Advanced Ternary Cathode Materials for High-Performance Lithium-Ion Batteries

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Abstract. The global shift from fuel-powered vehicles to electric vehicles (EVs) is accelerating, driven by the need to achieve zero emissions. As a cornerstone of this transformation, the development of advanced battery technology is crucial. Among the various components, ternary cathode materials are emerging as a dominant force in powering next-generation EVs. This paper explores the factors negatively impacting the cycling stability and electrochemical performance of nickel-rich ternary cathode materials. In response, it proposes several modification strategies, including ion doping, single-crystal structuring, and surface coating. By exploring these individual approaches, the paper highlights the need for future research to focus on integrating multiple modification techniques. The primary objective is to create batteries with high energy density, superior cycling performance, excellent electrochemical characteristics, and enhanced safety—paving the way for breakthroughs in this rapidly evolving field.

Keywords: Ternary cathode materials; modification strategies; lithium-nickel mixing; microcrack; surface side reactions.

1. Introduction

Lithium-ion batteries, which offer high energy density, stable operating voltage, and other advantages, have been the subject of extensive research and successfully deployed in a range of fields, including portable consumer electronics, new energy vehicles and storage systems. With the rapid development of new energy EVs, the energy density and cycle stability of lithium-ion batteries are increasingly demanding. Higher energy density means higher endurance mileage. To address the growing demand for improved energy density and extended cycle life in lithium-ion batteries, researchers have shifted their focus on the development of advanced cathode materials. The research has progressed from lithium cobalt oxide ($LiCoO_2$) to lithium iron phosphate ($LiFePO_4$) [1,2], continuously seeking cathode materials that offer higher specific capacity, enhanced cycle stability, and excellent rate performance. Among these, nickel-rich ternary cathode materials, specifically Li [$Ni_{1-x-y}Co_xMn_y$] O_2 (NCM, $x \geq 0.6$), have emerged as a promising option due to their superior energy density [3]. This type of lithium-ion battery can satisfy the current requirements of EVs as well as hybrid vehicles for long range. However, the cycle life of ternary cathode materials is much lower than that of the currently used lithium iron phosphate (LFP) [4]. Consequently, how to simultaneously consider the high specific capacity of nickel-rich ternary layered cathode materials as well as the high cycling stability has become one of the research hot topics in this field [5].

Tesla, the leading trolley company today, uses NCM and $LiNi_xCo_yAl_{1-x-y}O_2$ (NCA) nickel-rich ternary cathode materials for the manufacture of 4680 batteries [6]. Nickel-rich ternary cathode materials have high specific capacity and rate capacity, but they have poor cycle stability and high cost [4]. What people really want is for the EV batteries to have higher cycle stability rather than higher energy density. Therefore, this paper will discuss how cation mixing, microcrack and surface side reactions affect the electrochemical performance and cycling stability of Ni-rich ternary cathode materials. Then, this paper summarizes the development and characteristics of the modification strategies of nickel-rich ternary cathode materials in recent years, including ions doping, single crystalline and surface coating.

2. Development Progress and Unique Merits of Ternary Cathode Materials

Before the emergence of ternary materials, there were lithium nickel oxide, lithium cobalt oxide, and lithium manganese oxide, containing only a single element. This kind of cathode material cannot meet people's increasing requirements for high-performance lithium-ion batteries. Therefore, the researchers tried to combine these three elements, and the ternary cathode material Li $[Ni_{1-x-y}Co_xMn_y]O_2$ came into being.

In 1999, Liu et al. prepared Li layered cathode material Li $[Ni_{1-x-y}Co_xMn_y]O_2$ ($0 \leq x \leq 0.5, 0 \leq y \leq 0.3$) [7]. The ternary cathode system not only lowers costs but also significantly enhances specific capacity and cycle stability. In 2001, Ohzuku et al. successfully synthesized the Li $[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ ternary layered cathode material using the co-precipitation method. This material demonstrated a reversible specific capacity of 160 mAh/g [8]. In 2005, Liao et al. further increased the proportion of Ni and prepared a series of Li $[Ni_{0.6}Co_xMn_{0.4-x}]O_2$ materials. The initial discharge capacity of NCM622 ternary materials reached 178 mAh/g, indicating that the increase in nickel content was conducive to the improvement of specific capacity [9]. In 2006, Kim et al. synthesized Li $[Ni_{0.8}Co_{0.2-x}Mn_x]O_2$ (x=0,0.1) layered material and the initial discharge-specific capacity of Li $[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$ (NCM811) reached 198 mAh/g, and Mn partially replaced Co to improve the structural stability of the material [10]. In 2018, Yoon et al. prepared Li $[Ni_{0.95}Co_{0.025}Mn_{0.025}]O_2$ with co-precipitation method [11]. The synthesized particles showed excellent discharge-specific capacity and cycle performance. At 0.1 C times, the initial discharge capacity was 238 mAh/g. After 100 cycles, it still has an 85% capacity retention rate [11]. In 2021, Wang et al. compared LFP blade batteries and NMC/NCA batteries. The energy density of lithium iron phosphate batteries is only 180 Wh kg^{-1}, and the energy density of NCM / NCA cells has reached more than 250 Wh kg^{-1} [3].

Compared with layered oxides with single elements, ternary cathode materials feature high energy density, excellent rate capacity and high thermal stability.

3. Key Factors Affecting the Performance

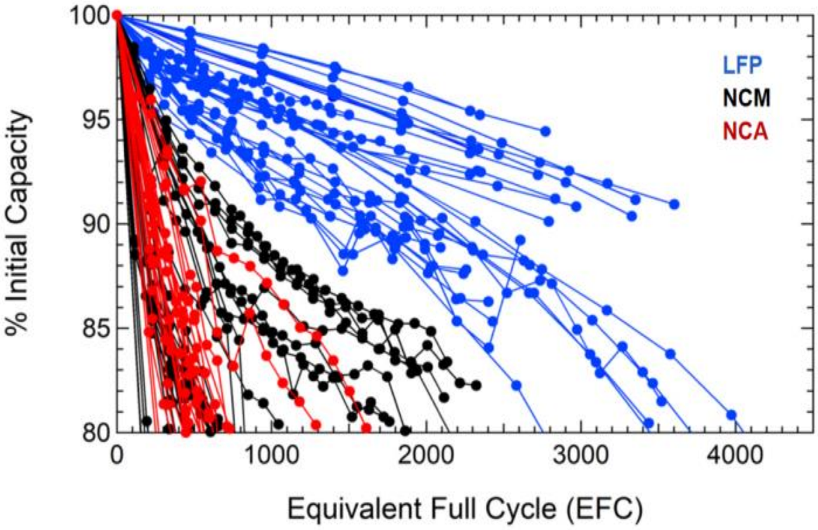

Fig. 1 Retention of discharge capacity compared to equivalent full cycle (EFC) count for LFP cells (blue), NCM cells (black), and NCA cells (red) [4].

Nickel in ternary materials mainly provides capacity for the battery. Manganese reduces material costs and enhances the thermal stability of cathode materials, while cobalt prevents the disordered mixing of nickel and lithium ions, thereby improving the conductivity of the cathode [12]. However, the lithium ions and nickel ions disordered arrangement will increase due to the high percentage of nickel. This phenomenon will reduce the lifespan of the battery, which is much lower than that of an LFP battery [4]. The comparison of the NCM / NCA cells and the LFP cells can be seen in Fig. 1. Inter-crystalline cracks can also cause poor stability of the electrode cycle [13]. The side reaction on the surface of the material will increase the lithium ions embedding and detachment resistance, thus reducing the electrochemical and safety performance of the battery [14].

3.1. Cation Mixing

The ternary layered cathode materials are prone to cation mixing during the material's calcination process and electrochemical cycle. Ni^{2+} ion radius is 0.69 Å, and Li^{+} ion radius is 0.76 Å. The two ions have similar radii, which can easily occupy each other's sites, causing Li^{+}/Ni^{2+} mixing [15].

The nickel ions and lithium ions disordered arrangement is illustrated in Fig. 2 [15]. In the NCM cathode material structure, lithium ions, oxygen and ternary materials are staggered like sandwiches. When nickel ions squeeze into the position of lithium ions, the thickness of each layer will be decreased because the radius of nickel ions is slightly smaller. Lithium-ion embedding becomes more challenging due to local space collapse caused by cation mixing. Furthermore, the structural collapse increases lithium ions embedding resistance, leading to the attenuation of the cycle performance [16].

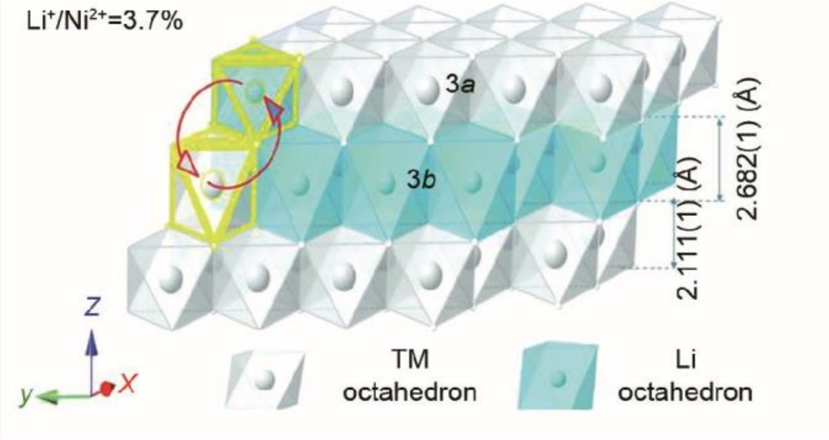

Fig. 2 Schematic diagram of Ni^{2+}/Li^{+} cation mixing [16].

3.2. Microcrack

Internal stresses caused by anisotropy during charging and discharging can result in cracks and pores forming between grain boundaries within the grains [17]. The presence of cracks leads to a decrease in the electrical conductivity of the secondary particles while continuously exposing new surfaces during cycling. Ni^{4+} produces a Ni-O rocksalt impurity layer between the electrode and electrolyte interface that is devoid of any electrochemical activity or electrical conductivity [14]. In addition, when the NCM layered cathode material is charged at high voltage, Ni^{2+} is easily oxidized to Ni^{4+}, and the ionic radius decreases, leading to the collapse of the crystal layer. The battery cycle performance is reduced due to the more challenging de-embedding of lithium ions.

3.3. Surface Side Reactions

Side reactions always occur during the process of Ternary cathode materials synthesis and electrochemical cycling. The by-products can seriously affect the cycling stability and safety performance of the battery. Yoon et al. prepared ternary cathode materials by the co-precipitation method. First, sulfate containing Ni, Co and Mn was used as raw material, NaOH as a precipitant and $NH_3 \cdot H_2O$ as a complexing agent, then mixed with LiOH for high-temperature calcination [11]. The LiOH during the preparation will react with the $LiPF_6$ in the electrolyte to form the HF, resulting in the deterioration of the battery performance. Besides, the nickel-rich ternary materials are prone to react with the CO_2 and H_2O in the air to generate LiOH and Li_2CO_3 on the surface of the materials, and they also react with the $LiPF_6$ to generate HF [18], which corrodes the electrodes and reduce battery cycle stability.

4. Advanced Modification Strategies for Performance Improvement

4.1. Ions Doping

Electrochemically inert ions can replace unstable Ni ions and make their binding to oxygen more stable, thus reducing the extent of Ni^{2+}/ Li^{+} mixing. Li et al. used the co-precipitation method to uniformly doped Mg^{2+} into the lattice to enhance the cycling performance and rate capacity of NCM811. Mg^{2+} doping in the lattice can reduce the nickel-lithium mixing row and inhibit the increase of resistance after circulation [19]. Li et al. tested NCM811 with Nb doping content of 0%, 0.5%, 1%, 2%, and 3%, respectively. They found NCM811 doped with 1% Nb had the highest initial discharge capacity and highest capacity retention after 100 cycles [20]. Nb not only reduces the lithium-nickel mixing but also serves as a pillar of the layered structure and stabilizes the structure during lithium-ion de-embedding [21].

4.2. Single-Crystalline Engineering

Fan et al. synthesized single-crystal $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ and demonstrated that the single-crystal structure was beneficial to mitigate intergranular cracking and inhibit the interaction between the electrode material and electrolyte interface, thus reducing the occurrence of side reactions [22]. Single crystal $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ strengthens the mechanical connection and effectively inhibits the formation of irreversible phase transition, thereby maintaining structural stability. Kong et al. found that impurities on the single-crystalline material do not grow to the interior of the material along the premier particles. Single-crystalline material exhibits a more excellent electrochemical performance than polycrystalline material [23].

4.3. Surface Coating

The surface coating of ternary cathode materials can be achieved by directly covering the surface with a capping agent. Li et al. directly capped zirconium on the surface of NCM811 using a simple wet chemical method. Zr was distributed on the crystal lattice and the surface of the material to form a homogeneous coating film, which not only reduces the Ni-Li mixing but also stabilizes the crystal lattice [24]. At the same time, the contact between the cathode material and electrolyte is reduced, which inhibits the occurrence of side reactions. It is worth mentioning that the capacity retention rate is still 92% after 100 cycles at 1 C. Therefore, the cycling performance is excellent.

5. Conclusion

This paper shows how these phenomena affect the cycle stability and electrochemical performance of nickel-rich ternary cathode materials from the aspects of nickel-lithium mixing, microcrack and surface side reactions. The progress of modification research in recent years is reviewed from the viewpoint of ions doping, single crystalline and surface coating. The following conclusions are listed below:

The modification method of doping with different ions can improve the cycle stability and rate capacity of nickel-rich ternary cathode materials to different degrees.

(2) Single-crystalline materials can effectively reduce the occurrence of side reactions, inhibit the formation of microcracks and maintain structural stability.

(3) The surface coating effectively mitigates Li-Ni mixing and minimizes side reactions between the cathode material and the electrolyte, thereby enhancing the battery's cycle life.

However, a single modification strategy cannot consider the improvement of multiple performances of a battery at the same time, so the modification strategies for nickel-rich ternary materials are often diverse. In addition to the single modification method mentioned above, the current popular research direction is the synergy of multiple modification strategies. The integration of various modification techniques offers innovative approaches for advancing the modification research of nickel-rich layered ternary cathode materials. In the future, this can significantly enhance the performance of lithium-ion batteries and potentially elevate the capabilities of other battery types to better meet daily needs.

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