The Failure Mechanisms and Modification Strategies of Li Ion Battery Ni-based Cathode

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Abstract. With the continuous advancement of the clean energy transition, Lithium-ion batteries are a kind of high-performance energy storage medium. However, high nickel content not only improve capacity of batteries, but also intensifies structure degradation and interface side reaction in the cyclic process, which contributes to capacity fade and decreased safety. This review systematic summarizes the basic structure and electrochemical reaction mechanism of Ni-based layered oxides, and highlights analysis on the primary failure mechanism in high-voltage cycling, which include oxygen release and the form of oxygen vacancy, surface phase transition and cation mixing. On this basis, this review conclude some research advance of mainstream modification strategies, including element doping, which means single anion/cation doping or mixed ion doping were applied to improve crystal lattice stability, restrain cation mixing and increase Li^+ migration rate, surface modification, i.e. isolating electrolyte and restraining side reaction or oxygen release by using metal oxides and carbon materials as coating or applying novel surface treatment method, microstructure engineering, i.e. enhancing surface stability and mitigating structure degradation by regulate the intragranular grain shape, size and arrangement to optimize the stability and electrochemical performance of NCM cathodes, especially for polycrystalline materials.

1 Introduction

The development and utilization of energy is a crucial driving force to promote the progress of human society. However, the large scale use of coal, oil and other disposable energy has caused severe environmental problems. Building a clean and low-carbon new energy system has become an inevitable trend as increasingly strict environmental protection policy in the world [1]. Among many energy storage technologies, lithium-ion battery (LIB) has become the current research hot spot because of its advantages, such as high energy density, low self-discharge rate and no memory effect. Cathode materials is core components of LIB, which directly determines the energy density and safety of the battery [2]. Layered $LiCoO_2$ is first commercial LIB. Though it has excellent electrochemical performance, the scarcity, potential toxicity and high price of Co limit its further application in the field of low-cost and high energy density lithium-ion batteries for electric vehicles. Therefore, layered LiNiO2 and

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other Ni-based cathode materials has attracted extensive attention because of lower cost, higher specific capacity and working voltage.

With the continuous development of research on Ni-based cathode materials, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$(NCM111),$LiNi_{1/2}Co_{1/5}Mn_{3/1}0O2$(NCM523),$LiNi_{3/5}Co_{1/5}Mn_{1/5}O_2$(NCM 622), etc. Ni-based ternary layered oxides have been developed successively, these kind of materials perform better electrochemical cycle stability by adjusting the proportion of Ni, Co and Mn compared with $LiNiO_2$. In order to further improve the electrochemical performance of ternary layered oxide cathode, increasing the content of Ni is conventional strategy, but the transition metal Ni and Li ions get a more thorough mix, which increases the possibility of phase transition and structural instability [3]. At the same time, these structural changes will also accelerate the interface side reactions and oxygen release, leading to the decline of structural stability and cycle performance of materials. Therefore, it is essential to, reveal the failure mechanism of Ni-rich layered oxide materials, which are basis and key to further optimize its performance and develop high reliability lithium ion power battery.

On the basis of the structure of Ni-based cathode materials and charge and dis charge principle, this review analyzes the failure causes of battery and the progress of modification strategies. Firstly, review systematically analyzes and summarizes the basic structure and reaction principle of Ni-based cathode materials. Secondly, review summarize failure mechanisms of Ni-rich cathode, including oxygen release and bulk oxygen vacancy, surface phase transition and cation migration. Then, this review summarizes modification strategies stem from failure mechanisms. By element doping, surface modification and microstructure engineering, the cycle life and safety of the battery have apparent improvement. Finally, review summarizes the difficulties and shortcomings of existing research and puts forward the feasible research direction of continuing to develop better performance batteries in the future.

2 Overview of Ni-based materials and reaction principle

Ternary Ni-rich cathode materials NCM, layered rock-salt structure (α-NaFeO2-type, space group R-3m), whose crystal consists of a cubic close-packed arrangement of oxygen atoms. The transition metal layer and Li layer are alternately arranged in this structure, forming a two-dimensional channel conducive to Li ion deintercalation. Ni, Co, Mn have synergistic effect in materials, affecting its electrochemical performance. Li ion deintercalation mainly dependent on redox electron pairs such as Ni^{3+}/Ni^{2+} or Ni^{4+}/Ni^{3+}.Therefore, Ni-rich cathode materials have higher energy density. The introduction of Co is conducive to enhancing the orderliness of the layered structure, reducing cation mixing, thereby improving structural stability. The thermodynamic properties can be enhanced at the same time, electronic and ionic conductivity of the material. Mn exists in the +4 valence state, which mainly aims to stabilize the crystal structure, improve electrochemical stability, and safety. However, excessive Mn may affect the layered structure to transform into the spinel phase, deteriorating the electrochemical performance [4].

During the battery charging process, transition metal ions undergo oxidation as the voltage increases. When the voltage is between 3.6-3.9V, Ni^{2+} is oxidized to Ni^{3+}.Ni^{3+} is further oxidized to Ni^{4+} when the voltage increases to 3.9-4.4V. When the voltage reaches 4.6-4.8V, Co^{3+} is oxidized to Co^{4+}. Over the entire charging voltage range, it is worth noting that the K-edge XRS of Co continuously changes, indicating that Co participates in the charge compensation process consistently. Mn maintains +4 valence state unchanged. Li^+ mainly escapes from the Li layer along the two-dimensional path of interlayer. Its diffusion energy barrier is related to the concentration. During the discharge process, transition metal ions undergo a reduction reaction. Co^{4+} is reduced to Co^{3+}. Ni^{4+} is reduced to Ni^{3+}, and further reduced toNi^{2+}. Li^+ embed into the Li layer at the same time.

3 Failure mechanisms

3.1 Oxygen release and loss in reaction

The main safety issue Li ion batteries is the release of oxygen during the reaction process [4]. O^{2-} ions are oxidized to O_2 during the charging process. This chemical process is exothermic and can easily trigger a series of chain reactions, which may pose significant dangers such as self-ignition of batteries. Oxygen release is a flexible phenomenon, which occurs during different phases of charge and discharge cycle of battery. Researchers studied the oxygen emission sources at different phases of NCM811 charge and discharge cycles by18O isotope labeled method. Then, three stage of oxygen release was summarized [5]. The voltage of first stage below 4.3V, below the standard cut-off voltage. There is no significant oxygen release at this time. The second stage has a little O_2 release and noticeable structural transformation of the material, accompanied by excessive Li deintercalation and transition metal oxidation, whose voltage between 4.3 to 5.5V. At third stage, the voltage is approximately equal to 5.5V. There is a large amount of O_2 release without obvious phase structure evolution. However, the accumulation of Li vacancies in the lattice causes significant internal stress, leading to microcracks inside and between particles, accelerating oxygen release. The removal of oxygen ions can lead to structural defects called oxygen vacancies [6]. Bulk oxygen vacancy is main reason of Li ion cathode degradation. Long term cycling can lead to the release of oxygen, forming vacancies on the surface of particles, and then diffusing into the bulk. Therefore, oxygen loss and oxygen vacancy formation are interrelated core defects, which not only trigger structural reconstruction but also affect the reversibility of Li^+ diffusion and redox reactions.

3.2 Structural instability and surface phase transition

When extensive Li^+ extract from cathode, Ni^{3+} is further oxidized to highly active Ni^{4+}, O^{2-} in lattice will lose its electrons because of strong oxidizing property of Ni^{4+}, leading to lattice oxygen to be released in the form of O_2. The result is that the original layered structure skeleton of the cathode material is destroyed, affecting the structural stability. At the same time, Ni^{4+} undergo intense redox reactions with organic components in the electrolyte, such as carbonate solvents, intensifying interface degradation [7].

The surface phase transition of Ni-rich electrodes is not a single process. Its phase type is strongly correlated with the charging cut-off voltage. When voltage lower than 4.5V, because of a limited number of Li vacancies, only a small amount of Ni^{2+} migrate into the tetrahedral interstices of the Li layer. They can form a structure similar to spinel with residual Li^+ and O^{2-}. This structure lacks long-range order, but its skeleton still partially maintains layered features. Conversely, when voltage higher than 4.5V, with further increasing Li^+ extraction and a large amount of lattice oxygen is released, resulting in utter chaos of atomic arrangement in transition metal layer and Li layer. Ni^{2+} occupy lattice site randomly. Forming rock salt facies similar to structure of NaCl. Research has shown that NCM811 can achieve a surface rock salt phase thickness of 20-30 nm at 4.8V cycle process. It can extend towards the interior of the particles, leading mass loss of cathode active site [8].

3.3 Cation migration

Cation migration mainly occurs during high-voltage cycling, where transition metal ions migrate from the transition metal layer to the vacancies of Li layer. The ions will form a shared octahedral structure with LiO_6, leading to cation mixing, damaging the original

layered structure. Cation mixing mains that transition metal ions, e.g., Ni, Co, Mn, partially occupy the 3a site which originally occupied by Li^+. At the same time, the layered structure on the cathode surface degrades into an inert phase, obstructing the transport of Li^+ and electrons while reducing the efficiency of charge transfer, and eventually resulting in a rapid capacity decay of battery. Li^+/Ni^{2+} mixing is the most typical situation in Ni-rich cathodes.

The mixing caused by the high temperature solid-phase synthesis process, coupled with the high kinetic activity of transition metal ions within the crystal lattice. Its ionic radius is similar to Li ions($r(Ni^{2+})$=0.069nm, $r(Li^+)$=0.076nm), which partially occupy 3a site, leading to cation mixing. In addition to this steric effect, researchers have also proposed a magnetic interaction mechanism [9]. Incorporating such mechanism offers a novel viewpoint to understand and interpret cation mixing. Due to unpaired electrons occupying the d orbitals of transition metal ions, nickel ions establish a 90 º superexchange configuration with neighboring transition metal ions and bridging oxygen ions. Besides, because of magnetic separation, the ion exchange between $Ni^{2+}$and Li^+ takes place inside the transition metal layer. This process obtains Ni^{2+}-O_2-Ni^{2+} /Mn^{4+}, which is thermodynamically stable linear superexchange configuration at 180 °.

4 Modification strategies

4.1 Element doping

Element doping not only improves the stability of crystal structure but also reduce cation mixing and irreversible phase transition by regulating the crystal structure, ion diffusion pathway and electronic conductivity of Ni-rich cathodes, which could enhance its electrochemical performance and structural stability effectively [10]. This strategy can be mainly divided into three categories. Cation doping, anion doping and mixed ion doping. The cation, e.g., such as K^+, Na^+, Mg^{2+}, which has small radius tend to occupy the Li sites, inhibiting the formation and propagation of microcracks. However, it is possible to smaller capacity. Large radius cation (such as Ti^{4+}, Ta^{5+}, Mo^{6+}) occupy the transition metal layer, enhancing bond strength between metal ions and oxygen atoms and improving the stability of lattice oxygen. Anion doping aims to replace some oxygen atoms with halogen, S^{2-} or Cl^- , reducing Li/Ni cation mixing and risk of transition metal dissolution while enhancing the acid and corrosion resistance of materials. Mixed ion doping aims to further optimize performance by simultaneously introducing cations and anions, combining the advantages of different ions to generate synergistic effects. Lee et al. discovered that the stability of NCM92 was significantly improved after double doping with Al^{3+} and Nb^{5+}.Al^{3+}contributes to enhancing the crystal structural stability, whereas Nb^{5+} plays a role in regulating the morphology of primary particles. Benefiting from the synergistic effect of these cations, the lattice ordering of the Ni-rich cathode is effectively enhanced, accompanied by a reduction in lattice strain [11].

4.2 Surface modification

The liquid electrolyte is in direct contact with the surface phase of the cathode material. And there are several adverse reactions, which exerts significant influence on the performance and safety of the battery, especially under high temperature and high voltage. Therefore,in order to get cathode material with excellent thermal stability and safer battery, it is essential to research on the surface or near surface of materials. Bulk doping primarily functions on cathode itself, so intervening in the problem that occur on the surface of particles is difficult. Surface modification is a available strategy to solve side reaction of surface. Functional

coatings or shells have been developed to effectively avoid interactions between cathode materials and organic electrolytes when using metal oxide and metal phosphate coatings. Considering surface protection effect, although a thick and uniform coating is beneficial for surface stability, it is not conducive to charge transport. In order to form a uniform coating or core-shell structure with well adhesion on the surface of Ni-rich cathode material particles, researchers have developed various synthesis methods. Precipitation Method aims to control pH or utilize charge interactions, depositing coating precursor on the surface and then forming a protective film through heat treatment. This method can achieve large scale use with low-cost. It can prepare concentration gradient structures while the disadvantage is that it is difficult to control the layer thickness.M Dong et al. cover surface of NCM811 grain with Al(OH)3 precipitate, then generate Al_2O_3 coating with high-temperature treatment. The modified NCM particles exhibit higher structural integrity and reduced cation mixing. It can resistance to HF corrosion while cycling performance and capacity retention have been improved [12]. Sol-Gel Method, the metal precursor is used to form a uniform sol in the solvent, which is converted into gel by evaporation and concentration, and then the organic components are removed by calcination, forming a high-purity, fine particle coating. The coating obtained by this method has the advantages of high purity and the ability to contain insoluble components, but it is easy to produce uneven coatings. J Xu et al. made use of electrostatic interaction between NCM523 nanoparticles and Y_2O_3 Compounds, promoting the anchoring of protective species on the positive electrode surface. A uniform coating with a thickness of 20mm was prepared, which significantly improved cycling stability under high-temperature [13]. Atomic Layer Deposition method (ALD) aims to alternately introduce two types of reaction precursors, a coating is deposited layer by layer at the atomic scale, and the deposition thickness can be precisely controlled (atomic level accuracy). The coating has excellent adhesion to the cathode surface. However, the problem is that the high equipment cost and difficulties of mass production. P Yan et al. used Li_3PO_4 to get coating, which was applied by ALD and annealing treatment. That coating not only covered the surface of the cathode, but also partially penetrated to the surface of the particles, strengthening the interfacial bonding [14].

4.3 Microstructure engineering

The aim of microstructure engineering is to homogenize the grain size and shape of individual particles, as well as to regulate the grain alignment within secondary particles. It can be effectively employed in polycrystalline NCM materials. This strategy optimize performance of cathode materials by changing gas release law and stress distribution of NCM grain. Reducing particle orientation and increasing grain boundary density can offer extra channels for oxygen diffusion in cathode materials, thus lowering the possibility of oxygen accumulation in charge-discharge cycling. The grain boundary can be considered as a stress relief zone, which adjust the lattice mismatch and reduce the interfacial strain between adjacent crystals. Then, the crack propagation is prevented, the mechanical stability as well as structural integrity are improved [15]. For Ni-rich cathode, structure design of single crystal prevent the intergranular crack caused by anisotropic stress, making it possible for materials to maintain original form. What's more, Ni-rich single crystal grain has smaller specific surface area, reducing the contact between the electrolyte and active material, leading to minimize the unfavorable reactions at the electrolyte-cathode interface.

5 Challenge and outlook

Ni-rich layered cathode materials is one of the most promising high energy density LIB system. Although it still faces challenges such as structural stability, interface compatibility

and safety, the increase of nickel atom content not only brings about high specific capacity of the battery, but also causes side reactions of electrolyte and phase transition of lattice oxygen, leading to lattice collapse and capacity fading on the structure. Through the strategies of element doping, surface coating and microstructure regulation, its comprehensive performance has been significantly improved.

In the future, the research of Ni -rich cathode materials should further focus on multi-dimensional key directions. For one thing, it is necessary to develop in-situ/ operando characterization techniques, revealing the structural evolution and failure mechanism of materials in the cycle process and providing accurate basis for targeted modification. For another, intelligent coating and doping system with adaptive functions should be developed, realizing dynamic protection at the electrode interface. Developing low-cost and large-scale preparation processes for single-crystal/ quasi-single-crystal materials simultaneously, resulting in breakthrough in bottleneck of mass production and application. What's more, theoretical calculation and machine learning technology should be combined to accelerate the design and screening of latest high-performance material systems. Through multi-scale and multi-strategy synergistic optimization, Ni-rich cathode materials are expected to further break the upper limit of energy density and promote the commercial application of the next generation of high energy Li-ion batteries on the premise of ensuring safety and cycle life.

6 Conclusion

This review summarizes the research progress of degradation failure mechanisms and modification strategies of Ni-rich cathode materials. The core degradation problem of NCM stems from the irreversible deterioration of bulk phase and surface, which is embodied in lattice vacancy, structural reconstruction, transition metal dissolution, etc. The degradation of bulk phase and surface is interactive and synergistic. The microcrack of bulk phase and cation mixing of Ni and Li can accelerated surface reconstruction and transition metal dissolution. Residual Li compounds on the surface can hinder Li ion transport. At the same time, Ni content has a significant effect on the failure mechanism. Residual stress induced by bulk phase transformation is main cause of degradation when Ni content ratio higher than 80%. Conversely, the influence of progressive surface degradation on capacity fading is more prominent. To above problem, modification strategies centered on bulk phase stability and interface stability have been formed. For bulk phase stability, composition engineering can be used to relieve mechanical stress and oxygen release. Also, microstructure engineering can be used to balance ion transport and maintain thermal stability. For interface stability, surface engineering such as residual lithium conversion and conductive coatings can be employed to suppress surface reconstruction and electrolyte erosion. The stability problem of Ni-rich NCM can be solved by synergistic effect of such two strategies. The key to the further development of NCM in the future lies in the precise regulation with multi-dimensional parameters, optimizing internal structure stability by bulk phase engineering, suppressing surface side reaction by interface engineering. At the same time, breaking through the process bottleneck with the help of interdisciplinary technology. Ultimately, achieving the goal of higher energy density, low cost and long cycle life, promoting wide application in the field of large-scale energy storage and electric vehicles.

References

1. S. Cao, J. Wang, F. Lu, et al., Research progress on failure mechanisms and modification of cathode materials for lithium-ion batteries. New Chemical Materials **53**, 7–14 (2025).

2. Y. Lyu, X. Wu, K. Wang, et al., An overview on the advances of $LiCoO_2$ cathodes for lithium‐ion batteries. Advanced Energy Materials **11**, 2000982 (2021).
3. J. Gao, et al., Single-crystal nickel-rich cathode materials: fundamentals, challenges and prospects. Chemical Communications **61**, 13780–13794 (2025).
4. D. Li, et al., Degradation mechanisms and modification strategies of nickel-rich NCM cathode in lithium-ion batteries. Materials Research Express **11**, 012006 (2024).
5. C.-G. Shi, et al., Investigation and suppression of oxygen release by $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode under overcharge conditions. Advanced Energy Materials **12**, 2200569 (2022).
6. S. Aslam, L. Hou, Q. Liu, W. He, D. Mu, L. Li, R. Chen, F. Wu, Lithium rich layered oxide: exploring structural integrity, electrochemical behavior, performance failures and enhancement strategies through doping and coating. Energy Storage Materials **79**, 104325 (2025).
7. Z. Cui, X. Li, X. Bai, X. Ren, X. Ou, A comprehensive review of foreign-ion doping and recent achievements for nickel-rich cathode materials. Energy Storage Materials **57**, 14–43 (2023).
8. F. Lin, I.M. Markus, D. Nordlund, T.C. Weng, M.D. A.H.L. Xin, M.M. Doeff, Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries. Nature Communications **5**, 3529 (2014).
9. J. Zheng, et al., Ni/Li disordering in layered transition metal oxide: electrochemical impact, origin, and control. Accounts of Chemical Research **52**(8), 2201–2209 (2019).
10. Z. Liu, Y. Zhang, S. Pan, et al., Addressing the fundamental issues in Ni-rich cathodes: degradation mechanisms and mitigation strategies. Energy & Environmental Science (2026).
11. S.B. Lee, N.Y. Park, G.T. Park, et al., Doping strategy in developing Ni-rich cathodes for high-performance lithium-ion batteries. ACS Energy Letters **9**, 740–747 (2024).
12. M. Dong, et al., Metallurgy inspired formation of homogeneous Al_2O_3 coating layer to improve the electrochemical properties of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material. ACS Sustainable Chemistry & Engineering **5**, 10199–10205 (2017).
13. J. Xu, X. Chen, C. Wang, et al., Nano-Y_2O_3-coated $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathodes with enhanced electrochemical stability under high cut-off voltage and high temperature. Ceramics International **43**, 11848–11854 (2017).
14. P. Yan, J. Zheng, J. Liu, B. Wang, X. Cheng, Y. Zhang, X. Sun, C. Wang, J.G. Zhang, Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries. Nature Energy **3**, 600–605 (2018).
15. Z. Wu, C. Zhang, F. Yuan, et al., Ni-rich cathode materials for stable high-energy lithium-ion batteries. Nano Energy **126**, 109620 (2024).