Transactions on Environment, Energy and Earth Sciences
ISSN: 2960-1924, eISSN: 2960-2300 | Volume 5
EMCEME 2025

Enhanced capacity retention of NCM batteries through doping optimization

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Abstract. Nowadays, People are very concerned about the range of electric vehicles, and scientists are also working hard to study how to increase the range. At present, among various methods to enhance energy density, replacing electrode materials is the most common. For instance, nickel get high capacity, the most common nickel-containing battery is NCM ($LiNi_xCo_yMn_zO_2$) battery. During the charging and discharging process of NCM batteries, lattice distortion is prone to occur, leading to the collapse of the layered structure and the generation of microcracks. By doping large-radius ions to support the lattice structure, phase transition is suppressed and stress accumulation is reduced. Herein, among several solutions, the doping methods are analyzed emphatically. By consulting literature, based on XRD and other images, various doped elements are analyzed, and the retention rates of capacitance is analyzed to theoretically verify the bias of NCM on doped elements. This paper also proposes a hypothetical combination of doping methods and nanotechnology, aiming to address the expansion of some doped elements, such as silicon, through the characteristics of nanometers.

Keywords: NCM battery, capacity retention, dopants.

1. Introduction

With the continuous growth of modern society's demand for portable electronic devices, electric vehicles, etc., the demand for high-performance batteries is becoming increasingly urgent. Traditional lead-acid batteries, nickel-metal hydride batteries, etc. are gradually failing to meet the requirements in terms of energy density, endurance and other aspects. Lithium-ion batteries have gradually become mainstream due to their advantages such as high working voltage and high energy density. However, early lithium-ion batteries like lithium cobalt oxide also had problems such as high cost (scarce cobalt resources and large price fluctuations) and safety. NCM ($LiNi_xCo_yMn_zO_2$) batteries have emerged as The Times require. By adjusting the proportion of the three elements, they can achieve balanced optimization in multiple aspects such as energy density, cycle life, safety, and cost.

However, NCM got a poor capacity retention due to bulk structure collapse and surface deterioration. such as Li^+ and Ni^{2+} cation mixing and irreversible phase transitions. In high-nickel materials, Ni^{3+} is easily reduced to Ni^{2+}, with an ion radius close to that of Li, leading to nickel ions invading the lithium layer and confusing the lattice sites. Consequently, the lithium-ion diffusion channel is blocked, causing microcracks. In addition, oxygen evolution is happened when the battery is charging, and it triggers the reconstruction of surface structure of NCM particles [1]. The structural stability collapses, the structure will change from a layered structure to spinel or rock salt structure. The structure reconstruction will lead to increasing the charge transfer resistance, resulting in premature cell failure. At present, the surface coating has a certain effect on stabilizing NCM-based anode materials. [2]. However, in contrast, the doping technology is not only relatively controllable in terms of price, but also has good effects in capacity retention, thermal stability and inhibition of oxygen release [1]. As more and more researchers use doping technology, they employ a wide variety of doping agents, such as Ba, Sr, V, Si and Y. After implementing the doping method, a stable main structure was obtained, which was strengthened by strong dopant ions-O bonds. This stable structure not only suppresses the anisotropic volume change caused by the repeated H2 to H3 phase transition,

but also maintains the overall structure to prevent the formation of microcracks and the occurrence of more side reactions [3].

In the current research on ternary cathode materials, element doping has been widely applied, the structural stability and electrochemical performance of high-nickel NCM materials have been enhanced. Previous studies have shown that by introducing heteroallene or is valent cations for bulk doping, the mixed arrangement of cations can be effectively suppressed, lattice stress can be alleviated, and cycling stability can be enhanced. For instance, Kim [1] regulated the Ni^{3+}/Ni^{2+} ratio by doping with Mg^{2+}, significantly reducing the degree of mixed arrangement of Li^{+}/Ni^{2+}. Gohar Shadi discovered that Ba^{2+} doping can optimize the lattice order of the layered structure and increase the cycle retention rate of NCM811 to 99.83% (500 cycles, 1C) [3, 4]; Similarly, Sr^{2+} doping has also been proven to improve rate performance while maintaining structural reversibility. The capacity retention rate of the 5% doped sample reached 65.72% at 2C, and after 500 cycles, the capacity retention rate was 99.84% [4].

These studies indicate that the influence of different doping elements on material properties varies, and the mechanism of action is closely related to ionic radius, valence state and lattice matching degree. However, at present, there is still a lack of systematic horizontal comparisons, making it difficult to determine the optimal doping strategy. Therefore, this paper aims to comprehensively compare the effects of typical doping elements such as Ba, Sr, and Si in high-nickel NCM systems, with a focus on analyzing their influence laws on structural stability, electrochemical reversibility, and capacity retention rate. It also explores whether nano-doping (such as nano-silicon) can further synergistically alleviate the structural degradation caused by volume expansion. This provides theoretical references and optimization paths for the design of high-performance cathode materials.

2. NCM battery materials and their principle mechanisms

A NCM battery is a type of lithium-ion battery that uses a cathode made of a mixture of nickel, manganese, and cobalt. These batteries are known for their high energy density, a high practical specific capacity exceeding 200 mAh g^{-1} [5], which allows them to store a large amount of energy in a relatively small and lightweight package. However, NCM cathode materials are typically composed of secondary particles, which are made up of aggregated, randomly oriented, layered primary particles. The microcracks that occur in the cathode material can be transgranular cracks or intergranular cracks. Consequently, the lifespan of battery is decreased [6]. NCM batteries are commonly used in electric vehicles, portable electronics, and renewable energy systems due to their performance and longevity. The charging and discharging principle of NCM batteries is that during charging, lithium ions are released from the positive electrode lattice, migrate through the electrolyte to the negative electrode and intercalate between the graphite layers. The discharge process proceeds in reverse, with lithium ions returning to the positive lattice [7].

3. Comparison of doping of different elements

3.1. Ba doping

Ba doping is of great significance in the field of battery materials. The selection of Ba doping is mainly based on the following reasons. On the one hand, Ba has a large ionic radius and a unique electronic structure. After being doped into the lattice of battery materials, it can effectively stabilize the crystal structure of the materials, reduce the structural crash caused by volume changes when the battery is charging and discharging, thereby significantly improving the cycle stability of the battery and further extending its service life. On the other hand, Ba doping can regulate the electrochemical properties of materials such as electronic conductivity and ion diffusion rate, optimizing the overall performance of the battery. Therefore, Ba doping is not only necessary for understanding how it improves the battery's service life, but also enables the selection of the best doping ratio through

comparison, such as the percentage of doping content. The set of percentages consist of 0%, 1.5%, 3% and 5% of Ba [4].

It can be seen from the Fig. 1a, 1b and 1c that for undoped NCM batteries, the diffraction peaks in their XRD patterns may be relatively wide or not sharp enough, indicating that the regularity of the crystal structure is slightly poor, and there may be a certain degree of lattice distortion or crystal defects, which will affect the diffusion channels of lithium ions and the overall stability of the material. For 1.5% Ba doping, the diffraction peak shape may not be as regular as that of 3% Ba doping, and the intensity of some peaks may be relatively weak or there may be some small impurity peaks. This suggests that there may be local atomic arrangement disorder or a small amount of impurity phase in the crystal structure, which affects the overall structural stability and electrochemical performance. For 5% Ba doping, peak shifts or intensified broadening may occur in the XRD pattern, indicating that excessive Ba doping has led to significant lattice distortion, disrupting the original crystal structure regularity, hindering lithium-ion diffusion, and affecting the rate performance and cycling stability of the material [4].

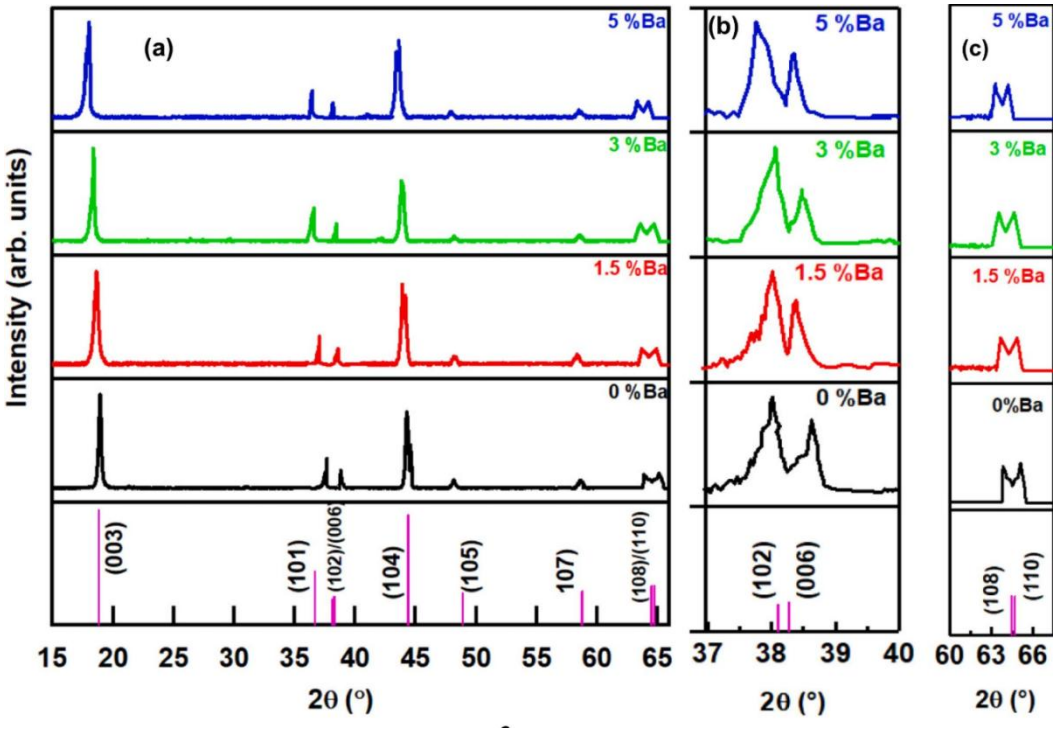

Fig. 1 (a) XRD patterns of $Ba_xLi_{1-x}Ni_{0.8}Co_{0.1}Mn_{0.1}O_2$ (x= 0, 0.015, 0.03, and 0.05), **(b)** enlarged (102) and (006) peaks, **(c)** enlarged (108) and (110) peaks [4].

Fig. 2 demonstrates that Voltage-capacity curve analysis: In Figures 2a and 2c, the voltage-capacity curve doped with 3% Ba shows relatively stable potential changes when the battery is charging and discharging, especially in the high-capacity range, indicating that it has good electrochemical stability during the the process of lithium-ion intercalation and deintercalation. In terms of polarization degree, compared with other doping ratios, the curve shape of 3% Ba doping is more regular and the polarization degree is relatively low. This means that during the charging and discharging process, the ohmic loss and polarization loss inside the battery are smaller, which is conducive to improving the charging and discharging efficiency and cycle performance of the battery. As for the capacity retention rate, it can be seen from Figure 2b that under different cycle times, the 3% Ba-doped battery exhibits a relatively high-capacity retention rate at 0.1C, 0.2C, 0.5C, 1C and 2C, indicating that it can maintain its initial capacity well during long-term cycling and has good cycling stability. For rate performance, in Figure 2d, the capacity retention rate of the 3% Ba-doped battery is relatively high at different rates, especially at high rates (such as 2C), it can still maintain a capacity of 64.8%, which is much higher than that of batteries with other doping ratios. This indicates that 3% Ba doping can significantly improve the rate performance of the battery, enabling it to maintain good performance

under high-current charging and discharging conditions. Based on the analysis of the above figures, 3% Ba doping shows obvious advantages in terms of voltage stability, polarization degree, cycle performance and rate performance. Therefore, it can be considered that 3% Ba doping is the best choice and can significantly improve the overall electrochemical performance of the battery. It is known that the capacity retention rate of the battery doped with Ba is 99.83% after 500 cycles at 1C [4].

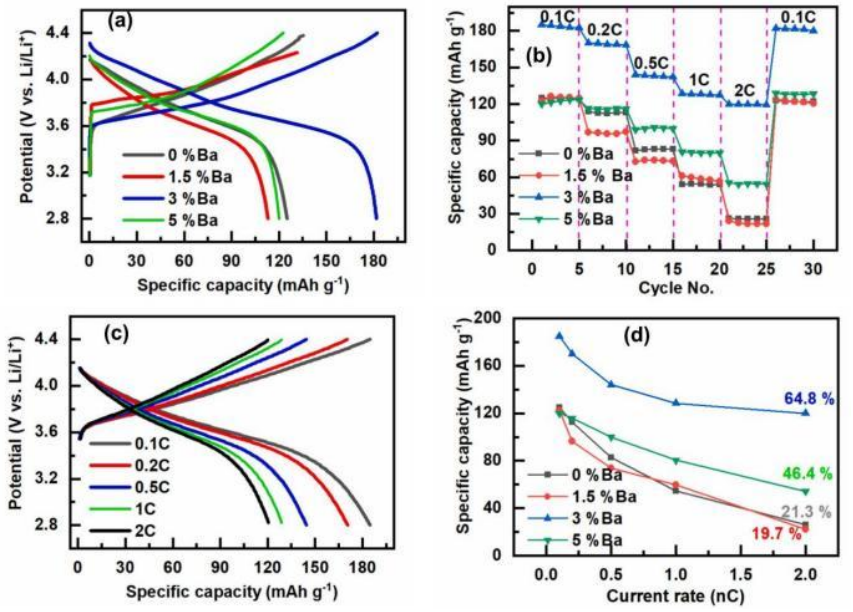

Fig. 2 (a) Initial charge/discharge curves at a current rate of 0.1C, **(b)** rate performance, **(c)** charge/discharge curves of 3 % Ba sample at various current rates, and **(d)** discharge specific capacity versus current rate [4].

3.2. Sr doping

From the given Table 1 and Fig. 3a and 3b, it can be known that for 1.5% Ba, the intensity of peak is lower than that of the 5% doping ratio, which indicates that the degree of cation mixing is relatively high. Higher cations mixed arrangement will disrupt the orderliness of the crystal structure, making the atomic arrangement no longer regular and thus affecting the structural stability. Its XRD diffraction peaks may be relatively broad or not sharp enough, which indicates that there is a certain degree of disorder in the crystal structure and there may be problems such as local lattice distortion, which is not conducive to the stability of the structure. Similarly, when 3% Sr is doped, the peak intensity ratio is lower than that when 5% is doped, indicating that the degree of cation mixing is still relatively high. The disordered distribution of cations such as Ni^{2+} in the crystal at positions like the lithium layer disrupts the regularity of the layered structure, leading to a decrease in structural stability. The shape of its XRD diffraction peaks may also show a certain degree of broadening or asymmetry, reflecting the presence of structural defects or local disordered regions within the crystal, which is not conducive to maintaining a stable structure.

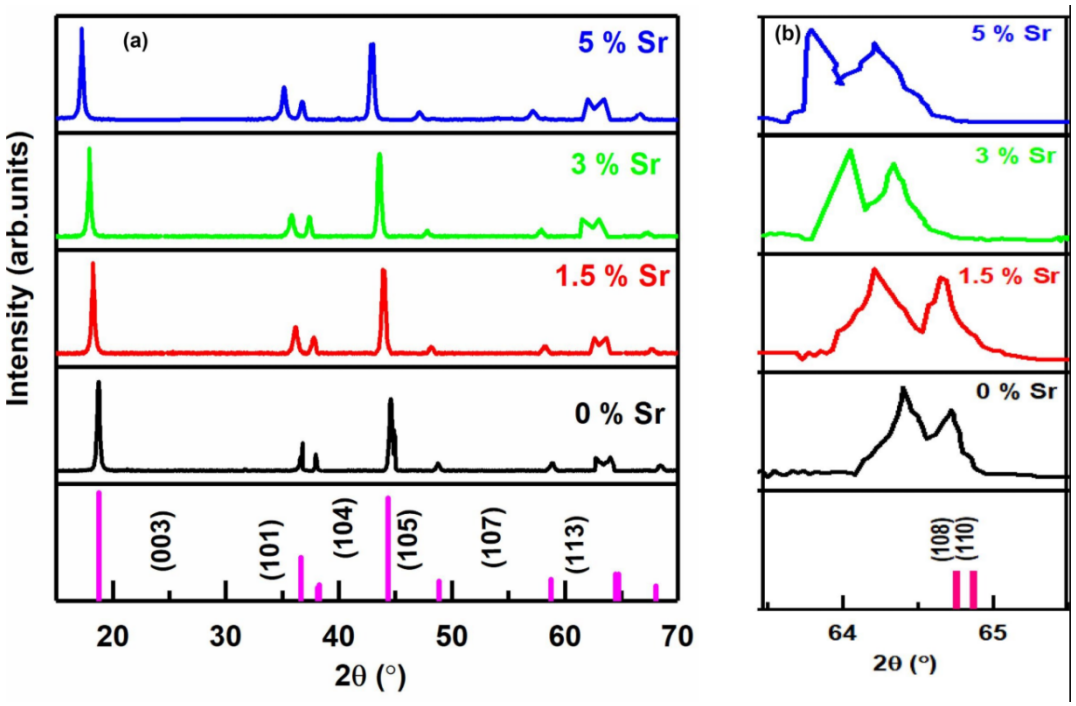

Fig. 3 (a) XRD patterns of $Sr_xLi_{1-x}Ni_{0.}8Co0_{.1}Mn_{0.1}O_2$ materials, **(b)** enlarged (108) and (110) peaks [8].

Table 1 intensity ratio of (003) and (104) peaks.

Sr Content	I003/I104
0%	1.23
1.5%	1.27
3%	1.34
5%	1.36

For the charge-discharge curves (Fig. 4a and 4c), under different discharge capacities, the 5% Sr-doped material (blue curve) exhibits a relatively stable potential plateau during the charge-discharge process, especially at high discharge capacities, where the potential drop is relatively small, indicating that it has good electrochemical stability. In contrast, materials with other doping ratios show a more significant potential drop at high discharge capacities, demonstrating poorer electrochemical performance. For cycling performance (Fig. 4b), at different cycling times, the 5% Sr-doped material (blue curve) maintains a relatively high specific capacity at different rates such as 0.1C, 0.2C, 0.5C, 1C, and 2C. With the increase of the number of cycles, the attenuation degree of the specific capacity of the 5% Sr-doped material is relatively small, showing better cycling stability. For rate performance (Fig. 4d), at different current rates, the 5% Sr-doped material (blue curve) can still maintain a high specific capacity at high current rates (such as 2C), demonstrating excellent rate performance. Its specific capacity retention rate is significantly better than that of materials with other doping ratios at high rates. For instance, at a 2C rate, the specific capacity retention rate of the material doped with 5% Sr is 15.83%, while that of materials with other doping ratios is even lower. Based on the above analysis, the 5% SR-doped material exhibits good potential stability during charging and discharging, good cycling stability during cycling, and excellent rate performance at high rates. Therefore, 5% Sr is the best doping option, which can significantly enhance the electrochemical performance of the material. The 5% Sr-doped sample maintains a stable discharge specific capacity of 114.4 mAh/g, achieving a capacity retention of 99.84% [8].

Ba doping and Sr doping both affect NCM811 cathode materials. At 3% doping, Ba improves structural stability. It stops cation mixing and prevents Li layer collapse. Ba doping gives 99.83% capacity retention after 500 cycles. XRD data shows Ba optimizes lattice order and strengthens structure. However, too much Ba (like 5%) causes problems. Large grains form. Lithium-ion paths

get longer. This lowers rate performance. Ba^{2+} has a large ionic radius which may distort the lattice. Sr doping at 5% gives different results. Initial discharge capacity reaches 150 mAh/g. Rate performance is better with 65.72% capacity retention. Sr reduces cation mixing and increases lithium-ion diffusion. After cycling, Sr shows 99.84% capacity retention, slightly higher than Ba. Sr keeps structural reversibility better. However low-concentration Sr doping (1.5%) weakens electrochemical performance. Sr^{2+} also has a large ionic radius. This may expand the lattice and build up local stress. Precising control of doping amounts is necessary for both Ba and Sr to work best.

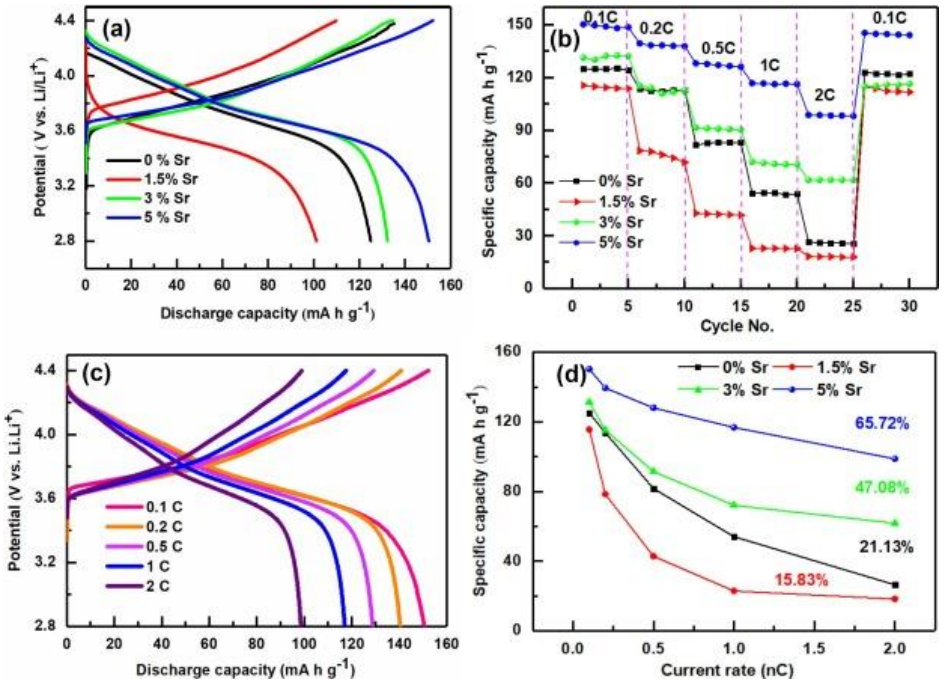

Fig. 4. (a) Initial charge/discharge curves at a current rate of 0.1C, **(b)** rate performance, **(c)** charge/discharge curves of 5%, Sr-NCM811 ($LiNi_8Co_1Mn_1O_2$) at various current rates, and **(d)** specific capacity versus current rate [8].

3.3. V doping

The XRD patterns of the original NCM and NCM samples doped with different contents of V (V-0.005 NCM, V-0.01 NCM, V-0.02 NCM) are shown in the Fig. 5. From the main observation results, all samples have obvious diffraction peaks on multiple crystal planes and the crystal structures are similar, but the peak intensities are different. V-0.005 NCM shows relatively high peak intensity in low-angle regions such as (003), (006)/(012), indicating its high crystallinity. The peak intensity of V-0.01 NCM is relatively low, while that of V-0.02 NCM lies between the two. In terms of validity analysis, for structural stability, V-doping affects the crystal structure, especially the peaks (003) and (006)/(012) are related to the stability of the layered structure. V-0.005 NCM has high intensity and good structural stability at these key peaks. From the perspective of crystallinity, V-0.005 NCM has high strength on multiple peaks, and high crystallinity is beneficial to electrochemical performance. Based on the above analysis, among these samples, V-0.005 NCM with a V doping content of 0.005 shows the best structural stability and higher crystallinity, and is the most effective.

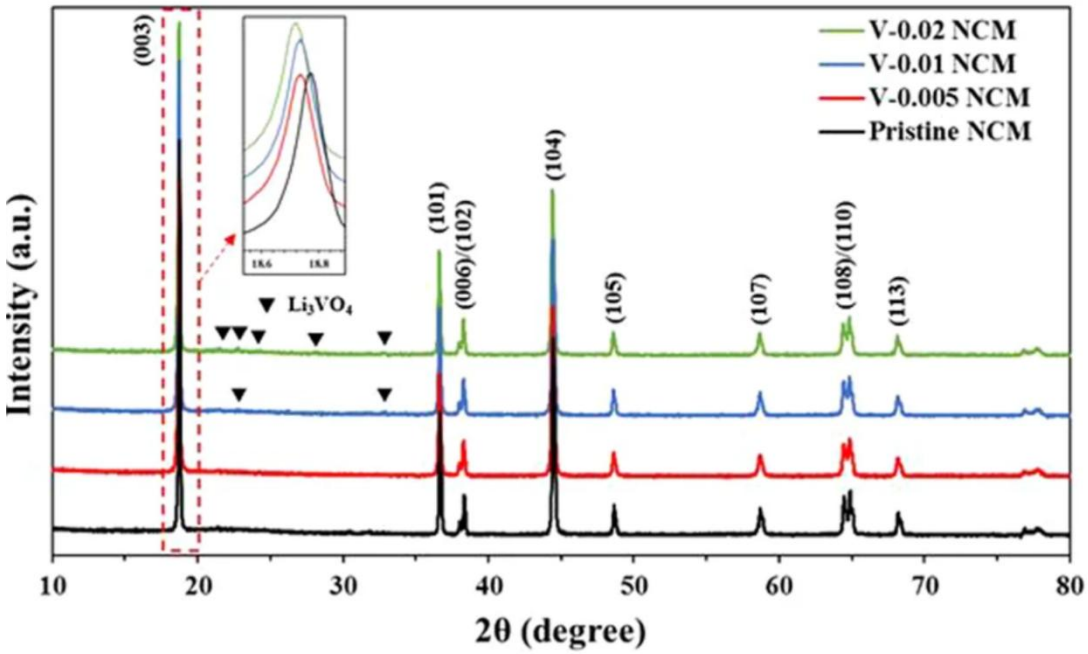

Fig. 5 shows XRD patterns of pristine and V-doped NCM samples [9].

3.4. Si doping

The reason for analyzing silicon is not only because silicon often appears in the field of batteries, but also because silicon can be combined with nanotechnology. It can be known from the references that the atomic radius and electronegativity of silicon and other properties make it highly compatible with the main lattice structure, allowing it to integrate into the lattice without causing excessive lattice distortion and maintain the stability of the crystal structure [1]. However, some other doped elements can cause significant lattice distortion. In high-temperature environments, silicon-doped materials exhibit excellent thermal stability and are more adaptable to high-temperature working conditions compared to other doped elements, demonstrating superior thermal stability. Silicon doping can effectively regulate the carrier concentration, and at the same time, it will not overly reduce the carrier mobility like some other doped elements, ensuring that the material has appropriate electrical conductivity. Not only that, the 5p orbitals of silicon can effectively couple and regulate energy levels with the valence band and conduction band of the main material, optimizing the energy band structure, while other doped elements may not be able to achieve such an ideal energy level regulation effect.

By looking at Fig. 6, it can be clearly seen in the SEM image that after adding silicon doping, the microcracks are visibly reduced, and even severe cracks are almost invisible. For the electrode without silicon doping, after 100 charge and discharge cycles, not only are there many microcracks, but also large holes. However, during charging and discharging, the expansion volume of silicon can reach 300%, which is very pessimistic [10]. This problem also occurs in silicon-carbon composite batteries. The proposed solution uses nanomaterials such as nano-silicon. Nanomaterials refer to materials that have at least one basic structural unit, particle, fiber or other component with a dimension less than 100 nanometers [11]. The absolute volume change of each nanoparticle is very small, and the resulting stress is dispersed, avoiding local stress concentration and greatly reducing the risk of electrode structure damage.

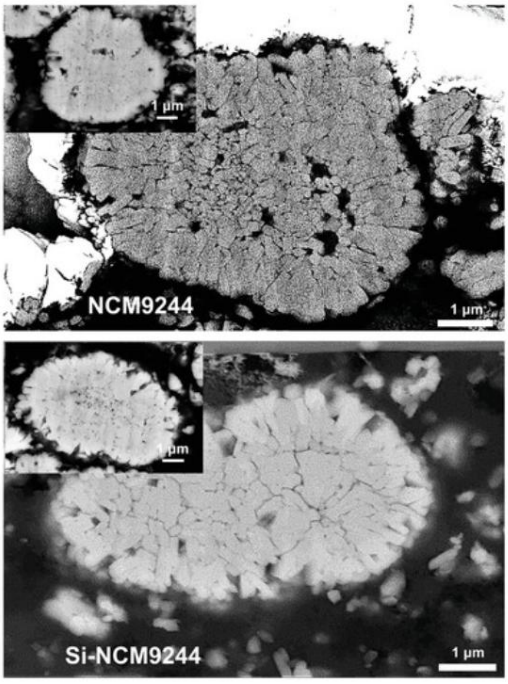

Fig. 6 Cross-sectional SEM images of secondary particles for NCM9244 ($LiNi_{0.92}Co_{0.04}Mn_{0.04}O_2$) and Si-NCM9244 before (inset) and after cycling (100 cycles) [1].

3.5. Y doping

In Figures 7a and 7b (related to XRD patterns), Figure 7a shows that the characteristic diffraction peaks of the NCM-OH and NCMY-OH precursors exhibit comparable characteristics. and free of impurities, both presenting a typical hexagonal layered structure. This indicates that Y successfully enters the $Ni(OH)_2$ lattice, laying a foundation for a good structure of the subsequent cathode material. The XRD patterns of the NCM and NCMY cathode materials in Fig. 7b show that both have a hexagonal NaFeO2 structure. Among them, NCMY has no impurity peaks, indicating that Y does not segregation or react with other substances to form heterogeneous phases during high-temperature calcination, maintaining the stability and uniformity of the cathode material structure. When the specific regions of both in Fig. 7b were magnified simultaneously, the double peaks of (006)/(102) and (018)/(110) were clearly split, indicating that both had good crystallinity and ordered layered structure. This stable, uniform and ordered structure helps to improve the capacitance retention rate, as the generation of disjunctions may disrupt factors such as ion diffusion channels that affect capacitance performance. Good crystallinity and an ordered layered structure can make ion diffusion smoother and reduce capacitance loss caused by structural defects, etc.

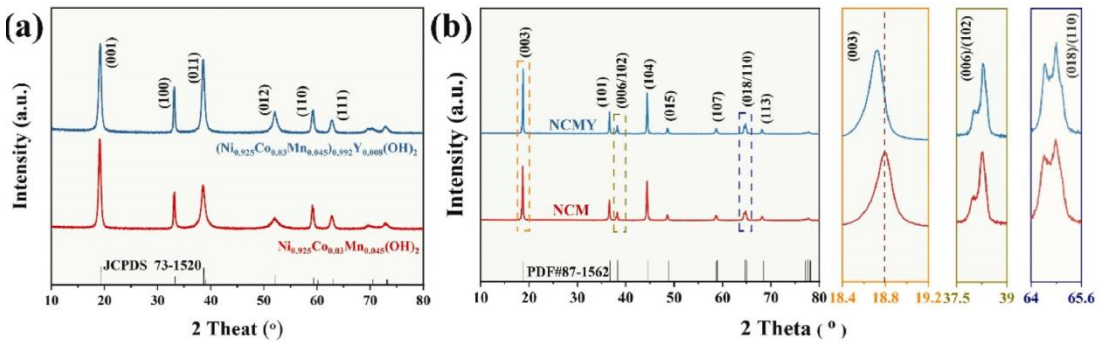

Fig. 7 XRD patterns of **(a)** the two precursors and **(b)** the corresponding cathode materials [12]

4. Conclusion

This study comprehensively evaluated multiple doping strategies such as ba, Sr, Si, Y and v to enhance the structural stability and electrochemical performance of high-nickel NCM cathode materials. The research results show that each dopant has different effects on cationic order, lattice integrity and capacity retention, and its best performance highly depends on the doping concentration and the inherent physicochemical properties.

In alkaline earth metals, 3% Ba doping effectively inhibits the mixing of Li^+/Ni^{2+}, stabilizes the layered structure, and the capacity retention rate is as high as 99.83% after 500 cycles. However, excessive Ba content can cause lattice strain and reduce rate performance. In contrast, 5% Sr doping not only demonstrates excellent cycling stability (99.84% retention rate), but also enhances rate performance (65.72% at 2C) and initial discharge capacity (150 mAh/g) due to improved lithium-ion kinetics and structural reversibility. Y doping has been proven to be particularly effective in enhancing crystallinity and phase purity. Y-integrated precursors generate impurity-free ordered layered structures, significantly alleviating irreversible phase transitions. Meanwhile, 0.5% V doping exhibits the best crystallinity and structural stability, with enhanced XRD peak intensity, confirming the minimal lattice defects and robust framework integrity. It is worth noting that silicon doping significantly reduces microcrack propagation during the cycling process, but its severe volume expansion (~300%) remains a key challenge, which can be addressed through nano-silicon integration to disperse mechanical stress and preserve the electrode structure.

Overall, although all dopants have improved capacity retention to varying degrees, Sr (5%) demonstrates the most balanced solution in terms of long-term cyclability, rate capability and initial capacity. Y and V doping offer promising alternatives for defect suppression and structural reinforcement, which is worthy of in-depth study. Future work should explore methods of mixed doping and nanoengineering to synergistically leverage the advantages of multiple elements. This comparative analysis provides valuable guidance for the rational design of advanced NCM batteries in high-energy, long-life lithium-ion batteries.

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