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The Progress and Prospects of Doping Modification of High-Nickel Ternary Cathode Materials

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Abstract. High-nickle ternary cathode materials(NCM) have become the core of high power density lithium-ion batteries by virtue of its outstanding specific capacity. But the lattice distortion caused by its deep lithium extraction, the disordered arrangement of lithium-ion and nickle-ion, interface side reaction restricted the cycle life and safety. This article systematically reviewed the latest advancements in the doping modification of element to enhance the structural-interface-dynamic stability of the NCM system: the impurity cations can expand the inter-layer spacing of the lithium layer, inhibit disordering, and reduce lattice strain by occupying the transition metal sites; the impurity anions noticeably enhance the transition metals and oxygen bonds, reduce oxygen vacancies and the mixed arrangement of transition metals; the multi-ion co-doping technology achieves a comprehensive performance improvement through the synergy of "structure + interface", indicating that element doping modification has advanced from the "trial-and-error of single atoms" stage to the stage of "structural-interface coordinated regulation" .This article summarizes the existing problems of element doping modification of high-nickel ternary materials, providing reference ideas for the future optimization of doping modification techniques.

1 Introduction

Fossil fuels have become the primary energy source used by humans currently because of their high energy density. However, their extensive use has caused significant damage to the environment: As of March 2024, the global CO_2 concentration reached 422.80 ppm, CH_4 concentration reached 1929.58 ppb, having increased by 1.26 and 1.17 times respectively compared to levels forty years ago [1]. At the same time, the reserves of fossil fuels have sharply declined, so developing sustainable new energy sources and efficient energy storage devices such as hydrogen, solar energy, and lithium-ion batteries has become the key to breaking the deadlock.

Lithium-ion batteries are the core energy storage devices. The cathode material determines their capacity and stability. Among them, high-nickel ternary materials have rapidly gained popularity with their excellent performance. Their global production share has

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increased from 10.8% in 2019 to 53.7% in 2023 [2]. In the current lithium-ion battery system, the positive electrode material is the main factor influencing the capacity of high-nickel ternary cathode materials. The capacity of high-nickel ternary materials at present can reach above 200 mAh g^{-1}, which can be comparable to the capacity of 372 mAh g^{-1} of commercial graphite anode materials [3, 4]. The high-nickel ternary cathode material prepared by Li et al. achieved a first-cycle Coulomb efficiency of 90.34% and a reversible capacity of 213.77 mAh/g, after 100 cycles of charging and discharging, the capacity retention rate of the battery reached 98.7% [5]. This indicates that the high-nickel ternary cathode battery can significantly improve the electrochemical performance of the lithium-ion battery. However, there are still some technical challenges at present, such as insufficient structural stability and unstable electrolyte-interface, which restrict the industrialization of high nickel ternary cathode materials [6, 7]. Therefore, modifying the high-nickel ternary cathode materials to enhance the stability of batteries has become a current popular research direction.

Element doping modification is an reliable method to solve the these issues of high-nickel ternary materials, the core principle is to introduce hetero ions of metals or non-metals into the layered lattice of the material, simultaneously optimizing the stability of structure and conductivity, ultimately enhancing the output power and cycle life of the battery. According to the type of doping ions, element doping can be classified into three categories: cation doping, anion doping, and multi-ion co-doping.

High-nickel ternary cathode materials are the core carriers for breaking through the bottleneck of lithium ion batteries. Element doping modification provides a targeted solution to the industrialization challenges of these materials. This article systematically summarizes the research progress in the field of element doping in recent years, reviewing the mechanism of action and performance optimization effects of different doping types. The aim is to provide theoretical references and technical ideas for the development of subsequent efficient modification strategies, and to facilitate the industrialization process of high performance batteries.

2 High-nickel ternary cathode material fundamentals

2.1 Material structure

The chemical formula of the high-nickel ternary cathode material is $LiNi_xCo_yMn_{1-x-y}O_2$ ($x \geq 0.6$, NCM). Its crystal structure is highly similar to that of $LiNiO_2$, and can be regarded as a derivative of $LiNiO_2$ after some Ni atoms are replaced by Co and Mn atoms. The core structural feature of this material is as follows: Three transition metals (TM), namely Ni, Co, and Mn, randomly occupy octahedron coordination sites. This TM layer alternates parallelly with the lithium-layer, and the inter-layer voids constitute a fast transmission channel.

2.2 The mechanism of lithium storage

The charge-discharge process of NCM is essentially a process in which the insertion/deposition of Li^+ between the cathode and the anode and the redox reactions of transition metal ions occur simultaneously. During the lithium removal charging process, Li^+ preferentially leaches out from the local Ni-O environment, resulting in the oxidation reaction of Ni^{2+} to Ni^{3+}. Subsequently, it leaches out from the Co-O or Mn-O environment, leading to the deep oxidation of Ni^{3+} to Ni^{4+}. Finally, it migrates through the electrolyte to the negative electrode and is embedded in the negative electrode material. During the entire charging process, for every Li^+ ion released, the transition metal layer will release one electron. And the electrons are mainly provided by the oxidation of Ni, Co and Mn only participate in oxidation in small amounts in the high-voltage range [8]. The lithium insertion discharge process is the opposite of charging. Lithium ions are released from the negative electrode, flow through the electrolyte back to the NCM positive electrode, and reinsert into the crystal lattice; The transition metal ions undergo reduction reactions, with their valence states returning to their initial levels.

3 Classification of element doping modification and its mechanism of action

3.1 Cation doping

Cation doping achieves the dual effects of "structural stabilization + kinetic enhancement" by introducing metal ions with the same valence or univalent metal ions (such as Na^+, Mg^{2+}, Al^{3+}, Ti^{4+}, Nb^{5+}, etc.) into the NCM lattice, thereby replacing some of the Ni, Co, and Mn lattice sites. Univalent ions (such as Ti^{4+} and Nb^{5+}) can establish a charge balance mechanism and inhibit the disordering of cations; The atomic radius differences of cations can adjust the lattice parameters, reduce the inter-layer volume strain during charge-discharge processes, and maintain the completeness of the layered structure; Some highly electronegativity cations (such as Al^{3+}) can enhance the transition metals and oxygen bonds, and inhibit the oxygen release process.

Zhao et al. successfully synthesized a nickel-cobalt-manganese-nickel alloy (NCMN) doped with 0-1.5% Nb^{5+} [9]. Among them, the 1% Nb^{5+} doped sample exhibited the best performance. The experiment shows that the 1% Nb^{5+} doped sample (NCMN1) has an first discharge capacity of 222.3 mAh g^{-1} at a high voltage of 4.6 V. After cycling at a current density of 1 C for 100 times, the capacity retention rate reaches 92.03%, which is much better than that of the undoped sample(74.3%);At the same time, the charge transfer impedance decreased to 88.13 Ω, and the lithium-ions diffusion rate increased by approximately 4 times.Further confirmation through first-principles calculations and density functional theory shows that doping with Nb^{5+} can expand the lithium layer spacing, reduce the band gap, and increase the electronic state density near the Fermi level, thereby enhancing the conductivity.

Yue et al. synthesized the $LiNi_{0.9}Co_{0.05}Mn_{0.05}$ material by high-temperature solid-state method by doping boron into the high-nickel ternary cathode material [10]. The results of XRD, SEM, TEM, CV, EIS, electrochemical cycling tests and particle compression experiments indicate that boron doping has changed the morphology of the primary particles of the material, making them longer and more closely arranged, the compressive strength has increased from 74.5 MPa to 104.4 MPa, it suppressed the formation of microcracks and particle fragmentation during the cycle, thereby enhancing the structural stability. The boron doping technology effectively enhances the rate performance, cycle stability and structural durability by optimizing the grain morphology, strengthening mechanical properties and promoting lithium-ion transport.

3.2 Anion doping

Anion doping mainly replaces O^{2-} in the NCM lattice with halogen ions such as F^- and Cl^-. By taking advantage of the high electronegativity of halogen ions, the TM-O bond interaction is optimized, achieving the dual effect of "structural stability + interface regulation". The electronegativity of F^- and Cl^- is higher than that of O^{2-}. This can enhance the ionicity of the TM-O bond, reduce the risk of lattice oxygen release, and inhibit the structural collapse during the charge-discharge process; Anion doping can also reduce the generation of oxygen vacancies, decrease the mixed arrangement of transition metal ions, and moderate the side reactions at the interface between the electrolyte and the cathode (such as electrolyte decomposition and instability of the CEI membrane).

Peng prepared fluorine-doped NCM811 (NCM811-1%F) by using the co-precipitation - high-temperature sintering method and the two-step low-temperature fluorination method [11]. The multi-scale characterization results show that fluorine successfully entered the lattice without disrupting the layered structure, the degree of lithium-nickel intermixing decreased, the particle morphology became more complete, and the element distribution was more uniform. The electrochemical performance tests show that the NCM811-1%F cathode material prepared by doping fluorine into the commercial NCM811 cathode material has a charge transfer impedance Rct of only 205 Ω. By introducing F- into the NCM811 lattice, the bond energy between transition metals and oxygen is enhanced, inhibiting the oxygen release process and the mixed arrangement of transition metals. This effectively alleviates the electrolyte erosion and side reactions, thereby significantly improving the stability of structure and cycle life of positive electrodes.

Zeng synthesized $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ high-nickel cathode materials doped with F^- or Cl^- elements [12]. The experiment revealed that both F^- and Cl^- entered the oxygen positions of the crystal lattice. Cl^- expanded the interlayer spacing of Li^+ while also extending and introducing mesoporous structures, and F^- formed stronger TM − F bonds, both reduced the lithium ion migration energy from 0.900 eV to 0.489 eV and 0.568 eV respectively. The gradient doping experiment indicates that appropriate doping can refine the primary particles, form a porous structure, and enhance the electrolyte infiltration and Li^+ transport; excessive doping, however, will exacerbate the mixing of Li^+ and Ni^{2+} and cause side reactions. Therefore, by adopting the "halogen anion doping + porous structure" technology, it is possible to simultaneously reduce the lithium ion migration energy, stabilize the transition metal layer, and shorten the ion transmission path in the high-nickel cathode, thereby significantly enhancing the rate and cycle property of the power battery.

Compared with the single-doping (cation or anion), multi-ion co-doping can achieve the synergistic effect of "structure regulation + interface stability": cations inhibit ion disordering, while anions strengthen the bond between metals and oxygen. The combination of these two can more comprehensively address the stability issues of high-nickel materials. For instance, Titanium ions can expand the diffusion pathway for lithium ions, while tantalum ions can reduce the disorder of cations and promote the radial growth of primary particles, as well as increase the rate of charge transfer. The synergistic effect of these two elements effectively enhances the initial discharge capacity and the long-term cycle stability [13].

Deepak Kumar et al. synthesized the 0.5%Ti-0.5%Ta co-doped sample LNMC-55 and the 1.0%Ti-1.0%Ta co-doped sample LNMC-11 by introducing Ti and Ta elements into the NMC811 material to replace some of the Co sites in the lattice [13].The experimental characterization indicates that the initial discharge capacity of LNMC-55 at 1 C reaches 161.1 mAh g^{-1}, and the capacity conversation ratio after 250 cycles is 87.1%, which is significantly higher than that of the original undoped sample (only 59.8%)； The lithium diffusion coefficient can be effectively maintained at a high level, and there are almost no microcracks that generate with NiO.The experimental results show that appropriate doping of Ti/Ta markedly reinforce both stability of structure and electrochemical performance by expanding the inter-layer spacing, refining the grains, inhibiting irreversible phase transformation, and stabilizing the CEI membrane.

Guo et al. used Al_2O_3 and B_2O_3 as doping sources to prepare the $Li-(Ni_{0.88}Co_{0.09}Mn_{0.03})_{0.985}Al_{0.005}B_{0.01}O_2$ [14]. The research has found that the boron element tends to remain on the surface of the NCM particles, forming a tetrahedral structure with the lattice oxygen, while aluminum is more likely to enter the transition metal layer. Due to the weakened shielding effect on the smaller radius of the B atom, the boron-oxygen bonds formed on the surface of the NCM particles have a higher bond energy, which can effectively inhibit the process of oxygen release during high-voltage charging, and simultaneously promote the formation of a highly reconstructed layered spinel-rock salt phase structure on the surface. By adjusting the doping depth and doping sites, the surface and the transition layer can be reconstructed, reinforcing the surface stability and cycling property of the material.

4 Current challenges and future directions

4.1 Current challenges

At present, the main problem we are facing is the unclear mechanism of the co-doping synergistic effect. The current research mainly focuses on the macroscopic correlation of "doping - performance", lacking dynamic evolution analysis at the atomic scale, and it is difficult to clearly identify the cooperative action paths of different doping ions. Meanwhile, the introduction of multiple ion doping may lead to unpredictable lattice defects, and the mechanism by which these defects negatively affect the material properties remains unclear.

Secondly, the process of doping and the control of doping concentration are very difficult. The high-nickel NCM material is extremely sensitive to doping concentration, and the optimal concentration range is usually narrow. Any deviation from the optimal concentration will lead to a sharp decline in performance. Furthermore, the current large-scale doping processes have the problems of "poor doping uniformity and high energy consumption", while the low-temperature solution method is unable to achieve the lattice-level embedding of doping ions, making it difficult to balance "precision" and "scale".

Finally, there are issues related to cost and compatibility. Some of the efficient doping elements are expensive, thereby increasing the cost of material preparation. Meanwhile, there is relatively little research on the interface compatibility between the doped materials and the electrolyte, as well as the negative electrode. This may lead to a contradiction where the performance of the lithium battery cathode material improves, but the overall battery performance deteriorates.

4.2 Future directions

To address the issue of unclear mechanism of co-doping synergistic effect, in-situ TEM four-dimensional imaging, in-situ XRD can be carried out simultaneously and in parallel to track the charge transfer path and bond length changes during the discharge process, and establish a database of doped atoms-defects; Introduce high-throughput machine algorithms to rapidly calculate the introduction of ionic charge compensation to screen the optimal doping ion combination, thereby reducing the amount of experiments.

Regarding the doping process and concentration control issues, a high-precision ion concentration detection model was introduced to keep the fluctuation of ion doping concentration within approximately 0.05%, quickly determining the optimal window; by introducing the plasma field to promote the lattice-level embedding of doping ions.

To address the issues of doping cost and compatibility, the doping elements are selectively leached using deep eutectic solvents, enabling a closed-loop recycling process and reducing industrial costs. To solve the compatibility problem, the positive electrode, electrolyte, and negative electrode can be designed as a single unit. A protective layer can be designed on the surface of the cathode to inhibit the mixed arrangement of transition metals.

5 Conclusion

Based on the existing research, cation doping significantly inhibits disordering and buffers volume strain through lattice occupation and charge balance mechanisms; anion doping enhances metal-oxygen bonds by virtue of its high electronegativity, reduces oxygen vacancies and transition metal dissolution; The multi-ion co-doping couples the advantages of both, demonstrating a multiplier effect in aspects such as expanding the inter-layer spacing, refining the grains, stabilizing the CEI membrane, and enhancing the Li^+ diffusion coefficient. Element doping, as a mature and effective modification method, has promoted the release of higher discharge capacity by high-nickel ternary cathode materials at high voltages and demonstrated excellent cycle stability. In the future, the design will continue to deepen in the direction of closed-loop computing-experimentation, gradient space distribution, and integration of process-doping, providing core support for high-nickel ternary materials to move towards ultra-high energy density battery power.

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