

# Research progress of ternary cathode materials in lithium-ion batteries

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**Abstract.** With the increasing global attention to environmental protection and sustainable development issues, the new energy vehicle industry is booming at an unprecedented rate, becoming a significant force in promoting the transformation of the green economy. As a core component of new energy vehicles, the performance optimisation and technological innovation of power batteries have become the top priority of industry research. The selection and optimisation of cathode materials are critical in determining the energy density, cycle life, safety performance, and cost-effectiveness of power batteries. Lithium nickel-cobalt-manganese (NCM), with its high specific capacity, high voltage platform, and cost advantage over other materials, stands out from many cathode materials and has become a hotspot of research in the field of power batteries and the preferred material for commercial application. NCM materials can achieve different performance balances by adjusting the ratios of the three elements, namely nickel, cobalt, and manganese, to satisfy the needs of various application scenarios. Therefore, this paper reviews the latest research progress in four aspects, namely, structural features, synthesis process, leading problems, and modification methods of several ternary materials with major compositions (NCM111, NCM523, NCM811), and also looks forward to and evaluates the prospect of their commercial application.

**Keywords:** LIBs, NCM, preparation, modification.

## 1. Introduction

In recent years, lithium iron phosphate batteries have been widely used in the field of new energy vehicles; their theoretical specific capacity of about 170mAh/g, structural stability, cycling performance, and safety performance, but due to their low specific energy (90120Wh/kg) limits the driving range of new energy vehicles, with the continuous improvement of electric vehicles on the range, the development of high specific energy lithium-ion batteries has become the lithium-ion battery industry. The development of high-specific energy lithium-ion batteries has become a hotspot for the lithium-ion battery industry. Lithium cobalt oxide batteries are mainly used in mobile phones, laptops, and other consumer electronics for their high specific energy performance advantages. Still, the scarcity of cobalt resources has led to a surge in the price of drilling in recent years; the cost of lithium cobalt oxide as the raw material for batteries is getting higher and higher, and thus, it cannot be popularized in the field of power batteries. Ternary material  $\text{LiNi}_x\text{Co}_y\text{Mn}_{(1-x-y)}\text{O}_2$  battery with its excellent overall performance and lower cost in the field of consumer electronics to replace part of the lithium cobalt battery market, so high specific energy, long life, and high-security ternary material power lithium-ion batteries have become a hotspot for research and development and attention of the world [1]. The proportion of nickel-cobalt-manganese in nickel-cobalt-manganese ternary anode materials can be adjusted within a certain range. Its performance changes with the different proportions of nickel-cobalt-manganese, so to further reduce the cobalt content and further improve the performance of cathode materials, countries around the world have done a lot of research and development in the research and development of ternary materials with different nickel-cobalt-manganese compositions, and have put forward several ternary materials with different nickel-cobalt-manganese proportions, including the NCMI (NCMI), the NCMI (NCMI) and NCMI (NCMI) [2]. A number of ternary material systems with different nickel-cobalt-manganese ratios have been proposed, including NCMI11, NCM424, NCM523, NCM622, NCM811, etc [3]. Some of these systems have been successfully realised in industry. Some of these systems have successfully achieved industrial

production and application. This paper mainly focuses on the three systems: NCM111, NCM523, and NCM811.

## 2. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111)

### 2.1. Crystal Structure

NCM111 belongs to the  $\alpha\text{-NaFeO}_2$  type crystal structure, a typical layered structure. In this structure, oxygen ions ( $\text{O}^{2-}$ ) and transition metal ions ( $\text{Ni}^{2+/3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+/4+}$ ) form lamellar units arranged longitudinally along the c-axis. The lithium ions ( $\text{Li}^+$ ) are located between these layered units, forming a typical ABC-type stacked cubic stacking structure. The crystal structure of NCM111 consists of alternating transition metal and lithium layers, and this layered structure facilitates the rapid embedding and detachment of lithium ions. The three elements Ni, Co, and Mn are uniformly distributed in the transition metal layer in a 1:1:1 ratio. This distribution helps to balance the electrochemical properties of the material and improve the cycling stability and safety. The layered structure provides a good diffusion channel for lithium ions, which enables lithium ions to be smoothly embedded and dislodged during the charging and discharging process [3].

### 2.2. Preparation Methods

As an essential ternary cathode material, NCM111 is prepared using various methods. The co-precipitation method is the most commonly used method to prepare NCM ternary materials in the industry. It belongs to the wet chemical method, which makes the transition metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ) co-precipitate by controlling the process parameters such as the pH value, temperature, and stirring speed of the reaction solution. It forms the precursor particles with regular shape, moderate particle size, and uniform distribution. The preparation process of this method is mature and easy for industrial production [4].

The high-temperature solid-phase method prepares products by interfacial contact reaction and nucleation growth between solids at high temperatures. Generally, transition metal salts, oxides, or hydroxides are chosen as raw materials, according to a certain proportion of the entire mixture, calcined at high temperatures to form high nickel ternary material products.

The sol-gel method is used through the hydrolysis and condensation reaction of metal alcohol salt or inorganic salt to form a sol. Then, after aging, drying calcination and other steps are used to prepare a powder material. The materials prepared by this method have high purity and uniform particle size.

In addition, there is the spray drying method. It is a kind of mechanical ball milling or sand grinding of metal oxides into a slurry, or soluble metal salts according to the stoichiometric ratio of a homogeneous solution, and then through the peristaltic pump will be slurry or solution into the spray drying equipment, rapid evaporation of solvents, spray granulation of the physical method. However, this method requires high control of raw materials and process parameters.

### 2.3. Modification methods

While seeking new synthesis methods, doping and coating NCM111 is also the primary way to improve the material's performance. Coating measures can reduce the contact area between cathode materials and electrolyte, effectively inhibit the decomposition of electrolyte on the surface of active materials and reduce the amount of dissolved Mn; at the same time, some metal oxide coating materials can stabilise oxygen atoms by combining with oxygen in the raw material lattice. The improvement effect of coating measures is pronounced in high-rate or high-temperature charge and discharge performance. The purpose of doping is to make the dopant ions enter the crystal lattice, replace some of the ions in the raw material, stabilise the structure of the raw material, and maintain the stability of the structure of the material in the charge-discharge process; secondly, doping metal will also have an impact on the conductivity and  $\text{Li}^+$  migration rate of the material.

Lin et al. homogeneously dispersed NCM111 powder in citric acid-ethanol solution, followed by vacuum to allow the citric acid to penetrate the pores of the porous powder, and obtained the carbon-

covered NCM111 material after high-temperature roasting. The composite material maintains the original layered structure of NCM111, and although the specific surface area decreases, the cycling performance and particular capacity of the material are greatly improved. The reason for the improved performance is mainly because the carbon coating increases the material's electrical conductivity, reduces the degree of electrode polarisation, effectively prevents oxygen loss under high current density charging conditions, and can lead to improved stability of the material in high-fold cycling [5].

### 3. $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523)

#### 3.1. Crystal structure

The crystal structure of NCM523 is a layered structure consisting of hexagonal, densely packed layers. In this structure, transition metal ions ( $\text{Ni}^{2+/3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+/4+}$ ) and oxygen ions ( $\text{O}^{2-}$ ) form alternating layers, while lithium ions ( $\text{Li}^+$ ) are located between these layers. Nickel, cobalt, and manganese are distributed in the lattice in a specific ratio (Ni: Co: Mn = 5:2:3). The different arrangements of these elements in the lattice form the crystal structure of NCM523 cathode material. The crystal structure provides a good diffusion channel for lithium ions, which enables lithium ions to be smoothly embedded and dislodged during the charging and discharging process, thus ensuring the battery's high discharge capacity and cycle stability. Moreover, the crystal structure of NCM523 can remain relatively stable during the charging and discharging process, which helps to extend the battery's cycle life and improve the battery's safety [6].

#### 3.2. Preparation Methods

As the most widely used high-nickel ternary material, NCM523 has the highest degree of industrialization. The synthesis process is relatively mature, mainly including chemical co-precipitation, high-temperature solid-phase, hydrolysis, hydrothermal synthesis, etc. The industrial ternary cathode material NCM523 is usually produced by combining indirect co-precipitation and high-temperature solid-phase sintering, and Li et al. synthesized NCM523 coated on the surface of  $\text{LiAlO}_2$  by hydrolysis hydrothermal synthesis [7]. Li et al. synthesized  $\text{LiAlO}_2$ -coated NCM523 by hydrolysis hydrothermal method; the thickness of the coating layer is 4 nm; meanwhile,  $\text{Al}^{3+}$  is gradient distributed in NCM523, and the internal  $\text{Al}^{3+}$  plays the role of doping, both of which improve the  $\text{Li}^+$  diffusion coefficient of NCM523, and show excellent cycling and multiplicity performance [8].

#### 3.3. Modification Methods

The advantages of high-nickel ternary materials are apparent. However, there are still many problems in successfully realizing industrial applications, such as the rapid battery capacity degradation after many charge/discharge cycles under high voltage ( $>4.3$  V) charging and discharging conditions. Therefore, synthesizing and modifying high-nickel ternary materials with excellent performance has become an important research direction in lithium batteries. Another major problem of high-nickel ternary materials is the rapid water absorption when exposed to air, which makes it easy to form  $\text{LiOH}/\text{Li}_2\text{CO}_3$  and other surface residual bases on the surface of the particles. These residual bases will quickly react with the electrolyte to form an electrochemical inert layer during charge/discharge cycling, increasing the impedance between the interfaces, reducing the transmission rate of electrons and ions, and thus causing the capacity to degrade. The direct contact between the materials and the electrolyte can be avoided through the surface coating and internal doping of high nickel materials, thus alleviating problems such as residual alkali on the surface and high voltage intolerance, as mentioned above. In recent years, NCM523 has been modified with Zr, Si, Al, and other oxides as the coating layer.

The main electrolyte lithium salt in lithium-ion batteries is  $\text{LiPF}_6$ , which is very sensitive to trace amounts of water;  $\text{LiPF}_6$  has poor thermal stability and decomposes quickly into  $\text{LiF}$  and  $\text{PF}_5$ , and

then reacts with water to produce HF, which erodes the anode material, causes the dissolution of metal ions in the material, and destroys the structure of the material, which results in the deterioration of the electrochemical performance of the material. The purpose of cladding modification is to form a thin isolation layer on the material's surface, preventing direct contact between the electrolyte and the primary material, thus suppressing the increase of interfacial impedance and improving the electrochemical performance of the material.

Kong et al. used the atomic layer deposition technique to coat an ultrathin layer of  $\text{ZrO}_2$  on the surface of NCM523. When this coating layer was 5 atoms thick, the NCM523 material showed the highest initial coulombic efficiency, excellent electrochemical performance, and high multiplicity performance in the 2.5 to 4.5 v range at room temperature [9].

In the doping modification of ternary materials, the commonly used doping elements are Mg, Ti, Al, Fe, Zr, Cr, etc. The principle of doping modification is mainly to reduce the content of unstable elements and replace Ni and Li with electrochemically stable or structurally stable elements, or the dopant atoms can stabilise the valence state of  $\text{Ni}^{+}$  and prevent its mixing and exclusion with  $\text{Li}^{+}$ ; or increase the bond length of metal atoms and oxygen atoms to reduce the release of oxygen, thus maintaining the structure of the layered oxide. Zr element has been used quite frequently in doping in recent years and has gradually become the most mainstream doping element.

Wang et al. doped NCM523 with Zr (1% Zr content). Although the initial capacity was lower than that of the undoped NCM523, the specific capacity of NCM523 was still 83.87% after 100 cycles of  $\text{IC}$  at a high pressure of 4.6 v, compared with 69.35% of the original material. The multiplicity performance of the doped material was also significantly improved [10].

## 4. $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811)

### 4.1. Crystal structure

The crystal structure of NCM811 belongs to the hexagonal crystal system with the space group  $\text{P6}_3\text{mc}$ . In this structure, each cell contains four  $\text{LiCoNiMnO}_4$  molecules, each consisting of a Li-ion and a Co, Ni, Mn, O quaternary. These four molecules are structurally identical, but the atoms are bonded differently, as Co-O, Ni-O, Mn-O, and Li-O bonds, respectively. The lengths and bond angles of these bonds are significant for the electrochemical properties of NCM811. The crystal structure of NCM811 is layered. The metal ions (cobalt, nickel, and manganese) within each layer are in a six-coordinated configuration, i.e., each metal ion is coordinated to six oxygen ions. In contrast, the layers are interwoven by lithium ions, and these Li ions are located in octahedral holes and surrounded by six oxygen atoms, forming an octahedral coordination structure. Since the Li ions in NCM811 occupy the octahedral holes, there are no excessive unoccupied holes, which effectively reduces oxygen penetration and electrode expansion, thus improving the cycle life of the electrode [11].

### 4.2. Preparation Methods

The preparation method is closely related to the structure and properties of the materials, and the materials obtained by different preparation methods have significant differences in microstructure, morphology, specific surface area, and electrochemical properties. Currently, the main preparation methods of NCM811 include the solid-phase method, chemical co-precipitation method, solution gel method, etc. The advantage of the solid-phase method is that the material can be prepared by the solid-phase method. The benefits of the solid-phase method are low preparation cost, easy industrial production, and simple process; however, in the preparation process, it is necessary to grind to make good contact between the reactants fully, and at the same time, it is essential to calcine at high temperature for a long time, with significant energy consumption, easy to mix impurities, and the cation mixing and discharge is also more severe. The chemical co-precipitation method, through the control of the reaction temperature, pH value, speed, and ammonia concentration (ammonia plays the role of chelating agent), etc., can be prepared to obtain a narrow particle size distribution of the spherical precursor and make the final product has a spherical microstructure, which is conducive to

the enhancement of the vibration density of the material. The sol-gel method was used to prepare NCM8. The gel method to prepare NCM811 anode materials, due to the gel in the drying and pre-cooking process, will escape a large number of gases so that the synthesized material particles have a porous nature and low degree of agglomeration characteristics; in addition, the decomposition of organic matter can produce additional heat, can be completed faster characterization, shorten the calcination time [12].

### 4.3. Modification Methods

Due to the high content of Ni in NCM811, the disadvantages are significant. Firstly, the problem of cation mixing (part of  $\text{Ni}^{2+}$  will occupy the  $\text{Li}^+$  position) is still severe; secondly,  $\text{Ni}^{4+}$  is not wholly reduced during the discharge process, and it is easy to react with the electrolyte, which affects the reversible specific capacity and the cycling performance of the material; lastly, the incomplete oxidation of  $\text{Ni}^{2+}$  is prone to form a 1-10 nm NiO layer on the surface, which hinders the migration of Li ions. These problems lead to the low first charging and discharging efficiency, fast capacity decay during cycling, and poor multiplicity performance of NCM811 cathode material, which essentially limits the application of this material in practical use, so the performance of NCM811 cathode material needs to be further improved by modification.

At high potential, the high oxidation state cations on the surface of NCM811 cathode material have high activity, easily dissolved in the electrolyte, destroying the surface structure. In contrast, the surface of the cathode material reacts with the electrolyte in a complex manner, forming a solid electrolyte (SEI) film unfavorable to the electrochemical performance. Coating a layer of inert material of suitable size on its surface can effectively inhibit the dissolution of active material in the electrolyte and improve the electrochemical performance of the material.

Ultra-thin solid electrolyte films, such as lithium phosphorus oxynitride (LiPON) films, are prepared on the surface of NCM811 electrodes using magnetron sputtering technology. This film can precisely coat the electrode surface, effectively inhibit the side reaction between the electrode and electrolyte, and improve the electrode's cycling stability and safety performance. The surface of NCM811 was modified by the sol-gel method and coated with cladding layers such as  $\text{Li}_2\text{SnO}_3$  (LSO) and  $\text{LiCoO}_2$  (LCO). This method can selectively coat the inner surface region of polycrystalline secondary particles, effectively preventing the degradation of the material in the environment and improving the electrochemical properties of the material [13].

Ion doping is an essential means to improve the electrochemical properties of NCM811. Cation doping can effectively reduce the mixing arrangement of  $\text{Ni}^{2+}$  in the  $\text{Li}^+$  site, which can stabilize the lamellar structure; in addition, the difference in ionic radius can also be used to change the spacing between the layers of NCM811 to provide a more convenient diffusion channel for  $\text{Li}^+$ . Anion doping can enhance the bonding energy of oxygen with other elements, reduce the amount of oxygen precipitation, and improve the safety performance [13].

Vu et al. doped and modified NCM811 with 0.2%  $\text{Na}^+$ , which maintained the layered structure and facilitated the movement of  $\text{Li}^+$  in the lattice, and finally obtained good multiplicity and cycling performance. The test shows that at a high cut-off voltage of 4.5 v and 1 C, there is still 132 mAh/g after 100 cycles, with a capacity retention rate of 69.1%, while the original material is 90.6 mAh/g, with a capacity retention rate of 49.5% [14].

## 5. Conclusion

NCM111 and NCM523, two crucial ternary cathode materials in lithium-ion batteries, have been widely used in many fields, such as electric vehicles and energy storage systems. These two materials have stable cycling performance and good safety performance, especially in preventing thermal runaway of the battery. With the continuous optimisation of the preparation process and the continuous improvement of cost control, NCM111 and NCM523 have become mainstream choices in the power battery market. However, with the rapid development of the new energy vehicle industry

and the urgent demand of consumers for higher ranges, the specific capacity of NCM111 and NCM523 has gradually approached its theoretical limit, which is unable to meet the current higher requirements for high energy density power batteries. In addition, cobalt, as an essential constituent element in these two materials, has seen its price rise sharply, increasing the manufacturing cost of batteries and further limiting their wide application. In addition, the cycling and thermal stability of high-nickel materials are relatively poor, which is prone to capacity degradation and thermal runaway.

It is necessary to develop effective and easy-to-implement modification means to address the problems of high nickel ternary cathode materials. This includes doping and capping modifications, efficient electrolyte additives, and developing high-pressure electrolyte systems. By doping other elements into the high-nickel material or coating a layer of stable compounds on its surface, the material's cycling and thermal stability can be improved. Meanwhile, the development of electrolyte additives with antioxidant and anti-corrosion functions can also reduce the side reactions between the electrolyte and the cathode material. In addition, as the battery voltage platform continues to rise, developing electrolyte systems that can withstand higher voltages has become an inevitable trend.

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