Research progress on lithium nickel manganese oxide cathode materials for lithium-ion batteries

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Abstract. Lithium-ion batteries (LIBs) play a key role in the global electrification of automobiles, and their long cycle life and high energy density make them the most widely used battery technology today. In LIBs, lithium-nickel-manganese oxide (LNMO) cathodes are becoming a hot research topic because this material, as an alternative to $LiCoO_2$, not only has higher energy density and lower cost, but also exhibits better safety performance. Compared to traditional $LiCoO_2$, LNMO can provide higher energy density, which means it can store more power in the same volume or weight, thus meeting the demand for long range in application scenarios such as electric vehicles. At the same time, LNMO is also relatively low in cost, which helps to reduce the overall manufacturing cost of lithium-ion batteries and promote their application in a wider range of fields. This paper first introduces the working principle of LIBs. Then, the crystal structure and electrochemical properties of LNMO are presented. Finally, the modification of LNMO by elemental doping and surface coating is emphasized to improve the performance of LIBs, aiming to serve as a reference for future research on LIBs.

1 Introduction

Against the backdrop of the global energy crisis, transportation electrification has not only become an effective means to cope with energy shortage, but also an important way to achieve environmental protection and sustainable development. In this transformation process, lithium-ion batteries, as the core component of electric vehicles, show great potential for application with their high operating voltage, high specific energy, long cycle life and environmental friendliness.

In lithium-ion batteries, the choice of cathode material has a decisive impact on the overall performance of the battery. Different cathode materials exhibit different characteristics in terms of specific capacity, energy density, cycle stability and safety. Therefore, the research and development of high-performance anode materials is the key to improve the performance of lithium-ion batteries and promote the electrification of transportation.

Currently, a variety of cathode materials have been used in lithium-ion batteries, such as $LiCoO_2$, $LiNiO_2$, $LiFePO_4$, and so on. However, each material has its inherent advantages and disadvantages, such as $LiCoO_2$ has a high specific capacity and cycle stability, but its cost is high and there are safety hazards [1]. $LiNiO_2$ has a high energy density, but its synthesis conditions are harsh and there are structural instability problems [2]. And although the olivine structure of $LiFePO_4$ is cheap and environmentally friendly, the low conductivity and lithium ion diffusion rate lead to its limited performance [3].

In recent years, lithium-nickel-manganese oxide has received much attention as a new type of anode material. Combining the advantages of nickel and manganese, LNMO have high energy density, good cycling stability and low cost [4]. At the same time, its unique crystal structure also makes a significant improvement in the safety of the battery, which is considered as one of the ideal choices of anode materials for lithium-ion batteries in the future. Therefore, this paper focuses on the progress of the application of LNMO in LIBs.

2 LNMO in LIBs

2.1. The basic structure of LNMO

$LiNi_{0.5}Mn_{1.5}O_4$ spinel has two main crystal structures: an ordered phase and a disordered phase. Both structures are based on a cubic framework, but the distribution of metal ions in them differs [5].

The crystal structure of the ordered phase ($LiNi_{0.5}Mn_{1.5}O_4$) is a primitive simple cubic structure (P4332). In this structure, Ni, Mn, and Li atoms occupy specific positions: the Ni and Mn atoms are located at the 4b and 12d octahedral positions, respectively, while the Li atoms are located at the 8a tetrahedral positions.O atoms occupy the 8c and 24e positions. This ordered arrangement gives the crystal structure specific stability and electrochemical properties.

On the other hand, the crystal structure of the disordered phase ($LiNi_{0.5}Mn_{1.5}O_4$-δ) is face-centered cubic (Fd3m). In this structure, Ni and Mn atoms are

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randomly distributed at the 16d octahedral positions without a specific order. Meanwhile, Li atoms are located at position 8a, while O atoms are located at position 32e. Due to the disordered distribution of Ni and Mn atoms, this structure differs from the ordered phase in physical and chemical properties.

It is worth noting that the transition between these two structures is affected by the annealing temperature during preparation. The ordered phase is usually formed at lower calcination temperatures, while the disordered phase is formed at higher temperatures. In addition, the disordered phase may also lead to oxygen loss and partial reduction of Mn^{4+} to Mn^{3+} to maintain electrical neutrality [6].

2.2 Electrochemical properties

LNMO spinel exhibits excellent electrochemical properties due to its unique crystal structure and constituent elements.

First, lnmo spinel has a high specific capacity of discharge. Its theoretical discharge specific capacity can reach 146.7~147 mAh/g, which means that the material is able to store and release a large amount of charge during the charging and discharging process, thus providing a high energy density.

Second, LNMO spinel has a high voltage plateau, usually around 4.7~4.8V. The high voltage plateau enables the battery to utilize the electrical energy more efficiently during charging and discharging, which improves the energy utilization of the battery.

In addition, LNMO spinel exhibits good cycling performance and multiplication performance. This is attributed to its stable crystal structure and excellent ion diffusion performance, which enables the battery to maintain good performance under long-time use or high-current charging and discharging conditions.

2.3 Preparation methods

At present, there are many methods for the preparation of LNMO, mainly including solid-phase method, hydrothermal method, vapor phase deposition method and solution method. Solid-phase method: the suitable proportion of Ni, Mn and Li solutions are first mixed and stirred in a certain way, and then the mixed solution is dried to obtain the precursor; then the precursor is annealed to form a spinel structure, and finally sintered to solidify and mold the crystals of spinel-structured LNMO [7]. Hydrothermal method: under high-temperature and high-pressure hydrothermal conditions, suitable precursors (such as nickel sulfate and manganese sulfate, etc.) are selected and added to hot water, and by controlling the appropriate reaction time and temperature, LNMO with single-crystal structure is finally obtained by dissolution, diffusion, and recrystallization reactions. vapor deposition method: suitable precursors (such as metal organics or metal oxides, etc.) are selected, and under appropriate temperature and atmosphere conditions, a thermal decomposition reaction is carried out to generate LNMO. Solution method: the raw materials are dissolved in a solvent to form a solution, and then the desired material is generated through a specific chemical reaction [8].

As a traditional preparation method, the high temperature solid phase method has the advantages of high technical maturity and controllable crystal structure type. However, the electrochemical properties of its finished products are relatively poor. The solvothermal method is a method derived from the hydrothermal method based on the metal salt solution as the raw material, adding precipitant, and then reacting at high temperature to produce the product. This method has the advantages of good quality of finished products and simple preparation process, and thus becomes the mainstream preparation method of lithium nickel manganate cathode materials. In addition, dry LNMO may have advantages over wet LNMO in some aspects. For example, the full cell of dry LNMO paired with graphite is able to maintain a high capacity retention rate after cycling and possesses stronger adhesion. Also, the use of conductive carbon with a smaller specific surface area within the dry LNMO helps to lower the electrolyte decomposition rate and reduce corrosion at the electrode-electrolyte interface. Overall, each LNMO preparation method has its own characteristics and applicable scenarios. Therefore, when selecting the optimal preparation method, a variety of factors need to be considered, such as equipment conditions, raw material costs, production efficiency, product performance, etc. In practical applications, it may also be necessary to improve or optimize the preparation method according to specific needs in order to achieve the best preparation results.

3 Modification strategy

3.1. Adulterate

Doping modification can not only inhibit the occurrence of the Jahn-Teller effect, but also enhance the bond energy between metal ions and oxygen, and slow down the side reaction between the electrolyte and the electrode material. The doping of transition metal elements can replace part of Ni^{2+}, thereby inhibiting the formation of $Li_xNi_{1-x}O$ and other heterophases, increasing the unit cell parameters, promoting the transport of ions and electrons, and improving the comprehensive properties of the material. Arunkumar et al. [9] reported that the doped material forms different cubic phases during the charge-discharge process, and the unit cell parameters become smaller, which may make the doped modified $LiNi_{0.5}Mn_{1.5}O_4$ cycle performance is improved. Doping modification can be divided into two categories: anionic doping and cationic doping. The main elements of anionic doping are F, S, etc., mainly at the O position. The main elements of cationic doping are Na, Cu, Mg, Co, Cr, Al, Fe and Si, etc., mainly at the Ni or Mn position.

Doping modification is a method to improve the properties of materials by introducing different ions, especially in the study of cathode materials for lithium-

ion batteries, which is widely used. By doping different metal ions or non-metal ions, the electrochemical properties of the material can be effectively improved, including increasing the specific capacity, cycling stability, and rate performance, while inhibiting undesirable side reactions and structural changes. The effects of different types of ion doping on the properties of $LiNi_{0.5}Mn_{1.5}O_4$ materials can be mainly divided into anionic and cationic hybrids.

3.1.1 Cationic hybrid

The cationic hybrids mainly include Na^+, Cu^{2+}, Mg^{2+}, Co^{3+}, Cr^{3+}, Al^{3+}, etc. For cationic hybridization, various metals can improve their performance in many aspects, mainly focusing on the performance improvement of Li, such as Na^+ hybridization to reduce the conduction band to improve conductivity, Mg^{2+} to improve the movement speed of Li^+, Co^{3+} to impurity, effectively improve the cycling performance and rate performance, Jang et al. [10] roperties and rate properties of $LiNi_{0.5-x}Co_{2x}$ $Mn_{1.5-x}O_4$ materials were improved compared with those before doping. Especially in the sample with x = 0.05, the best performance was shown. And for non-metallic cations, Bini et al. [11] prepared $LiNi_{0.5}Mn_{1.5-x}Si_xO_4$ doped with Si4+ sample (0. 00≤x≤0. 35), and it was found that Si^{4+} doping not only stabilized the Fd-3m crystal structure, but also increased the disorder in the cationic region. Si occupies the tetrahedral position, and the corresponding amount of Li moves to the octahedral position. The addition of silicon can control and limit the growth of particles, and the smaller the particle size, the more favorable it is for the diffusion of Li^+ and improve the electrochemical performance.

3.1.2 Anionic Hybrid

F-anion doping: It reduces the change of unit cell volume and structural stress during Li^+ memorcastization, and improves the charge-discharge performance and thermal stability at high magnification. Anionic doping (e.g., F^- or S^{2-}substituting partial O) can reduce the unit cell volume change and structural stress during Li^+ intercalation, and shorten the electron and ion transport path. F^-doping can also inhibit the reaction of hydrofluoric acid (HF) corrosion electrode materials, reduce the dissolution of Ni and Mn ions, and improve the charge-discharge performance and thermal stability of the materials at high rates. Oh et al. [12] prepared F-doped $LiNi_{0.5}Mn_{1.5}O_{4-x}F_x$ material. With undoped $LiMn_{1.5}Ni_{0.5}O_4$ ratio, the discharge specific capacity of the half-cell prepared by $LiNi_{0.5}Mn_{1.5}O_{4-x}F_x$ decreases. The possible reasons for this are: Li-F bond (bond energy of 577 kJ/mol) is stronger than Li-O bond (bond energy of 341 kJ/mol), and Li^+ is difficult to detach from the matrix structure; When cycled at a high magnification greater than 3C, $LiNi_{0.5}Mn_{1.5}O_{3.9}F_{0.1}$ than undoped $LiMn_{1.5}Ni_{0.5}O_4$ has a high capacity retention rate. It may be due to the fact that the unit cell parameters of Li^+ change less during the repeated mosaicing process, so that the structural strain is smaller and the structure is more stable.

3.1.3 Compound doping

For example, Mg^{2+} and Si^{4+} are co-doped, which shows a long cycle life and good rate performance. Ti-La co-doping enhances the stability of the crystal structure and improves the Li^+ diffusion coefficient. The ternary doping of Cu^{2+}, Al^{3+} and Ti^{4+} increased the diffusion coefficient of Li^+, and improved the stability and chemical properties of the materials. Mg^{2+} and Si^{4+} composite doped LiNi0.47Mg0.03Mn1.47Si0.03O4 was produced by Shu et al. [13]. The sample had good rate performance and a lengthy cycle life. The Mg-Si co-doped sample had a discharge specific capacity of 121 mAh/g and a capacity retention rate of 98.86% after being charged and discharged at 0.5C and 3~5V. In contrast, the undoped LiNi0.5Mn1.5O4 samples had a capacity retention rate of just 79.17% after 100 cycles. Mg^{2+} and Si^{4+} enter the spinel structure, which will slightly improve the unit cell parameters, so the co-doped samples have better rate performance and lower charge transfer resistance. The co-doping of Mg^{2+} and Si^{4+} inhibited the abnormal grain growth to a certain extent, and the particle size distribution of the obtained samples was more uniform.

3.2 Wrapping

In cathode materials such as $LiNi_{0.5}Mn_{1.5}O_4$, surface coating can effectively inhibit the dissolution of Mn, reduce the side reaction between the surface electrolyte and the electrode, avoid the erosion of the electrode by corrosive substances such as HF, and reduce the self-discharge ability of the material. Through the use of nanotechnology and metal doping, the electrochemical properties of the battery have been significantly improved.

Researchers have explored a variety of materials as surface coatings, including Al_2O_3, Bi_2O_3, SiO_2, ZnO, ZrO_2, $FePO_4$, $AlPO_4$, $Li_4P_2O_7$, Au, Ag, carbon, polyimide, and graphene oxide, among others. The effects of these coating materials on $LiNi_{0.5}Mn_{1.5}O_4$ varied, but they all showed a trend of improving battery performance. It can be mainly divided into oxide coating and non-oxide coating.

3.2.1 Oxide coating

The oxides commonly used to coat $LiNi_{0.5}Mn_{1.5}O_4$ materials include Bi_2O_3, SiO_2, ZnO, AL_2O_3, etc. For common oxides, such as Al_2O_3 coatings, Zn and Co-doped $LiNi_{0.5}Mn_{1.5}O_4$ show the ability to inhibit solid electrolyte interface (SEI) layer formation and reduce charge transfer resistance. The Bi_2O_3 coating inhibits electrolyte decomposition and reduces the dissolution of transition metal ions on Ti-doped $LiNi_{0.5}Mn_{1.5}O_4$, and effectively inhibits the capacity attenuation. The porous and nanostructured SiO_2 coating can effectively protect $LiNi_{0.5}Mn_{1.5}O_4$ particles from HF erosion, and improve

the capacity retention rate of the coating at high temperatures. The effect of ZnO coating is similar to that of SiO_2, and it has higher discharge capacity and good capacity retention, but its stability during cycling still needs to be verified. ZrO_2-coated $LiNi_{0.5}Mn_{1.5}O_4$ has better cycling performance compared to bare samples, which may be due to limited surface reactivity and reduced charge transfer resistance. However, some studies have shown that the coating may impair the accessible capacity of $LiNi_{0.5}Mn_{1.5}O_4$ due to the poor kinematics of lithium-ion transport [14]. Noguchi et al. calcined $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ and $Bi(OH)_3$ at 600 °C, and the Bi_2O_3 film was evenly coated on the surface of $LiNi_{0.5}Mn_{1.5-x}Ti_xO_4$ [15]. After 500 cycles at 45°C, the capacity retention rate of the clad material reached 70%, while the capacity retention rate of the unclad material was only 60%. The $LiNi_{0.5}Mn_{1.5}O_4/SiO_2$ composite synthesized by Fan et al. had a capacity retention rate of 86% after 100 cycles with a specific capacity of nearly 130 mAh/g (55°C, 5 C) for the first discharge. Metal oxide coating can prevent $LiNi_{0.5}Mn_{1.5}O_4$ from reacting with the electrolyte and dissolving the active substance to a certain extent, but the acid resistance of the metal oxide is poor, and it cannot effectively prevent the erosion of the material by HF.

3.2.2 Non-oxide coating

$FePO_4$ and $AlPO_4$-coated $LiNi_{0.5}Mn_{1.5}O_4$ exhibited significant capacity retention and electrochemical reversibility, which may be due to the inhibition of SEI layer formation and enhanced surface charge transport. $Li_4P_2O_7$-coated $LiNi_{0.5}Mn_{1.5}O_4$ rarely formed Li_3PO_4 impurities during cycling, and showed less state reaction, and showed significantly improved cycling performance.

In addition, studies have explored the use of precious metals such as Au and Ag as coating materials. Through specific chemical reactions, the coating of Ag and Au can be obtained, and these precious metal coatings may bring new possibilities for improving battery performance due to their unique electronic properties and chemical stability.

4 Conclusion

LNMO has many advantages in lithium-ion batteries, such as high energy density, high operating voltage, excellent multiplication performance, good thermal stability, lower cost, and environmental friendliness. These advantages make LNMO have a wide range of application prospects in electric vehicles, portable electronic devices and other fields. This paper summarizes the crystal structure and preparation method of LNMO. It also describes the optimization of the crystal structure of LNMO through doping, coating and other modification means to improve its ion diffusion rate and electronic conductivity, so as to achieve higher energy density and better multiplicity performance.

However, at present, LNMO also faces the problem of fast capacity decay, especially under high temperature conditions. This is mainly due to the dissolution of transition metal ions in the material and the side reactions between the electrode material and the electrolyte. It will not only affect the cycling performance and stability of the battery, but also reduce the capacity and energy density of the battery. On the other hand, in order to fully utilize the performance advantages of LNMO, a more complex production process may be required. This may increase production costs and affect the commercialization of the battery. Although LNMO itself has better safety, it may cause some safety problems if the process and conditions are not strictly controlled during the manufacturing and use of the battery.

To overcome these shortcomings, future research can optimize the synthesis conditions, improve the material structure, and develop new electrolytes in order to improve the stability, capacity retention, and cycle life of LNMO. In addition, strengthening the quality control of the battery production process to ensure the safety and reliability of the battery is also an important direction to promote the application of LNMO in lithium-ion batteries.

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