empty state. The basic principle of energy storage for $LiMn_2O_4$ is the diffusion and migration of Li movement between the cathode and anode during the charging and discharging processes, thereby storing and releasing electrical energy. It has the advantages of high energy density, high efficiency, and long cycle life, so it is widely used in LIBs, energy storage systems, and other electrochemical fields.

## 2 CHARACTERISTIC OF $LiMn_2O_4$

### 2.1 Morphology and Structure of Spinel LiMn2O4

As a key LIBs cathode material, Spirel-type lithium-type manganate ($LiMn_2O_4$) has a cubic crystal structure and a space group of Fd-3m (Jian et al., 2018). The crystal cell parameter is a = 8.142 Å, and each crystal cell contains 8 $Mn^{3+}$ ions and 16 $Li^+$ ions. In the crystal structure, lithium ions and Mn ions occupy the octahedral and tetrahedral voids respectively, forming a structure similar to spinel.

Spine-type lithium manganate has a variety of morphology, and different preparation methods can control its morphology. Common morphologies include spherical, rod-shaped, laky and nanowire-like. The differences in these morphologies are mainly due to factors such as preparation conditions, methods, types and proportions of reactants. By adjusting the morphology of spirel-type lithium manganate, its electrochemical properties, charge and discharge characteristics and cyclic stability can be adjusted (Zhang, 2021).

Spherical spinite-type lithium manganate is often used in the preparation of composite cathode materials, possessing a substantial surface area and outstanding electrochemical characteristics; rod-shaped spine-type lithium manganate is usually used in high-power lithium-ion battery cathode materials, with good electrical conductivity and fast ion transmission rate; sheet-shaped lithium manganate can improve electrode filling Charging density, which enhances the mechanical stability of materials, is suitable for high-capacity LIBs; nano-wired spinel-shaped lithium manganate can increase the electrode surface area and ion transmission rate, improve cycle performance and stability, and is suitable or lithium-ion batteries characterized by both high power and high energy density (Cen et al., 2021).

## 2.2 Preparation Method of Lithium Manganate of Spine

Solid-state reaction method: This method uses solid-state reactions at high temperatures to generate spinite-type lithium manganese salts and lithium salts. It is usually necessary to calcine the reaction product at high temperature to improve its crystallinity and purity. Although it requires high temperature and long-term reaction, it is suitable for mass production (Guo et al., 2019).

Hydrothermal method: Under high temperature and high pressure conditions, spine-type lithium manganate is generated by hydrothermal synthesis. By adjusting the reaction ratio, reaction time and reaction temperature and other conditions, the structural characteristics such as the morphology and crystal size of the material can be controlled. This method has high preparation efficiency and controllability.

Solvent thermal method: This method is to react manganese salt with lithium salt in an organic solvent to form a spinerite-type lithium manganate. Compared with the solid reaction method and the hydrothermal method, the solvent heat method has a lower reaction temperature and a shorter reaction time, and can control the structural characteristics such as the morphology and crystal size of the material. This method has high preparation efficiency and controllability (Guo et al., 2019).

Other methods: There are also other synthesis methods, such as coprecipitation process, microwave method, vapor deposition method, etc. These methods have their scope of application, and appropriate methods can be selected according to the research needs.

## 2.3 Application Prospect of Spinel Lithium Manganate

As a positive material for lithium-ion batteries, Spire-type lithium manganate ($LiMn_2O_4$) shows important application prospects in the fields of wearable devices, smart homes, electric automobiles and energy storage solutions.

In the field of electric vehicles, with the increasing global attention to environmental protection, the electric vehicle market is developing rapidly. Spine-type lithium manganate is widely used in the field of electric vehicles with its high energy density, long cycle life and cost advantages. At the same time, as components of the energy storage setup, the spinet-type lithium manganate is also favored in the fields of home energy storage infrastructure, photovoltaic energy storage infrastructure and wind power energy storage system because of its high discharge voltage platform, excellent circulation performance and fast charging and discharge characteristics.

In terms of wearable electronic products, with people's attention to health and the rapid rise of the wearable device market, spinel lithium manganate, as a battery cathode material suitable for small electronic devices, is favored for its high energy density and long cycle life. It is widely used in the field of wearable devices such as smart watches, smart bracelets and smart glasses (Abaas et al., 2020).

As an excellent lithium-ion battery cathode material, spine lithium manganate has a wide application prospect in the future in the fields of renewable energy, intelligent equipment, electric cars and energy storage facilities

# 3 MODIFICATION METHOD OF LIMN$_2$O$_4$

## 3.1 Doping Modification

Doping modification stands in an efficacious manner approach to enhance the electrochemical behavior of spinel lithium manganese oxide. Through the introduction of dopant elements, regulating the crystal structure and electrochemical traits of spinel lithium manganese oxide can enhance its lithium-ion diffusion rate, electrical conductivity, structural stability, and cycling performance. Doping modification can introduce dopant elements into the spinel lattice of manganese oxide, occupying the octahedral or tetrahedral voids in the crystal structure, thereby changing the electronic structure and charge distribution of the material, and optimizing its electrochemical performance. Commonly used doping elements include transition metal ions, alkali metal ions, alkaline earth metal ions, rare earth metal ions, and non-metallic elements. Doping modification can increase the electrical conductivity of spinel lithium manganese oxide, reduce the diffusion resistance of lithium ions, and improve the charge and discharge rate and power performance of the battery. Doping modification can stabilize the spinel structure of lithium manganese oxide, suppress its volume expansion and structural damage during charge and discharge cycles, and improve the cycle life and stability of the battery. Doping modification can optimize the crystal structure of lithium manganese oxide, control the grain size, morphology, and crystallinity of the material, and improve its electrochemical performance and energy density. Doping modification additionally allows for the adjustment of the redox potential and charge transfer kinetics of LIBs, optimizing the charge and discharge voltage platforms, thus enhancing the energy utilization efficiency and rate performance of the battery.

Metal and non-metal doping is a prevalent tactic aimed at enhancing the galvanic process characteristics of LiMn$_2$O$_4$ cathode materials. These doped elements include metal elements such as cobalt (Co), nickel (Ni), copper (Cu), and non-metallic elements such as fluorine (F), phosphorus (P) and silicon (Si). Through doping, the crystal and electronic structure of lithium manganate can be changed, thus improving its electrochemical properties (Li, 2022). In addition to the physical and chemical properties of the material itself, the preparation process is also a key factor, which can be used to improve the stability and capacity decay rate of the material. Research shows that the prepared material has the advantages of uniform particle size, high crystallinity and large specific surface area, which can effectively improve its electrochemical activity. Therefore, while adopting the element doping strategy, it is usually necessary to optimize the synthesis method and process.

The solid-phase method conducted at elevated temperatures involves the preparation of spinel-type lithium manganate cathode materials after mixing raw materials in a certain proportion and after many high-temperature calcination and grinding processes. The sol-gel method typically employs citric acid as a complexing agent to prepare materials through stirring., dissolving, drying and curing, grinding into powder, calcination heat treatment and other steps. In contrast to the thermal solid-state processing approach., the wet chemical method of sol-gel synthesis offers advantages such as lower solution viscosity, improved uniformity, and enhanced quantification and the preparation conditions are relatively mild (Cen et al., 2021).

Using Li$_2$CO$_3$, Mn$_3$O$_4$ and SiO$_2$ as raw materials, a series of Si-doped LiMn$_2$-xSi$_x$O$_4$ (x=0,0.005,0.010,0.020) positive electrode materials were synthesized using the high-temperature solid-state approach. The research the outcomes demonstrate that Si$^{4+}$ 的、doping has no effect on the initial spine composition of the sample, but the lattice constant increases along with the rise of silicon doping, optimizing the crystal structure. The charge and discharge performance test shows that Si$^{4+}$ doping effectively improves the initial discharge ratio capacity of lithium manganate. At room temperature and 0.2 C, along with the rise of silicon doping, the initial discharge ratio capacity of the sample is increased from 122.5 mAh/g to 127.7mAh/g. It shows the best cycle stability at x=0.010. The capacity retention rate post 100 cycles under ambient conditions and 1C is 94.30%, and the retention of capacity post 50 cycles at high temperature 55℃ and 1C is as high as 89.08% (Lu et al., 2023).

The sol-gel method is used to analyze lithium dihydrate acetate and manganese tetrahydrate acete as lithium and manganese sources, and ethyl silicate as silicon sources to prepare spinite-type lithium manganese cathode materials. XRD and XPS spectra show that Si$^{4+}$ has successfully replaced part of the Mn$^{4+}$ in the lattice, resulting in a slight contraction of the lattice and producing a small amount of impurity peaks, indicating that the silicon element has not been completely doped and Li$_2$SiO$_3$ has been generated. At 10mA/g current density and 1.5-4.8V voltage, the initial discharge ratio capacity of the sample is 147mAh/g, and the capacity retention rate is 60% after 51 cycles (Lu et al., 2023).

The template orientation method is used to modify the silicon ions mixed in the microsphere nickel-doped lithium manganate ($LiNi_{0.5}Mn_{1.5}O_4$). EDX analysis shows that silicon ions are successfully incorporated into the lattice of lithium manganate, but a small amount of salt phase impurities appear in the XRD spectrum. SEM characterization shows that the microspheres doped with silicon ions are uniform in size and about 15mm in diameter. Compared with undoped samples, the capacity retention rate increased from 93.1% to 99.4% after 100 cycles at 1 C.

In the process of single silicon element doping modified spinite-type lithium manganate, TEOS is often used as a silicon source. The particle size obtained after doping is evenly distributed, the shape is regular, and the edges and corners are clear. $Si^{4+}$ mainly replaces $Mn^{4+}$ at the octahedron 16d position in lithium manganate crystal cells, thus obtaining a high first discharge ratio capacity. The primary synthesis approaches employed include the high-temperature solid-phase method and the sol-gel method. Both methods have an optimized effect in micro-particle morphology control, but the synthesis conditions are relatively strict, such as high temperature (450-800℃), long-term (roaking time takes 10-25 hours), and cumbersome operation (long-term stirring). Mixing and grinding multiple times) and the stoichiometric ratio is difficult to control (Lu et al., 2023).

## 3.2 Surface Modification

Surface modification is another effective method to enhance the electrochemical performance of spinel lithium manganese oxide the electrochemical performance of $LiMn_2O_4$. Through the introduction of surface functional groups or coating layers, the surface properties and electrochemical reactivity of $LiMn_2O_4$ can be regulated to improve its lithium-ion diffusion rate, surface wettability, interfacial compatibility, and structural stability. Surface modification can introduce surface functional groups such as hydroxyl groups, carboxyl groups, amino groups, sulfhydryl groups, and phosphonate groups onto the surface of lithium manganese oxide, thereby changing its surface chemical composition and surface energy, and optimizing its surface electrochemical performance. Surface modification can also deposit coating layers such as carbon, metal oxides, conductive polymers, and ceramic materials onto the surface of lithium manganese oxide, forming a surface protective layer or conductive network, improving its surface structural stability and electrochemical activity, and enhancing its cycle life and rate performance. Surface modification can regulate the surface morphology and roughness of lithium manganese oxide, control the particle size, shape, and distribution, and optimize its surface reactivity and interfacial compatibility. Surface modification can also enhance the surface adsorption capacity and catalytic activity of lithium manganese oxide, promote the formation of solid-electrolyte interface (SEI) films, and improve the stability and safety of the battery. Surface modification can improve the surface charge transfer kinetics and electrochemical reaction kinetics of $LiMn_2O_4$, reduce the charge transfer resistance and polarization of the battery, and improve its energy efficiency and power density.

## 3.3 Composite Modification

Composite modification is a comprehensive method to improve the electrochemical properties of $LiMn_2O_4$. By combining $LiMn_2O_4$ with other functional materials, the composite material's overall electrochemical performance can be synergistically improved, achieving complementary advantages and overcoming individual shortcomings. Composite modification can combine spinel lithium manganese oxide with carbonaceous materials like graphene, carbon nanotubes, carbon black, and carbon fibers to form a conductive network, improving the electrical conductivity and charge transfer rate of the composite material, and enhancing its rate performance and power density. Composite modification can combine spinel lithium manganese oxide with metal oxides such as titanium dioxide, iron oxide, cobalt oxide, and nickel oxide to form a heterojunction structure, improving the electrochemical activity and redox reaction kinetics of the composite material, and enhancing its capacity and energy density. Composite modification can combine spinel lithium manganese oxide with conductive polymers such as polyaniline, polypyrrole, polythiophene, and polyacetylene to form a hybrid material, improving the electrochemical stability and structural flexibility of the composite material, and enhancing its cycle life and mechanical properties. Composite modification can combine $LiMn_2O_4$ with ceramic materials materials like aluminum oxide, silicon dioxide, zirconium dioxide, and boron nitride to form a protective layer or skeleton structure, improving the structural stability and thermal conductivity of the composite material, and enhancing its safety and reliability. Composite modification can also combine spinel lithium manganese oxide with nanostructured materials such as nanoparticles, nanowires, nanosheets, and nanopores to form a nanostructured architecture, improving the surface area and reaction activity of the composite material, and enhancing its specific capacity and energy density.

# 4 CONCLUSION

Spine-type lithium manganate is considered one of the most potential cathode materials of LIBs at present due to its significant advantages in performance and application range. In the realm of LIBs, it is crucial to develop high-performance positive materials suitable for large-scale commercial applications, essential for advancements of lithium-ion battery technology. Compared with other cathode materials such as $LiFePO_4$, $LiCoO_2$, $LiNiO_2$ and ternary NCM, lithium spinite manganate has the benefits of affordability and environmental friendliness, environmental protection, strong stability, simple preparation and excellent performance, so it has attracted much attention. It is an excellent cathode material for LIBs due to its high energy density, long cycle life, and high electrochemical stability. However, unmodified $Mn_2O_4$ positive electrode materials may encounter some problems in LIBs, for example low electrical conductivity, slow lithium ion diffusion rate, poor structural stability, and limited specific capacity. Modification methods such as doping modification, surface modification, and composite modification can effectively enhance the electrochemical behavior of $LiMn_2O_4$, optimize its crystal structure and surface properties, and enhance its charge and discharge rate, cycle life, and safety performance. The research and development of modified spinel lithium manganese oxide positive electrode materials are of great significance to the progression of LIBs technology and the advancement of new energy applications.

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