Research Status of Ni-rich Ternary Cathode Materials for Lithium Ion Batteries

Xiaohui Li¹², Hongyan Xie¹²³⁷, Huixin Jin¹², Qiang Zhang¹², Yaqing Zhang¹², Yezhu Li¹², Kaifeng Li¹² and Chongjun Bao³⁴

¹College of Material and Metallurgy, Guizhou University, Guiyang, 550025, China
²Guizhou Province Key Laboratory of Metallurgical Engineering and process Energy Saving, Guiyang, 550025, China
³State Key Laboratory of Pressure Hydrometallurgical Technology of Associated Nonferrous Metal Resources, 650503, China
⁴Kunming Metallurgy Research Institute, Kunming, 650500, China

*Corresponding author email: hyxie@gzu.edu.cn

Abstract. Ternary cathode material LiNiᵸCoᵧMn₁₋ₓ₋ᵧO₂ (NCM) has been widely studied as a kind of cathode material with high voltage, high theoretical capacity, good cycling performance and high thermal stability, which is one of the most popular cathode materials for lithium ion battery. Nickle-rich NCM (x≥0.5) can meet the market demand for high-specific capacity power batteries due to its high nickel content and large charge-discharge capacity. But the safety and thermal stability are poor. Therefore, this paper mainly studies how to obtain Ni-rich NCM with high specific capacity and good thermal stability from three aspects of precursor preparation, surface coating and doping.

1. Introduction

In the 21st century, as the economy enters the stage of rapid development, the consumption of petroleum resources gradually increases. With the goal of protecting the environment and reducing the consumption of non-renewable energy, the development of new energy materials rises rapidly[1]. Due to its high theoretical capacity, high safety and good cycling performance, LiNiᵸCoᵧMn₁₋ₓ₋ᵧO₂ (NCM) is considered as one of the most suitable new energy materials to replace petroleum energy[2]. NCM combines the characteristics of LiNiO₂, LiCoO₂ and LiMn₂O₄. Nickel based materials have high specific capacity, cobalt based materials have good cycling performance and manganese based materials have high safety[3]. Among them, the actual capacity of LiNiᵸCoᵧMn₁₋ₓ₋ᵧO₂ (x≥0.5) (Ni-rich NCM) can reach 60~80% of the theoretical capacity (about 280mA·h/g). However, with the increase of nickel content, its safety and stability will be reduced. Taking NCM523 as an example, the capacity retention rate of unmodified NCM523 is about 65~75% after 100 cycles[4]. With the increase of nickel content, the capacity increases, but the cycling efficiency also decreases[3]. For the emergence of the above problems, the preparation, surface coating and phase doping of Ni-rich NCM precursor were studied in this paper.

2. Preparation of NCM Precursor by Coprecipitation

In the preparation process of the ternary cathode material, the structure and morphology of the precursor are the main factors affecting the ternary cathode material, and 40~60% of the technical
2.1. Influence of Precipitant on Precursor

Common precipitators are hydroxide and carbonate precipitators. When the hydroxide is used as the precipitant, the reaction speed is faster, it is easier to control the particle size, specific surface area and morphology, and the density of the particles is good. He\(^{[7]}\) used sodium hydroxide as precipitant to prepare NCM523, the particles are uniform, sphericity is good and the surface is smooth. When the voltage is 3-4.5V, the specific capacity reaches 175.2 mA·h/g at 0.2C, and the capacity retention rate is 82.53% after 210 cycles.

When carbonate is used as a precipitant, the process performance is relatively poor. The obtained particles have rough surface, uneven particle size and poor compactness. However, due to its slow reaction speed, large specific surface area, simple reaction conditions and low cost, it has been widely studied and applied\(^{[8]}\). Ma\(^{[1]}\) prepared Co-Mn carbonate with micro pore structure by carbonate precipitation method, and obtained LiNi\(_{0.6}Co_{0.2}Mn_{0.2}O_2\) by maceration method and high temperature solid phase method; Its specific capacity reaches 154.7 mA·h/g at 0.2C, and after 100 cycles, its capacity retention rate is 83.09% (100.77 mA·h/g).

2.2. The Precursor was Prepared by Concentration Gradient Coprecipitation

During co-precipitation, the precursor of a special core-shell structure can be prepared by the concentration gradient method. This structure will be more stable during use and the possibility of cracks will be reduced. Hou\(^{[9]}\) used the concentration gradient co-precipitation method to obtain LiNi\(_{0.5}Co_{0.2}Mn_{0.3}O_2\) with double shell structure. Its morphology was observed under scanning electron microscope, as shown in fig.1. Compared with the common structure, the double shell structure had obvious microporous structure, which increased the specific surface area of particles. When the voltage is 3-4.3V and the current density is 20 mA/g (1C = 160 mA/g), the discharge capacity is 171.5 mA·h/g (ordinary structure is 168.7 mA·h/g), and the initial coulomb efficiency reaches 89%.

![Figure 1. SEM images of precursors(a) normal structure (b) Core-shell structure\(^{[9]}\)](image)

2.3. Influence of Feeding Speed on Precursor

In addition, reaction temperature, stirring speed and time, PH value and feeding speed in co-precipitation all directly affect the morphology and particle size distribution of the precursor. The above conditions have been studied by a large number of scholars and are basically mature. However, few literatures have mentioned the titration rate. Titration rate can directly affect the particle size and distribution, and particle size is too wide will directly affect the vibration density and specific surface area of the material. Hua\(^{[10]}\) obtained LiNi\(_{0.5}Co_{0.2}Mn_{0.3}O_2\) by rapid precipitation method without the assistance of surfactant, and showed that the surface of spherical particles had nanoscale flower structure under scanning electron microscope. These nanoscale flower structures increased the specific surface area of the particles, And the structure is more stable. When the voltage is 2.5-4.6V and the discharge current density is 1C, the specific capacity reaches 158 mA·h/g. After 50 cycles, the
capacity retention rate reaches 98.27% and there is basically no attenuation. SEM image as shown in Figure 2.

![Figure 2](image)

**Figure 2.** Schematic illustration for the formation of NL333’s intermediate at different stages of the co-precipitation reaction (a) 0.5 h, (b) 1.5 h, and (c) 3 h; (d) Photo for a rose.

3. Surface Coating Modification

It is well known that properly increasing the cut-off voltage can improve the battery charge and discharge specific capacity. Due to the battery in the process of charging and discharging, between the electrolyte and cathode materials can produce side effects, This side effect is more severe at high voltage, capacity attenuation caused by serious, can also affect the thermal stability of the cathode materials, produce safe hidden trouble [7, 11]. To solve this problem, in addition to the use of high-pressure electrolyte, the cathode material will also be modified by surface coating. The coating can reduce the contact between the cathode material and the electrolyte and reduce the occurrence of side reactions and improve its thermal stability. Common coating materials include metal oxides, metal fluoride and mineral salts [12].

3.1. Metal Oxide Coating

Al$_2$O$_3$ is a representative metal oxide coating material. Due to its strong stability, This effect of Al$_2$O$_3$ coating is shown in Figure 3. Al$_2$O$_3$ is often used as a coating material for the surface coating of cathode material [13].

![Figure 3](image)

**Figure 3.** Schematics illustrations for the coating process of Al$_2$O$_3$ on NCM523 surface [14].

Chen [13] used Al$_2$O$_3$ nanoparticles obtained after ultrasonic treatment to surface coat LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$. This method is different from the previous wet chemical coating process such as sol-gel method and chemical precipitation method, which is simple and environmentally friendly. When the voltage is in the range of 3–4.5V and the discharge current density is 0.2C, its specific capacity reaches 197.1 mA·h/g (uncoated is 187.6 mA·h/g), the initial coulomb efficiency reaches 91.2% (uncoated is 84.9%), the irreversible capacity decreases, and the capacity retention rate reaches 91.0% (uncoated is 82.9%) after 30 cycles. The side reaction between LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ and electrolyte decreases after Al$_2$O$_3$ coating, It also increases the orderliness of layered structures.
Other metal oxide coating materials include WO$_3$\cite{15}, Ta$_2$O$_5$, ZrO$_2$, TiO$_2$, etc.

3.2. Phosphate Coated
The inert chemical properties of transition metal phosphates were effective in preventing side reactions between the cathode and the electrolyte. In addition, the strong covalency of the PO$_4^{3-}$ polyanions may improve the thermal stability of the materials\cite{16}. Lee\cite{17} coated LiPO$_3$ on the surface of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ by sol-gel method. In situ TR-XRD test results show that the LiPO$_3$ coating increases the temperature of all the phase transitions, thus inhibiting the phase transitions and improving the thermal stability of the cathode material. The specific capacity reaches 192.7mA·h/g (uncoated is 184.8mA·h/g) at 0.1C. After 100 cycles, the capacity retention rate is 79.7% (uncoated is 63.9%). LiPO$_3$ not only protects LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ from HF corrosion in the electrolyte, improves the ionic conductivity of Li$^+$, thereby improving the rate performance of cathode materials.

4. Phase Doping Modification
Nickel-cobalt-manganese ternary positive electrode material is a typical $\alpha$-NaFeO$_2$ structure. This layered structure has the characteristics of large capacity and good cycling performance. However, in the process of forming the layered structure, the difference between the radius of Li$^+$ and the radius of Ni$^+$ is very small, which is easy to cause the cation mixing arrangement phenomenon, which leads to the disorder of the layered structure, which reduces the diffusion channel of Li$^+$. Therefore, the specific capacity is reduced and the cycle performance is reduced. Bulk doping is the most effective method to enhance structural stability. Doping is generally divided into cationic doping, anion doping and cation mixed doping. Na doping is a typical cationic doping, because the radius of Na$^+$ ($r_{\text{Na}^+} = 1.02\text{Å}$) is larger than that of Li$^+$ ($r_{\text{Li}^+} = 0.76\text{Å}$), and Na$^+$ replaces part of Li$^+$, which can not only increase Li layer spacing, but also reduce cation mixing\cite{19}. Hua\cite{20} compares LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ before and after Na doping. XRD results show that the c-axis side length of the sample after Na doping proves that the Li layer spacing has increased. Through the electrochemical performance test, the first discharge specific capacity increased by about 35mA·h/g compared with undoped, and the rate performance also increased, which further shows that sodium doping increases the spacing between the Li layers, speeding up the transmission of Li$^+$ between the lattices.
Other cationic doped elements include Mg, Al, Fe, Cu, etc.

5. Conclusion
The study of Ni-rich NCM cathode materials is mainly to obtain high specific capacity, and high specific capacity also means that a part of safety and stability is lost, and how to compensate for the loss is mainly studied from two aspects of precursor preparation and modification. The preparation of the body mainly affects the particle size, specific surface area and other morphologies of the cathode material. Choosing the appropriate precipitant and preparation conditions is the key to preparing a good morphology precursor. Modification includes surface coating and doping. Coating material should have good chemical stability, and the thickness of coating is the key. Too thick coating will affect the electrochemical performance of the cathode material. Proper cationic doping can not only reduce the cation mixing of cathode material, improve the order of lattice, but also accelerate the diffusion of Li$^+$ and improve its rate performance.

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