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Coating and Doping Modification Strategies for Ni-rich layered NCM cathode materials

by Liang Hong

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Certificate of Original Authorship

I, Liang Hong declare that this thesis, is submitted in fulfilment of the requirements for the award of Master of Science (Research), in the School of Mathematical and Physical Sciences, Faculty of Science at the University of Technology Sydney.

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heartfelt appreciation,

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Abstract

Nickel cobalt manganese oxide (NCM) materials are commonly used as lithium-ion battery cathode materials. The thesis first reviews different modification methods and effects of NCM cathode material. It discusses the effects of different modification strategies on the electrochemical properties and crystal structure of NCM cathode materials. Ni-rich layered NCM cathode material is one of important NCM cathode materials. Therefore, it is necessary to construct protective layers for Ni-rich layered NCM cathode materials. Notably, the thesis introduces a cerium (Ce) element to modify the NCM90 ($LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$) cathode material. The NCM precursor reacts with cerium hydroxide and lithium hydroxide at high temperature and generates a modification strategy for Ni-rich layered NCM cathode material with cerium oxide (CeO_2). This strategy can enhance the specific capacity of NCM cathode materials, improve the energy density and stabilize the lattice structure of Ni-rich layered NCM cathode material. In this thesis, 2%-CeO_2@NCM90 cathode material exhibits better electrochemical performance than the pristine NCM90 cathode material at different current densities. Some Ce^{4+} ions are reduced to Ce^{3+} ions, and some Ni^{2+} ions in the NCM cathode material are also converted to Ni^{3+} ions. The modified NCM90 cathode material has better electrochemical performance because the diffusion rate of lithium ions in the material is increased, the mixing of cations is reduced, and harmful interfacial phase transitions are reduced. In addition, cerium weakens the volume change of the NCM cathode material, reduces the release of active oxygen, and increases the stability of the transition metal and lithium layers in the NCM cathode material.

Keywords: Lithium-ion batteries; Surface modification; Doping; Coating; Ni-rich layered NCM cathode material

Introduction

The gradual reduction in the use of traditional fossil fuels because of environmental demands has made the development of renewable energy increasingly important and urgent. This has driven the rapid development of lithium-ion batteries. In daily life, NCM cathode materials, which have high energy density, low cost, and can be produced on a large scale, play a significant role in electric vehicles, portable electronic products, and electrochemical energy storage devices. Among NCM cathode materials, Ni-rich NCM cathode materials offer higher energy density and specific capacity because of their high nickel content. Additionally, the layered structure of Ni-rich NCM cathode materials positively impacts their performance. This layered structure provides unique planar ion channels, increasing the specific surface area of NCM cathode materials, enhancing the efficiency of ion insertion and extraction reactions during charge and discharge processes, and improving the electrochemical reaction kinetics. Consequently, NCM cathode materials exhibit better rate performance and cycle stability. Ni-rich layered NCM cathode materials can also operate at higher voltages (around 4.3V) and achieve high efficiency at lower costs (with nickel content greater than 80% and relatively low nickel metal prices) for various applications in everyday life.

However, Ni-rich layered NCM cathode materials face several challenges. Despite their ability to withstand higher working voltages and offer high specific capacity and energy density, they suffer from poor thermal and structural stability. Furthermore, side reactions frequently occur during electrochemical cycling, leading to high irreversible capacity values, ultimately negatively impacting their electrochemical performance. Therefore, various modification methods are needed to enhance the properties of Ni-rich layered NCM cathode materials.

This thesis focuses on NCM cathode materials with a composition of 90% nickel, 5% cobalt, and 5% manganese (NCM90). Firstly, it investigates the synthesis methods, characterization, and electrochemical properties of the pristine NCM90 cathode materials. Then, it designs a modification strategy through solid-state reactions between metal hydroxides and NCM90 cathode material precursors at high temperatures. The electrochemical testing and characterization of the modified NCM90 cathode materials are compared and analyzed with the pristine NCM90 cathode materials. The effects of the modification strategy on the electrochemical performance of Ni-rich layered NCM cathode materials are analyzed, exploring various dimensions to identify performance influencing factors and methods to enhance the performance of NCM90 cathode materials through modification strategies. The contents of each chapter are summarized as follows:

Chapter 1 summarizes the research progress of different modification strategies for NCM cathode materials. This chapter introduces several traditional modification strategies, including cation doping, coating, washing, excess lithium source, cathode electrolyte interphase (CEI) and solid electrolyte interphase (SEI) construction, and crystal face exposure modification strategies. Detailed explanations of cation doping and coating modification strategies are provided, highlighting their applications in NCM cathode materials. By constructing CEI film, we can reduce the degree of cation mixing in NCM cathode materials, reduce the proportion of irreversible phase transitions, and inhibit the release of lattice oxygen, thereby improving the electrochemical performance of NCM cathode materials.

Chapter 2 is about experiments and methodology. First, the methodology required for the study is proposed, and then the Ni-rich layered NCM cathode material is modified using cerium in the experiment and the electrochemical performance and physicochemical properties of the modified Ni-rich layered NCM90 cathode material are compared with the pristine NCM90 cathode material.

Chapter 3 analyzes the electrochemical test and characterization results. The feasibility of using cerium to modify the Ni-rich layered NCM90 cathode material is demonstrated by comparing the two materials. In addition, through the comparison of physical and chemical properties, it is also found that the modification strategy of cerium reduces the degree of cation mixing of Ni-rich layered NCM cathode materials and improves the cycle stability and rate performance of lithium-ion batteries.

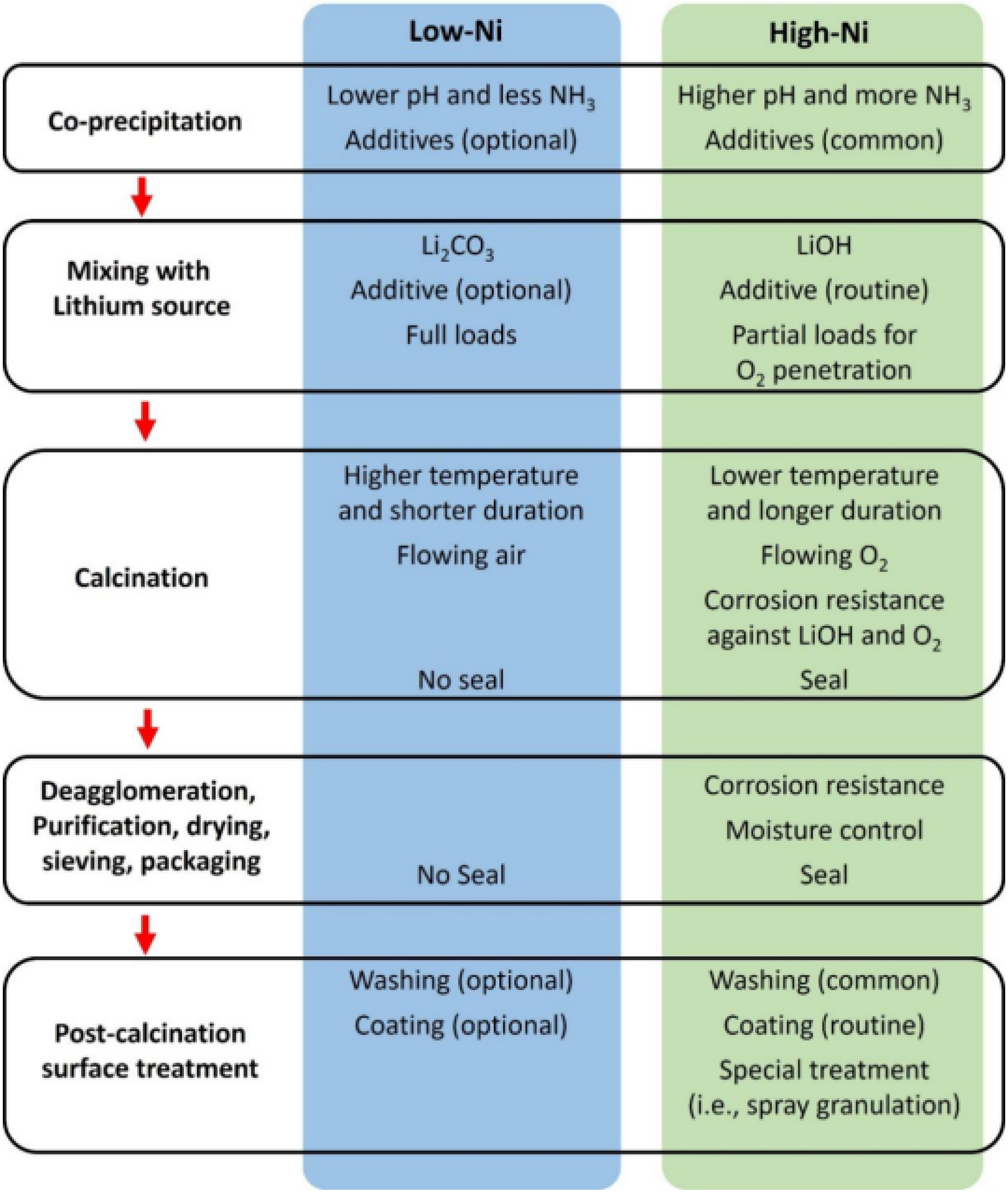
Chapter 4 summarizes the problems and solutions mentioned in the entire thesis, and gives the application prospects and methods of NCM cathode materials modified by cerium element.

Chapter 1 Literature Review

1.1 The development of Ni-rich NCM cathodes in lithium-ion batteries

As the global demand for sustainable energy increases (Blomgren, 2017), the development of new energy technologies has become one of the frontier areas of scientific research (Schipper et al., 2016). Lithium ion batteries (LIB) have become a very important part of new energy technology and have also become the research object of many scientists (Li et al., 2015), and lithium ion batteries have made great progress and development (Scrosati et al., 2011). Lithium ion batteries have become the first choice for energy storage batteries in portable electronic devices because of their high Coulombic efficiency and low cost (Myung et al., 2016). Electric vehicles (EVs) usually use lithium-ion batteries as energy storage, and some of the mobile devices also use them (Kim et al., 2018). In some research of lithium-ion batteries, cathode material is very important for the energy density, and NCM cathode materials have become a new important material in lithium-ion batteries (Manthiram et al., 2015). NCM cathode materials have good development potential and application (Li et al., 2020). The study found that the current Ni-rich layered NCM cathode materials can provide a discharge capacity of up to $240\text{mAh}\cdot\text{g}^{-1}$ (Yoon et al., 2018).

Figure 1 shows the synthesis conditions and differences between high-nickel content NCM cathode materials and low-nickel content NCM cathode materials.



	Low-Ni	High-Ni
Co-precipitation	Lower pH and less NH_3 Additives (optional)	Higher pH and more NH_3 Additives (common)
Mixing with Lithium source	Li_2CO_3 Additive (optional) Full loads	LiOH Additive (routine) Partial loads for O_2 penetration
Calcination	Higher temperature and shorter duration Flowing air No seal	Lower temperature and longer duration Flowing O_2 Corrosion resistance against LiOH and O_2 Seal
Deagglomeration, Purification, drying, sieving, packaging	No Seal	Corrosion resistance Moisture control Seal
Post-calcination surface treatment	Washing (optional) Coating (optional)	Washing (common) Coating (routine) Special treatment (i.e., spray granulation)

Fig. 1. Schematic illustration of the industrial synthesis of nickel-based layered oxide cathode materials, showing unique challenges and requirements for high-nickel cathode materials.

1.2 The properties of Ni-rich NCM cathodes

Nickel content is an important factor to determining the specific capacity of Ni-rich layered NCM cathode materials. However, at the same time, the nickel content will also affect the structure of Ni-rich NCM cathode materials (Zhang, 2020). Ni-rich layered NCM cathode materials contain more than 60% nickel. Although they have extremely high energy density and specific capacity, they perform poorly regarding cycle performance and thermal stability (Jo et al., 2016). Analyzing XRD patterns, the reflection peaks of Ni-rich NCM cathode materials can be indexed according to the α-NaFeO2 structure of the hexagonal crystal system, with different metal ions occupying different sites. In Ni-rich layered NCM cathode materials, increasing the nickel content will reduce the manganese and cobalt content. Manganese in Ni-rich NCM cathode materials can improve the thermal stability of the material and reduce the degradation of electrochemical performance caused by temperature changes during charge and discharge (Li et al., 2019). In the phase transition process of NCM cathode materials at high temperatures, manganese can help NCM materials to avoid structural collapse (Pender et al., 2020). If manganese was added to the NCM cathode material, it can help the NCM cathode material stabilize the layered structure and reduce microcracks on the surface of the material.

The role of cobalt is partially the same as that of manganese in Ni-rich NCM cathode materials. Both elements can improve the structural stability of Ni-rich NCM cathode materials to a certain extent, but cobalt also has other roles in the crystal structure of Ni-rich NCM cathode materials. During the cycle, cobalt can affect the charge and discharge process, specifically by reducing the degree of structural changes in the NCM cathode material, thus improving the cycle performance of lithium-ion batteries (Ryu et al., 2018). Since there are different ions in the NCM cathode material, different ions with similar ionic radii are more likely to replace each other. In Ni-rich NCM cathode materials, the ionic radii of nickel ions (0.72Å) and lithium ions (0.76Å) are similar, so Ni^{2+} ions may migrate to Li^{+} sites during the synthesis and recycling process, causing cation mixing, which is one of the main reasons for battery capacity attenuation (Lin et al., 2018). The presence of manganese and cobalt can effectively suppress the phenomenon of cation mixing because the ionic radius of manganese ions and cobalt ions are closer to that of lithium ions, which can effectively maintain the crystal structure of Ni-rich NCM cathode materials.

Based on the modification strategies for NCM cathode materials mentioned above, we can determine the objectives for modifying NCM cathode materials and identify current research gaps and potential solutions. First, we need to understand the reaction mechanism of Ni-rich layered NCM cathode materials in lithium-ion batteries. Higher voltage induces more complete redox reactions of transition metals during charging (lithium ion de-intercalation), with the chemical reaction:

$Li\ (Ni_x^{2+}+Co_y^{3+}+Mn_z^{4+})O_2 \rightarrow Li_{1-x}\ (Ni_x^{3+}+Co_y^{3+}+Mn_z^{4+})O_2 + xLi^+ + xe^-$

Further charging causes nickel ions to continue oxidizing with the following reaction:

$Li_{1-x}\ (Ni_x^{3+}+Co_y^{3+}+Mn_z^{4+})O_2 \rightarrow Li_{1-x}\ (Ni_x^{4+}+Co_y^{3+}+Mn_z^{4+})O_2 + xLi^+ + xe^-$

This generates more highly oxidative Ni^{4+} ions in Ni-rich layered NCM cathode material. Because of the high oxidative nature of Ni^{4+} ions, they readily undergo redox reactions to acquire electrons, forming Ni^{2+} ions through the following reactions:

1. $Li_{1-x}\ (Ni_x^{4+}+Co_y^{3+}+Mn_z^{4+})O_2 + xLi^+ + xe^- \rightarrow Li_{1-x}\ (Ni_x^{3+}+Co_y^{3+}+Mn_z^{4+})O_2$
2. $Li_{1-x}\ (Ni_x^{3+}+Co_y^{3+}+Mn_z^{4+})O_2 + xLi^+ + xe^- \rightarrow Li\ (Ni_x^{2+}+Co_y^{3+}+Mn_z^{4+})O_2$

More complete lithium ion reactions and redox reactions of transition metals can effectively increase the output capacity of Ni-rich layered NCM cathode materials.

However, maintaining the lattice and surface stability of these materials presents significant challenges. Enhanced lithium ion de-intercalation leads to the migration of a substantial number of transition metal ions to Li^+ sites, causing lattice changes and the formation of microcracks within the crystal. Additionally, higher voltages result in deeper phase transitions of Ni-rich layered NCM cathode materials, generating anisotropic internal stress and microcracks between crystals, and altering the layered structure. This not only promotes surface phase transitions, shifting from layered structures to rock salt or spinel phases, and increasing interfacial impedance, but also facilitates the release of lattice oxygen during intense redox reactions. This adversely affects the electrolyte performance at the interface, negatively impacting the cycle performance of Ni-rich layered NCM cathode materials.

Doping and coating strategies are common methods to improve the electrochemical performance of Ni-rich layered NCM cathode materials. The strategy of achieving both coating and doping is prevalent in research. Chemical reactions produce lattice doping and surface coating, which can reduce the instability of the lattice structure while increasing surface stability. Common materials for coating strategies include various metallic and non-metallic compounds that remove the alkalinity caused by lithium compound residues during sintering, reduce contact between the electrolyte and cathode material, and enhance Li^+ ion diffusion rates at the interface. During sufficient redox reactions, Ni-rich layered NCM cathode materials generate highly active Ni^{4+} ions, which readily undergo redox reactions to capture electrons from lattice oxygen, increasing lattice oxygen release and ultimately decreasing electrochemical performance.

During the electrochemical process, the H2→H3 phase transition is a key factor affecting the performance of Ni-rich NCM cathode materials. During the phase transition, NCM cathode materials will undergo severe anisotropic deformation along the *c*-axis (Kondrakov et al., 2017). Huge volume changes occur, resulting in microcracks inside and on the surface of the crystal. The continuous growth of microcracks greatly affects the structural stability and cycle stability of Ni-rich NCM cathode materials. At the same time, the huge volume change during the phase transition will also cause surface reactions between the Ni-rich NCM cathode material and the organic electrolyte on the surface. If the surface is not coated to reduce the reaction intensity, it will greatly affect the electrochemical properties of Ni-rich NCM cathode material. Therefore, many attempts have been made to avoid the above problems and solve the problems caused by the impact of deformation and cracks in the H2→H3 phase transition on the performance of Ni-rich layered cathode materials (Liang et al., 2016).

Figure 2 uses titanium to modifiy NCM cathode material. By observing the *dQ/dV* curves of the modified NCM cathode material and the pristine NCM cathode material, it can be seen that the modification strategy using titanium reduces the irreversible capacity during the phase transition process, thereby improving the cycle stability of the lithium ions batteries.

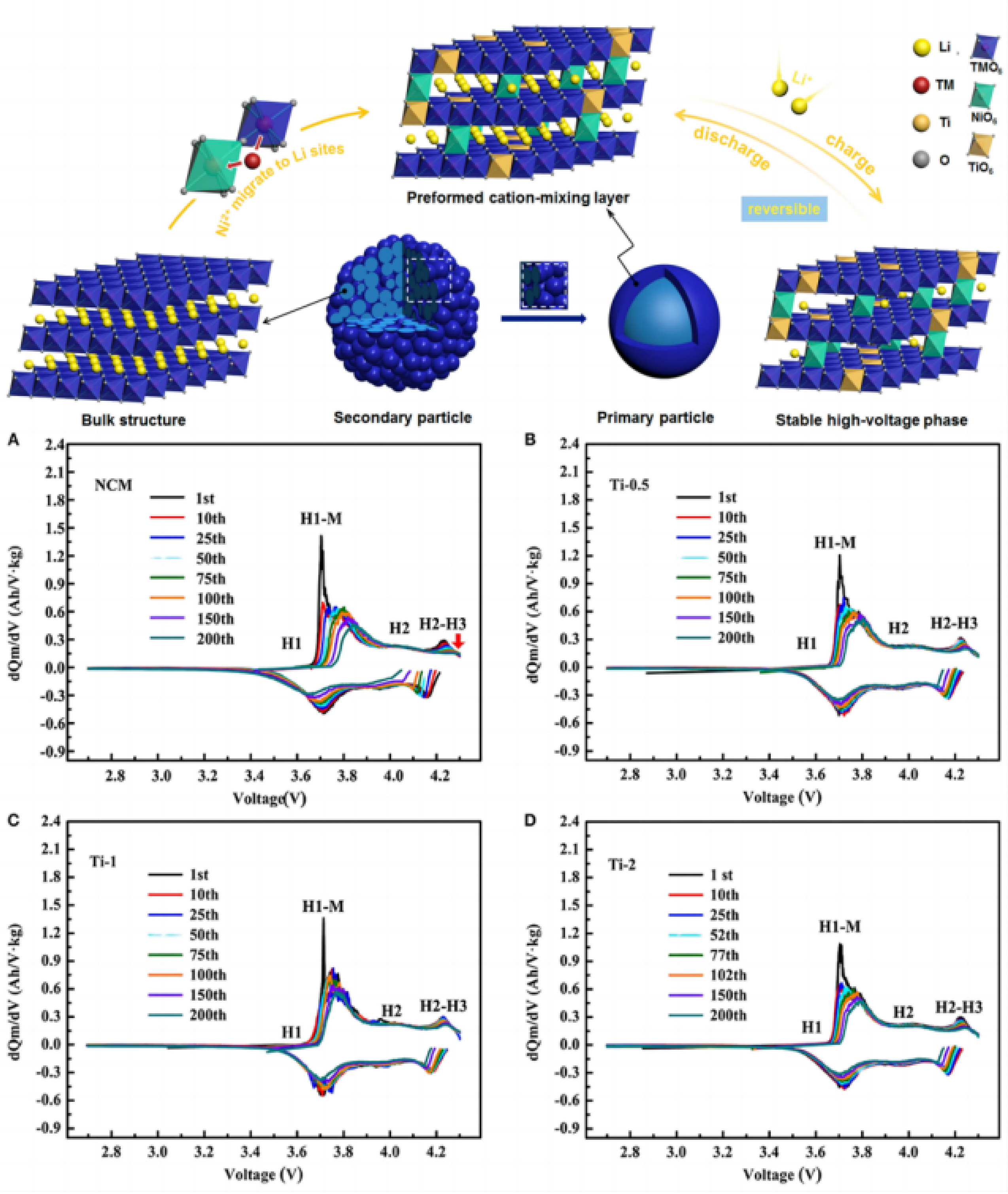


Fig. 2. Modification reaction process of titanium element (F. Wu et al., 2019b) and differential capacity versus cell potential curves of different numbers for the NCM (A), Ti-0.5 (B), Ti-1 (C), and Ti-2 (D) electrodes (Chen et al., 2019).

1.3 Modification strategies for Ni-rich NCM cathodes

First, in synthesizing Ni-rich NCM precursor materials, the precursor is a spherical secondary particle porous material formed by stacking primary particles synthesized from three materials (manganese sulfate, nickel sulfate, and cobalt sulfate). Reaction time, higher reaction speed, longer aging time, and slower reaction flow rate can build Ni-rich NCM precursor materials that align with standard spherical morphology, thus the crystal structure stability of Ni-rich layered NCM cathode material would be improved. Although in the research by Koshika's team, the more uniform spherical material did not have a very significant impact on the rate performance of the NCM cathode materials (Koshika et al., 2022b). However, more uniform spherical materials are more conducive to a more stable structure during coating reactions and doping reactions (W. G. Ryu et al., 2019).

Some research also found that when the NCM precursor is converted into a Ni-rich NCM cathode material through a co-sintering process under a high temperature environment, the electrochemical properties of the Ni-rich NCM cathode material can be changed by controlling the lithium content (Xiao & Sun, 2018). Excess lithium content greatly impacts the electrochemical performance of the $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ cathode material (Wang et al., 2020). Increasing the usage of part of the lithium element will cause certain problems. For example, because of the excessive usage of lithium hydroxide, the surface of the NCM cathode material of the reaction product becomes a highly alkaline surface (Zhang, 2020a). It causes a defluorination reaction with the organic binder polyvinylidene fluoride (PVDF) in the subsequent battery manufacturing process. The electrolyte N-methylpyrrolidone (NMP) is relatively stable under neutral conditions. However, NMP has a pyrrole ring, so the partial degradation may occur in a highly alkaline environment, it is necessary to prevent the surface from being too alkaline. In addition, if an excessive amount of lithium content is used in the synthesis of NCM cathode materials, some negative effects will also occur. Moreover, excessive lithium usage can lead to a decrease in the diffusion rate of lithium ions (Abebe et al., 2021b), thereby affecting the performance of Ni-rich NCM cathode materials (Teichert et al., 2020). Therefore, the degree of lithium excess has a significant impact on the electrochemical performance of NCM cathode materials. In the research of Liu's team (Liu et al., 2023d), excess lithium was used in the sintering process of solid-state reaction, and it was found that when the excess lithium was about 3%, the cation mixing degree of NCM90 cathode material decreased and the electrochemical performance of the material improved. A high proportion of Ni^{3+} ions in the transition metal layer can enhance the diffusion rate of lithium ions (Cui et al., 2015).

Noh's team also studied the relationship between the conditions of solid-state reactions and the NCM cathode materials (Noh et al., 2013). The sintering temperature of NCM cathode materials decreases with the increase of nickel content. The sintering temperature of NCM90 cathode material is generally 730-750℃, while the sintering temperature of NCM811 material is generally 770-800℃. There are reasons for using different lithium contents in the sintering process of different NCM cathode materials. Since the melting point of lithium hydroxide monohydrate is only 471℃, it is appropriate to use lithium hydroxide monohydrate in the synthesis of Ni-rich NCM cathode materials, because the temperature during sintering is likely to be below 750℃. However, the melting point of lithium carbonate is 720℃, so during the sintering process, the sintering temperature of Ni-rich NCM precursor materials is sometimes below 800℃, so lithium hydroxide monohydrate can be completely molten, while lithium carbonate will remain solid. Molten lithium hydroxide monohydrate can be more evenly and thoroughly mixed with the Ni-rich NCM precursor material, reducing the lithium residue on the surface after the reaction, thereby improving the performance and structure of the NCM cathode material. The usage of lithium carbonate is for NCM cathode materials with low nickel content. The synthesis temperature of these materials generally exceeds 900℃, so lithium carbonate can also be completely melted. So using lithium carbonate generally requires the sintering temperature of the NCM precursor to be above 900°C (Dixit et al., 2017). After reacting the Ni-rich NCM precursor through a co-sintering process, surface-side reactions are prone to occur because of surface instability. In the sintering process described above, excess lithium can improve the electrochemical performance and crystal structure stability of Ni-rich NCM cathode materials. However, there will still be problems with residual lithium and excessive alkalinity on the surface (Yu et al., 2018). During electrochemical testing of Ni-rich NCM cathode materials, these problems will induce the formation of residual lithium impurities on the cathode surface and severe side reactions with the electrolyte (Guéguen et al., 2016). To solve this problem, Ryu's team (Ryu'su et al., 2023) used a variety of different solvents to clean the surface residues of the Ni-rich layered NCM cathode material. Co-solvents were used to clean and form a protective coating on the NCM material cathode to solve the problem of surface residues of the Ni-rich layered NCM cathode material after the sintering process because after sintering the residual lithium and alkalinity are too high on the surface of the NCM cathode material. By comparing the cleaning process with water and fluorine-containing liquid, the fluorine-containing liquid can react with the residual lithium compound to form a protective coating, preventing the electrolyte from direct contact with the NCM cathode material surface, hindering the decomposition of the salt and preventing a series of problems caused by excessive surface alkalinity and surface side reactions have improved the electrochemical performance and cycle performance of Ni-rich NCM cathode materials.

Two important modification methods for NCM cathode materials are doping and coating strategies. The two strategies can greatly improve the electrochemical performance and structural stability of NCM cathode materials, reducing the occurrence of side reactions. The structural stability of Ni-rich layered NCM cathode materials is enhanced by doping and coating with different cations and anions, such as Li_3PO_4-based coating materials (Song et al., 2011). Li_3PO_4 coating solutions facilitate the formation of coatings with enhanced electrochemical performance. The lithium phosphate coating is in the amorphous phase, and the $Li_{3-x}Ni_{x/2}PO_4$ coating is generated by the crystalline phase covering the amorphous phase Li_3PO_4, which improves the cycle performance of the NCM cathode material. Li_3PO_4-based coating materials effectively increase the rate performance and thermal stability of NCM cathode materials under high pressure. Research by Schipper's team has found effective lattice doping of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622) using zirconium (Zr) element and found that through the zirconium element doping strategy, the structure of the doped NCM cathode material will not undergo a partial layered structural change like the pristine NCM cathode material, which transforms from a layered structure to a spinel structure, leading to a decrease in cycle performance and structural instability. This change happens to the pristine NCM622 cathode material during the electrochemical cycle process (Schipper, Dixit, et al., 2016).

1.3.1 Cation doping strategies

Atom doping strategy is a very effective strategy to treat the performance of Ni-rich layered NCM cathode material. Using different types of atoms for doping reactions can reduce the occurrence of surface side reactions of Ni-rich layered NCM cathode material, improve the structural stability of Ni-rich layered NCM cathode material, and inhibit the huge volume change during the phase transition process and the subsequent collapse of the crystal structure (Xu et al., 2020). Compared with other common cathode materials used in lithium ion batteries, such as lithium cobalt oxide, lithium manganese oxide and lithium iron phosphate, Ni-rich layered NCM cathode materials can exhibit better cycling performance and electrochemical properties. In Ni-rich layered NCM cathode materials, increasing the nickel content in the cathode material enhances the specific capacity of the battery. However, this also reduces the stability of the Ni-rich layered NCM cathode material. Doping with various elements is an effective strategy to improve thermal stability, electrochemical performance, structural stability, and cycle performance of Ni-rich layered NCM cathode materials.

Figure 3 shows the degradation mechanism of Ni-rich NCM cathode materials, electrolyte erosion, lattice oxygen release, side reactions caused by CEI film, and microcracks produced in NCM cathode materials after electrochemical cycles, which will damage the electrochemical properties of NCM cathode materials. Therefore, we need to modify the NCM cathode materials, and cation doping is a very important modification strategy for NCM cathode materials.

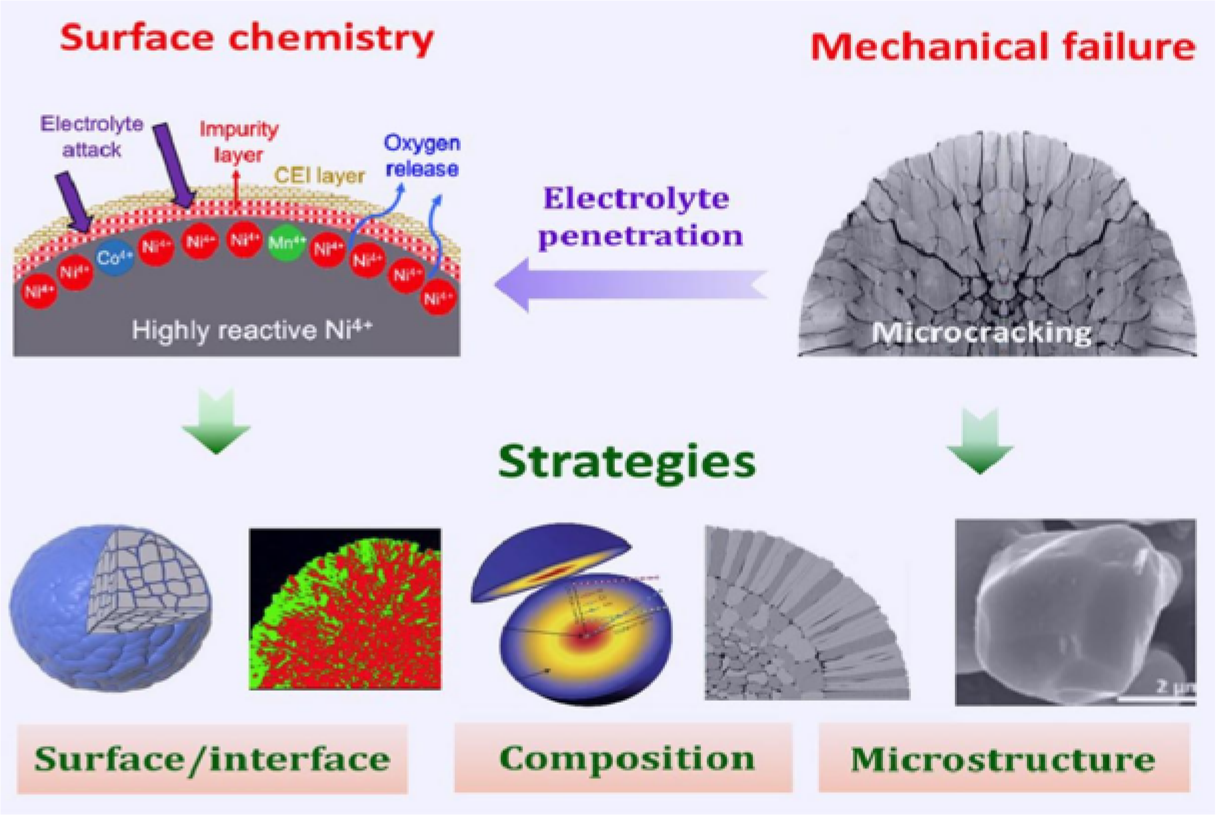


Fig. 3. The degradation mechanism and corresponding solution strategies of Ni-rich cathodes (Yang et al., 2023).

Cation doping and anion doping are two different modification strategies for Ni-rich layered NCM cathode materials. This thesis mainly reviews various cation doping strategies. Since metal elements have a radius similar to that of lithium ions and nickel ions, they can enter the lattice of NCM cathode materials to occupy the sites of lithium and nickel elements. Metals occupying the sites of lithium or nickel elements can stabilize the layered structure of NCM cathode materials and improve the cycle stability of NCM cathode materials. However, anion doping may face some problems. After some anions are doped into the lattice, it may cause lattice defects in NCM cathode materials, reduce electron transfer efficiency and lithium ion diffusion efficiency, and affect the performance of NCM cathode materials. Cation doping can reduce the degree of cation mixing and increase the diffusion efficiency of lithium ions.

The strategy study of cation doping modified NCM cathode materials has shown that various cations can undergo doping reactions, including alkaline earth metals, transition metals, and lanthanide metals. Modification strategies for cathode materials include Al, Zr, Mg, Mn, La, Gd, Nb and other elements. Research on Ni-rich layered NCM cathode materials found that different metal cations replace different sites in NCM cathode materials. Different metal cations have different effects on the performance of NCM cathode materials.

1.3.1.1 Magnesium doping strategy

Research by the Li's team shows (H. Li et al., 2019) that after doping with the magnesium (Mg) element as the doping element of the Ni-rich layered NCM cathode material, magnesium ions will enter the lattice of the Ni-rich NCM cathode material. The ionic radii of magnesium and lithium ions are relatively close so that magnesium ions will occupy the sites of lithium ions. Magnesium ions will occupy the sites of lithium ions, thereby improving the mixing degree of cations. Although cation mixing has a negative impact on the performance of Ni-rich NCM cathode materials, the cycle and rate performance of Ni-rich NCM cathode materials doped with magnesium elements does not undergo significant negative changes. However, the entry of magnesium ions can enhance the migration of nickel ions to interlayer lithium ions to stabilize the structure of crystals. For Ni-rich NCM cathode materials, high voltage will cause a large number of cracks to appear at the grain boundaries, causing mechanical damage to the crystal structure, and the cracks will continue to grow, causing irreversible structural changes, ultimately leading to electrochemical changes in the Ni-rich NCM cathode materials, thus it will have loss of performance and collapse of structure. At the same time, the high oxidation state of the nickel element will undergo an exothermic reaction at high voltage, causing huge volume changes, irreversible phase transitions, and loss of electrochemical performance. The crystal change during the phase transition of Ni-rich layered NCM cathode materials can be effectively changed through the doping strategy of the magnesium element. The standard operating voltage of Ni-rich NCM cathode materials is between 2.7 and 4.3V, the NCM cathode material doped with magnesium element showed almost no lattice change after 100 electrochemical cycles at a high voltage of 4.7V, and the irreversible phase transition during the H2→H3 phase transition process also decreased (Lim et al., 2017). Xie's team proposed in the study of magnesium doped modified NCM cathode materials that the thermal stability and electrochemical performance of NCM cathode materials can be improved through magnesium element modification strategy (Xie et al., 2019). During the process of doping NCM cathode materials with magnesium elements, magnesium ions preferentially replace the positions of lithium ions in the lattice and become the structural skeleton of the NCM cathode. During the phase transition process, the volume change of NCM cathode material decreases, which improves the structural stability of NCM cathode material (Zhang, 2020d).

1.3.1.2 Aluminum doping strategy

The doping modification of aluminum (Al) element is different from that of magnesium element. Firstly, the substitution sites of aluminum element during doping modification are different from those of magnesium element. Aluminum element mainly replaces the position of transition metal (TM), replacing manganese, cobalt, and nickel sites. Among them, it can be known from the Perdew, Burke and Ernzerhof functional (PBE) calculation that the most likely substitution site of the aluminum element is the position that replaces nickel sites. At the same time, aluminum ions, like many transition metal ions or lanthanide metal ions, have a very high oxidation state and form powerful Al−O bonds with oxygen ions in the Ni-rich layered NCM cathode material. These strong Al−O bonds significantly impact the lattice stability of Ni-rich layered NCM cathode material. The research by Jeong's team also elaborated on the impact of aluminum doping on Ni-rich layered NCM cathode material (Jeong et al., 2020). The doping modification of aluminum elements on Ni-rich layered NCM cathode material can improve electrochemical performance by replacing nickel sites. With the wide inter-plate thickness of the LiO_6 structure, the increase in the inter-plate thickness can improve the ions diffusion of lithium ions. Secondly, it can also improve lithium ions insertion and deinsertion reactions. The lithium ion insertion and deinsertion reactions can ultimately suppress the anisotropic changes in the Ni-rich layered NCM cathode material, thereby reducing the lattice changes during the phase transition during the reaction during battery cycling at high voltages, so it also plays a important role in stabilizing structures. In addition, the doping modification strategy of aluminum ions, by replacing the weak Ni−O bonds with strong Al−O bonds, can delay the starting temperature of the thermal decomposition reaction and, therefore, reduce the starting temperature of the phase transition. By suppressing the formation of rock salt phase and spinel phase in the thermal decomposition reaction, the thermal stability of Ni-rich layered NCM cathode materials is improved (J. Lin et al., 2023). In the research on doping modification strategies in many directions, research on various nickel cobalt manganese aluminum (NCMA) oxide materials also illustrates the positive impact of aluminum doping modification on Ni-rich layered NCM cathode material. The research by Kim's team (U. Kim et al., 2023) found that after the aluminum element is introduced into the Ni-rich layered NCM cathode material, the unique structure of the NCM cathode material will cause aluminum to accumulate at the grain boundaries continuously, so during high-voltage electrochemical cycling, the NCM cathode material does not produce excessive cracks. The cracks generated during the electrochemical cycle can allow the electrolyte to penetrate different particles, and continue to grow and cause side reactions, thereby damaging the structural integrity of the Ni-rich layered NCM cathode material. During the phase transition process of aluminum doped NCM cathode materials, the volume change decreases, and the number of cracks also decreases. These changes can have a positive impact on the electrochemical performance of NCM cathode materials.

1.3.1.3 Zirconium doping strategy

The Gao's team doped $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) cathode material with zirconium (Zr) element. Zirconium, unlike aluminum and magnesium, can react simultaneously on the surface and lattice of NCM cathode materials. The doping of zirconium element will cause the lattice of NCM811 cathode material to expand, thereby increasing the diffusion rate of lithium ions in NCM811 material. During the H2→H3 phase transition of the NCM cathode material, the zirconium element can inhibit the phase transition process from the layered structure to the spinel structure and improve the structural stability of the NCM811 cathode material (X. Li et al., 2018). The solubility of zirconium compound is generally poor. Therefore, different types of zirconium compounds can be used for doping modification strategies at the same time. The zirconium element can enter the lattice and improve the stability of the NCM cathode material (Schipper, Dixit, et al., 2016b). Li's team (X. Li et al., 2018b) also found through experiments that zirconium modification has multiple effects on NCM cathode materials. Part of zirconium element enters the lattice of NCM crystals and reduces the mixing effect of cations, to improve the stability of the Ni-rich NCM cathode material structure; other part of zirconium element forms a coating on the surface of the NCM cathode material, thereby reducing the contact between the Ni-rich NCM cathode material surface and the electrolyte, and reducing harmful interface reactions.

1.3.1.4 Titanium doping strategy

The doping modification strategy of the titanium (Ti) element is more complicated than that of Al, Mg, and Zr elements. Because of the difference in atomic radius, titanium ions will not only replace a specific type of element in the Ni-rich layered NCM cathode material. The titanium element will simultaneously replace the lithium sites and transition metal sites in the crystal structure, and the substitution ratio depends on the Ni-rich NCM cathode material structure. The substitution of titanium element for Ni-rich layered NCM cathode material will increase the interlayer spacing between different lithium layers and reduce the disorder of cations. The ordered cation arrangement will significantly improve electrochemical performance and structural stability of Ni-rich layered NCM cathode material. The research by Zhang's team (D. Zhang et al., 2019) used titanium element to modify the NCM811 cathode material because the ionic radius of titanium (Ti) ions depends on its oxidation state. The standard oxidation states of titanium are +4, +3, and +2. The ionic radii of titanium ions in different oxidation states are also different. Ti^{2+} ion is about 0.86Å, Ti^{3+} ion is about 0.67Å, and Ti^{4+} ion is about 0.61Å. The radius of Ti ions is larger than the radius of transition metal ions. However, the radius of Ti^{4+} ion is lower than the radius of lithium ions. Therefore, in the research by Zhang's team, titanium ions will be more inclined to occupy the lithium ions position in the lattice. Additionally, higher oxidation state titanium ions can oxidize some Ni^{2+} ions to Ni^{3+} during doping modification. The ionic radius of titanium element is also very close to that of transition metal ions. For example, the ionic radius of nickel ions is approximately 0.69Å, and that of cobalt ions is approximately 0.74Å. Consequently, Titanium ions can partially occupy the sites of transition metal ions during the doping modification process. Regarding Ni-rich layered NCM cathode materials, the strategy of Ti element entering the lattice is shown in **Figure 4**. By replacing different sites, the phase transition process is suppressed and a superlattice is generated. In the study by Sun's team, it was observed that Ni-rich materials doped with titanium exhibited higher first-round charge and discharge efficiency and rate performance when the titanium element ratio was low, such as 0.5% or 1%. However, a higher titanium element ratio, such as 2%, will reduce the performance of the Ni-rich NCM cathode material (Y. Sun et al., 2023).

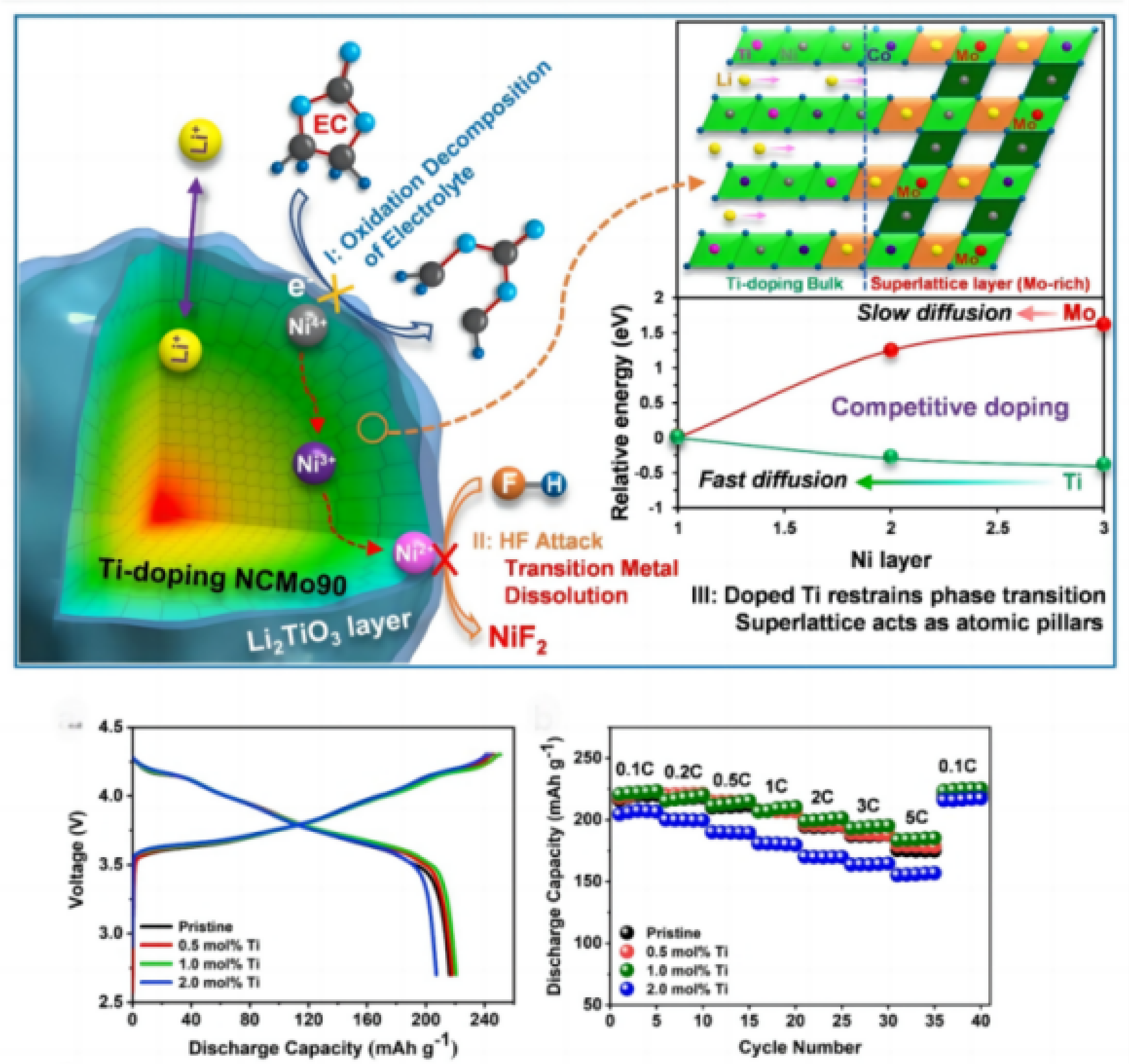


Fig. 4. Schematic illustration of the structural design concept for bulk-to-surface modified $LiNi_{0.9}Co_{0.09}Mo_{0.01}O_2$ cathode material (Y. Sun et al., 2023).

1.3.1.5 Other metals doping strategies

Other metal elements can also be used as modification strategies for NCM cathode materials, such as tin (Sn), lanthanum (La), gallium (Ga), tantalum (Ta), niobium (Nb) and tungsten (W). Su's team used molybdenum (Mo) element for doping modification of NCM cathode materials (Su et al., 2018). Mo^{6+} ions have strong oxidizing properties, so they can oxidize Ni^{2+} ions to Ni^{3+} ions. The Ni^{3+} ions generated from this can increase the electrochemical activity of NCM cathode materials, improve the diffusion rate of lithium ions, and the doping of molybdenum (Mo) element can also change the phase transition process, promoting the formation of surface rock salt phase. Nguyen's team used tin (Sn) element for doping modification of NCM cathode materials (Nguyen et al., 2021). Tin element enters the lattice to replace nickel sites, suppressing the formation of microcracks during the transformation process and improving the cycling stability of NCM cathode materials. The research by Wu's team (Wu et al., 2020) modified the NCM cathode material by doping amounts of gallium (Ga) ions in the study. Gallium ions will replace some of the manganese ion sites, improving the performance of the NCM cathode material. After gallium ions enter the lattice of the NCM cathode material, they inhibit the release of lattice oxygen and make the cations more ordered during the phase transition process of the cycle process. In the doping modification of NCM811 cathode material, which prevents the structure collapse of the structure during the redox process of nickel element, so electrochemical performance of the NCM811 cathode material is significantly improved. The research by Chu's team conducted relevant research on the doping modification strategy of NCM cathode materials with tantalum (Ta) element (Chu et al., 2020), and proposed a new strategy for doping and modifying NCM622 cathode materials with tantalum ions. Because of the tantalum ionic radius, the sites replaced after entering the crystal lattice of the Ni-rich layered NCM cathode material are lithium ion sites, which act as a supporting structure, thereby inhibiting the cation mixing that damages the cycle and rate performance of the NCM cathode material. Since the bond energy of the tantalum and oxygen bond is very high, the tantalum element and the oxygen element can form a very strong chemical bond, thereby improving the stability of the NCM cathode material structure modified by tantalum ion doping because of high dissociative bond energy. In addition, during the doping strategy of Ni-rich layered cathode NCM cathode materials using niobium (Nb) elements, single-crystal NCM cathode materials can be doped, and the doping strategy of polycrystalline NCM cathode materials can also be carried out smoothly. The research by Levartovsky's team modified the polycrystalline NCM85 (nickel content is 85%) material by doping it with the niobium element. Niobium ions entered the crystal structure, inhibiting the formation and growth of cracks during the cycle during the phase transition of the Ni-rich layered cathode NCM cathode material and reducing the occurrence of surface side reactions, thereby improving the cycle performance of Ni-rich layered NCM cathode materials (Levartovsky et al., 2021c). The configuration deformation of the electron cloud of nonlinear molecules with multiple degenerate states in the molecule's ground state is called the Jahn-Teller effect (JTE), and the JTE mainly occurs in metal complexes. During the doping modification process, because of the JTE, nickel ions in the Ni-rich layered NCM cathode material are converted from Ni^{3+} ions to Ni^{2+} ions. The highly oxidized niobium ions form strong chemical bonds with oxygen ions because the JTE can distort the octahedral structure composed of transition metals and oxygen atoms (Lv et al., 2021), and an irreversible phase transition occurs, thereby reducing the cycle performance and crystal structure stability of the Ni-rich layered NCM cathode material (Gao et al., 2020). The reduction effect caused by the doping niobium element can effectively reduce the JTE. The change in the combined state of nickel ions in the Ni-rich NCM cathode material caused by the effect, and the conversion of high-valence nickel into a low-valence state itself is one of the most important sources of the capacity of the Ni-rich layered NCM cathode material.

1.3.1.6 Mixed doping strategies

There are many studies that use mixed doping of multiple elements in Ni-rich layered NCM cathode materials. Tan's team illustrated the Ti element is often co-doped with other elements in Ni-rich layered cathode materials. The Ni-rich layered NCM cathode material was modified with $ZrTiO_4$ (Tan et al., 2023). After the modification of NCM90 cathode material by $ZrTiO_4$, it can effectively suppress the internal strain of the Ni-rich layered cathode material during the H2→H3 phase transition. At the same time, it will significantly reduce the release of lattice oxygen during the phase transition process, thereby reducing the volume change of the NCM90 cathode material during the phase transition process and improving the structural stability of the Ni-rich layered NCM cathode material. Comparing titanium with other metal elements, titanium tends to concentrate on the NCM cathode material surface, forming a coating rather than being fully integrated through doping modification. In contrast, $ZrTiO_4$ doping modification primarily targets lattice oxygen in the crystal structure. During phase transitions, lattice oxygen release during heat treatment and high-pressure cycling creates vacancies, leading to crystal structure defects, crack formation, and ultimately irreversible structural changes. These changes can degrade electrochemical performance, resulting in poorer cycle performance and reduced maximum capacity. Under the combined action of Ti and Zr elements, the Ni-rich layered NCM cathode material forms a stable lattice framework, reduces lattice oxygen release, and improves performance. Tan's research demonstrates that the rate performance and cycle performance of NCM90 cathode material can be effectively enhanced using an appropriate amount of Zr and Ti for joint modification.

Figure 5 describes using $ZrTiO_4$ doping strategy to dope NCM90 cathode material, and the *dQ/dV* profiles of the modified NCM90 cathode material and the pristine NCM90 cathode material show that the irreversibility of the phase transition process is significantly reduced because of this modification strategy, with almost no noticeable irreversible capacity loss. The reversibility of the phase transition remains at a high level after 100 electrochemical cycles, while the irreversibility of the phase transition of the pristine NCM90 cathode material is much higher than that of the modified NCM90@ZTO-x (NCM90 cathode material after $ZrTiO_4$ doping) material.

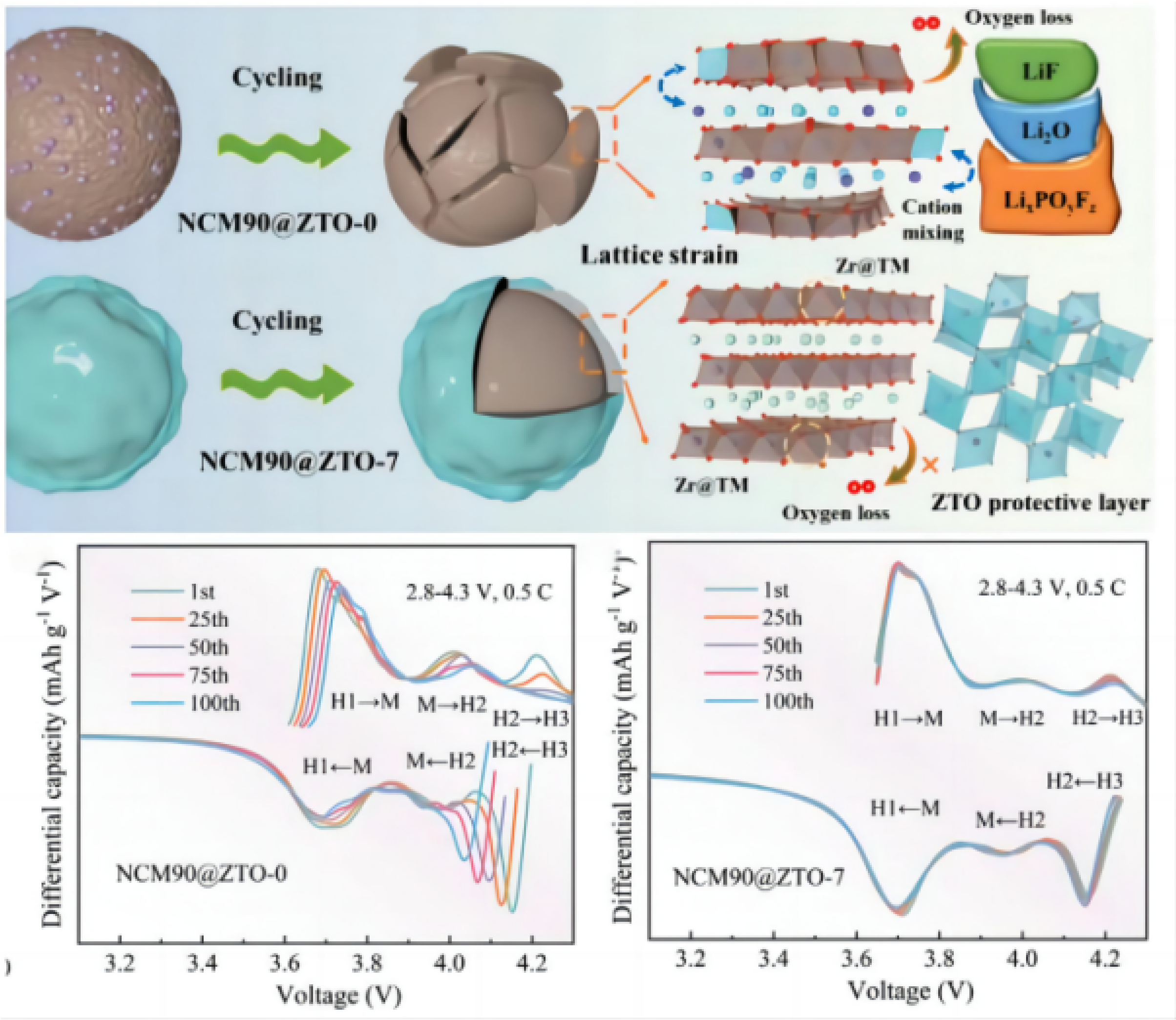


Fig. 5. Schematic illustration of the structural design concept for bulk-to-surface modified $LiNi_{0.9}Co_{0.09}Mo_{0.01}O_2$ cathode material and *dQ/dV* profiles of NCM90@ZTO-x (NCM90 cathode material after $ZrTiO_4$ doping) conducted at 25 °C in the range between 2.8 and 4.3V (Tan et al., 2023b).

The doping modification strategy using titanium (Ti) can be more complex than that of Al, Mg, and Zr. Because of the difference in atomic radius and charge, Ti ions replace both Li-ion sites and transition metal sites in Ni-rich layered NCM cathode materials, with the substitution ratio depending on the material's structure. Ti element can also have a mixed doping effect with alkaline earth metal elements. He's team (He et al., 2023) discovered the mixed doping effect of Mg and Ti elements in their research. Since the ionic radius of Mg^{2+} ions is about 0.72Å, more significant than the ionic radius of transition metal ions, through and Ti co-doping of elements can increase the interlayer distance, which is beneficial to the insertion and de-insertion of lithium ions. The reversibility of the Ni-rich layered NCM cathode material battery modified with Ti and Mg elements is better than that of the original NCM cathode material (Park et al., 2019). XRD analysis shows that some Ti^{4+} ions occupy the position of Mn^{2+} ions, while some Mg^{2+} ions occupy the position of Ni^{2+} ions. This co-doping reaction can reduce the degree of cation mixing, decrease the proportion of Ni^{2+} ions, and increase the proportion of Ni^{3+} ions. And Ni^{3+} ions are an important factor in improving the electrochemical performance of NCM cathode materials, which is better consistent with the cycling and rate performance of modified NCM cathode materials.

Li's team studied the modification of Ni-rich layered NCM cathode materials by tungsten (W) element (Z. Li et al., 2023d). During the electrochemical cycling process of NCM cathode material, a phase transition process occurs, which produces microcracks that lead to a decrease in electrochemical performance and damage to the layered structure. In the thesis, they proposed a modification strategy for NCM95 cathode material using tungsten and fluorine elements. The doping of tungsten element can improve the reversibility of the phase transition process of NCM cathode materials, reduce irreversible capacity, and decrease the occurrence of microcracks during the reaction process. Especially during the phase transition from H2 phase to H3 phase, the stress and lattice oxygen release of the crystal are suppressed, reducing the irreversible capacity loss during the phase transition process. In addition, compared with NCM95 cathode materials doped with only tungsten element or only fluorine element, higher specific capacity and better rate performance are also obtained.

Figure 6 shows that the charge-discharge curves, rate performance, and cycling stability of the NCM95 cathode material are all improved after mixed doping. The incorporation of both tungsten and fluorine elements enhances anisotropy and mitigates lattice oxygen release during the H2 to H3 phase transition, thereby reducing irreversible capacity loss. This results in a higher specific capacity and better rate performance compared to materials doped solely with either tungsten or fluorine element.

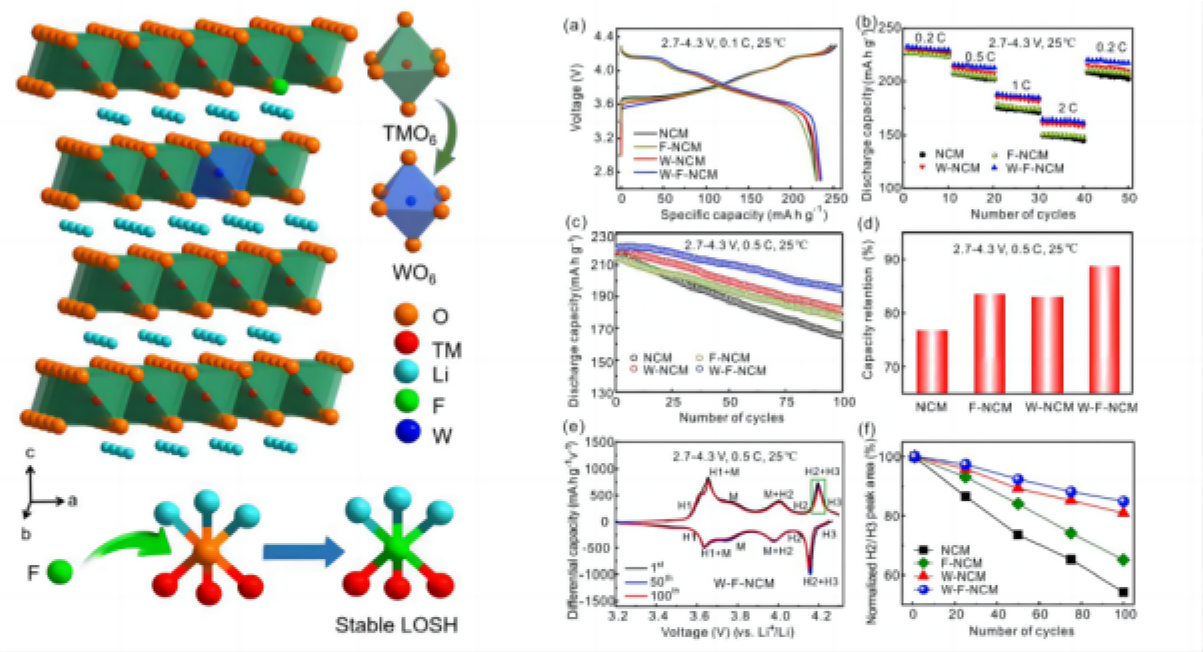


Fig. 6. Schematic illustration of W and F co-doped layered structure materials (Z. Li et al., 2023f).

1.3.2 Coating strategies

In related research on Ni-rich layered NCM cathode materials, the coating process generated by coating reactions is also an essential modification strategy. Oh's team used spinel-structured $LiMn_{1.9}Al_{0.1}O_4$ to cover the surface of cathode materials (Oh et al., 2016), thereby alleviating the structural and surface instability of NCM70 (nickel content is70%) during storage. The pristine NCM cathode material reacts with water and carbon dioxide in the air, forming an insulating surface layer composed of lithium hydroxide and lithium carbonate, resulting in surface deterioration and hindering the electrochemical cycle of the battery by affecting the charge transfer rate and electron mobility. Coating is considered an important modification strategy for NCM cathode materials because it involves surface engineering, which prevents excessive contact between the NCM cathode material and the electrolyte. This reduces surface side reactions and enhances overall battery performance. The coating layer, typically composed of metal oxides, provides high thermal stability, thereby improving the safety of lithium-ion batteries. In addition, the coating reaction of the NCM cathode material can form a stable interface on the surface of the NCM cathode material, thereby increasing the ion conduction rate and the lithium ion diffusion rate. In the redox reaction of lithium-ion batteries with the NCM cathode material as the cathode, the coating layer can inhibit the occurrence of side reactions on the material surface and improve the cycle stability.

1.3.2.1 Aluminum oxide coating strategies

Alumina is commonly used in coating reactions of various lithium-ion battery cathode materials. Using aluminum oxide coating can effectively protect the electrochemical performance of NCM cathode materials in high-pressure and high-temperature battery reactions, significantly reduce side reactions between NCM cathode materials and electrolytes, and will not excessively impact the Li ions migration. Because of the coating protection, surface side reactions of transition metal ions in coated electrodes are significantly reduced, and the highly active nickel element can effectively carry out battery reactions to ensure the battery's reversible performance and stable structure. Han's team has also achieved many results in the coating modification strategy of aluminum oxide coating for Ni-rich layered NCM cathode material (Han et al., 2017). In the thesis, they illustrated the coating reaction mechanism of NCM622 cathode material and NCM811 cathode material. In NCM cathode materials with different nickel and lithium contents, the higher surface lithium concentration and the strong diffusion effect of aluminum oxide make the coating of the NCM811 material smoother without excess aluminum oxide gathering on the surface. In addition, reducing the manganese content in the NCM cathode material can also improve the diffusion effect of alumina, making the surface of the NCM cathode material smoother. The coating modification strategy of alumina is different for NCM cathode materials with different nickel contents. When the nickel content is low, there will not be any aluminum element inserted into the lattice of the NCM cathode material because the lithium content on its surface is low, high-temperature annealing will generate a protective layer of $LiAlO_2$ that will not enter the crystal lattice, and excess aluminum oxide will accumulate on the surface of the NCM cathode material. For the NCM811 material, because of the low manganese content, when the Ni-rich layered NCM cathode material reacts with alumina at high temperature, the hindrance to the insertion of aluminum elements into the crystal lattice process of the NCM cathode material will be reduced. The aggregated aluminum oxide particles make the surface smoother, and some aluminum elements are doped into the crystal lattice. The doping modification of Ni-rich layered NCM cathode materials by aluminum element is introduced in detail above. For the NCM cathode material coating modification, the doping of aluminum will also cause specific adverse effects on the performance of the alumina coating on the surface. It has an impact on the structure of the coating and the ordering of molecules. In the coating modification strategy of Ni-rich layered NCM cathode materials, the sol-gel method can also be used in addition to the high-temperature eutectic method mentioned above. The research by Wu's team used the sol-gel method with polymers as an assistant. The gel method, using a polyvinyl alcohol polymer additive, generated a uniform γ-Al_2O_3 coating on the NCM622 cathode material surface (Y. Wu et al., 2019). Additionally, tiny pores are formed on the NCM cathode material surface after the sintering process, thereby reducing the obstruction of the aluminum oxide coating to the migration of lithium ions in the NCM622 cathode material, ensuring the ion transmission rate and thus reflecting the electrochemical cycle-excellent performance, especially under high-pressure work. The aluminum oxide coating also reduces the occurrence of side reactions of transition metal ions, thereby inhibiting the dissolution of some transition metal ions and battery degradation. In their research, Neudeck's team also constructed a liquid alumina system for Ni-rich layered NCM cathode materials. For the NCM811 material, the strong water absorption of trimethylaluminum was used to construct an aluminum oxide coating on the NCM811 cathode material surface (Neudeck et al., 2019).

1.4.2.2 Titanium oxide coating strategies

Titanium dioxide is a common coating material and can also be used as a coating modification strategy on the Ni-rich layered NCM cathode material surface. Similar to aluminum oxide coating, titanium dioxide coating can also decrease the accumulation of particles on the Ni-rich layered NCM cathode materials surface to a certain extent, can make the interface more stable, and protect active transition metal ions from interacting with The electrolyte reacts during battery cycling, mitigating the dissolution of some transition metal ions. This kind of coating, as mentioned above, also partly reflects the role of grain boundary engineering in modifying Ni-rich layered NCM cathode material. The coating process and grain boundary engineering can improve the cycle and rate performance of lithium ion batteries, and can also improve the safety of NCM cathode materials. Through such reactions, the grain boundary reaction can be effectively controlled, the proportion of surface degradation of the crystal structure can be slowed down, and the collapse of the crystal structure can be prevented. The above factors are all key factors affecting the performance of NCM cathode materials (Cheng et al., 2019).

1.3.2.3 Rare earth metal oxide coating strategies

Lanthanide oxides play an important role in the coating modification strategy of NCM cathode materials. Shen's team use lanthanide metal gadolinium (Gd) as the coating material (Shen et al., 2023). Gd_2O_3 coating changes the phase transition process of the NCM cathode material, adjusting the H1→H2 phase transition to an approximate single-phase reaction, reducing the irreversible process during the phase transition, thereby improving the electrochemical performance of the NCM cathode material. As a coating layer of NCM cathode material, Gd_2O_3 can also reduce the direct contact between NCM cathode material and electrolyte and reduce unnecessary side reactions. This method regularizes the diffusion of lithium ions, avoiding disordered diffusion and thereby improving conditions during phase transitions. During the H2→H3 phase transition in NCM cathode materials, the Gd_2O_3 coating suppresses the loss of lattice oxygen. Lattice oxygen positively affects repulsion, inhibiting the H2 to H3 phase transformation ratio and harmful H3 phase transformation, thus minimizing structural stability loss in NCM cathode materials. Additionally, the Gd_2O_3 coating delays the temperature required for phase transitions and increases the activation energy needed for the release reaction of surface lattice oxygen, reducing the release ratio of lattice oxygen and improving thermal stability. **Figure 7** shows that in the Gd element modification strategy for Ni-rich layered NCM cathode materials, Gd occupies different micro-sites in the layered structure across various components. XRD analysis shows an increased $I_{(003)}/I_{(104)}$ in the modified Ni-rich layered NCM cathode material, indicating a reduction in cation mixing. TEM imaging also reveals distinct coatings and lattice structures, illustrating that this modification strategy effectively protects Ni-rich layered NCM cathode materials.

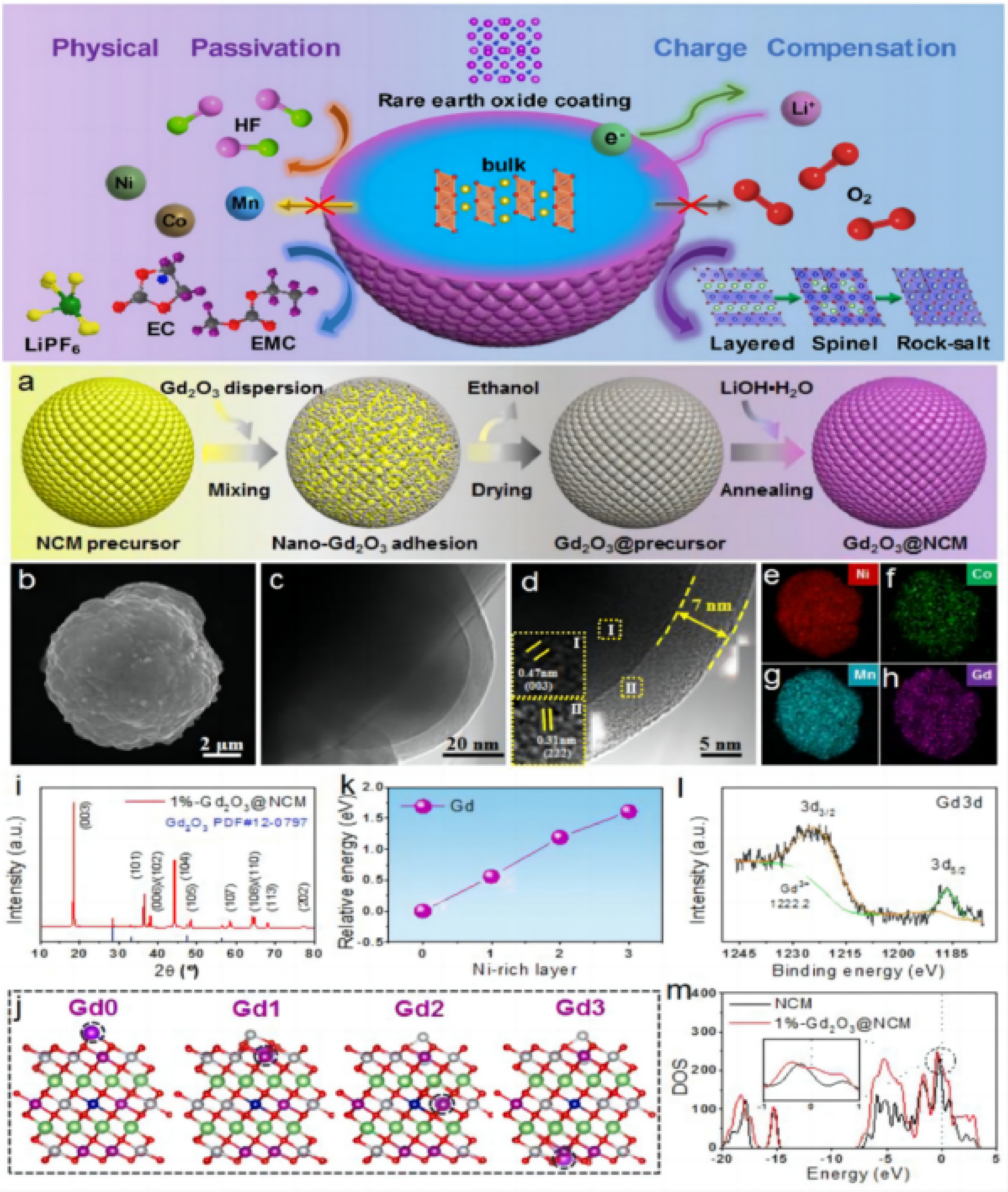


Fig. 7. Schematic of the rare earth oxide (Gd_2O_3) coating NCM cathode materials (Shen et al., 2023b).

1.3.2.4 Fluorine-related compound coating strategies

While studying the coating modification effect of magnesium oxide on Ni-rich layered NCM cathode materials, Hu's team found that the coating deposition formed on the material's surface did not significantly affect its electrochemical performance. For example, a thicker SEI film formed by lithium fluoride deposition does not increase the resistance of the material surface, nor does it negatively impact charge transfer (Hu et al., 2021). However, high-frequency surface erosion, such as that caused by hydrofluoric acid, significantly increases resistance during surface charge transfer, leading to decreased electrochemical performance. Their experiments show that larger grain boundary areas and smaller primary particles provide more pathways for electrolyte penetration, benefiting Li ion transport. However, this also increases the proportion and likelihood of interfacial side reactions. Conversely, larger particles with smaller grain boundary areas experience fewer side reactions, improving cycle stability, but polarization effects may occur under high currents. Fluorine element-related coating modification strategies are crucial for Ni-rich layered NCM cathode materials. Liu's team used $LiPF_6$ as a precursor to perform surface coating modification of NCM material with a lithium fluoride coating and partial fluorine element doping. At the same time, because the chemical bond energy formed by the metal ion and the fluorine element is higher than the chemical bond formed by the oxygen element when using the fluorine element for modification strategy, it will generate a part of the metal-fluorine chemical bonds with higher bond energy changes the crystal structure of the NCM cathode material to a certain extent, thereby modifying the electrochemical performance of the Ni-rich NCM cathode material (K. Liu et al., 2018). As a coating, lithium fluoride is enriched on the surface of the NCM cathode material, which can effectively protect the surface active transition metal ions of the NCM cathode material. The generated SEI film will significantly reduce the occurrence of surface-side reactions. At the same time, through part of the fluorine, The element enters the crystal for doping modification and interacts with the fluorine element on the lithium fluoride coating on the surface of the

NCM cathode material, which can increase the specific surface area of the NCM cathode material and lithium fluoride coating, and improve the performance of NCM in different electrolyte environments. This synergistic effect occurs in many elements, such as the modification strategy of lanthanide metals and some transition metals, which both produce surface oxide coatings and elements in the crystal internal structure. It enters and replaces the Li, Ni, Co, and Mn sites in the original NCM cathode material to modify the structure of the Ni-rich layered NCM cathode material (Sun et al., 2018).

1.3.2.5 Combination of coating and doping strategies

For Ni-rich layered NCM cathode materials, doping and coating reactions often coexist. In their research, Du's team used the harmful thermal expansion material ZrV_2O_7 as the coating material of the NCM622 cathode material (Du et al., 2021). The coating enables the physical separation between the NCM cathode material and the electrolyte while suppressing irreversible surface side effects. In addition, The Zr element in the metal oxide is chemically bonded to the cathode material structure of NCM622 material to a certain extent, and part of the Zr element enters the lattice structure of the NCM cathode material. Because of the presence of the pentavalent vanadium element, the stability of the NCM622 cathode material structure is effectively stabilized, and the cation mixing effect of lithium and nickel ions is also reduced. Surface oxygen is also degraded by 6%, and lower surface oxygen means a more stable crystal structure. This transition metal oxide can also provide a three-dimensional framework on the NCM cathode material surface to promote lithium ions transport at the interface. More importantly, deposited transition metal oxide coating effectively neutralizes the volume instability of the active NCM cathode material through its unique negative thermal expansion characteristics, limiting the NCM622 cathode material from electrochemical cycling at high temperatures and voltages when the volume expansion effect occurs during phase transition. This limits the volume expansion effect during phase transition, allowing the NCM622 cathode material to maintain stability during electrochemical cycling at high temperatures and voltages.

1.3.3 Other strategies

1.3.3.1 Cathode electrolyte interphase film construction strategies

The cathode electrolyte interface (CEI) is an important direction for the study of NCM cathode material modification. One of the modification strategies for NCM cathode materials is the design of CEI film. By constructing better CEI films, the reactivity of NCM cathode materials can be effectively improved. Good CEI film can reduce interface side reactions and enhance the thermal stability of materials. However, some CEI films may reduce charge transfer efficiency due to inappropriate thickness or material properties, and ideal CEI layers are generally inorganic and insulating (Y. Wu et al., 2021). The formation of CEI film is not only related to the material, but also to the electrolyte. Zhao's team added dilithium (trifluoromethanesulfonyl) imide and dilithium (oxalic acid) borate ester to the electrolyte (W. Zhao et al., 2018), and generated effective CEI film through the reaction of the electrolyte. This film can protect NCM cathode materials, reduce direct contact between the electrolyte and NCM cathode materials, and suppress the transition of the layered structure of NCM cathode materials to disordered rock salt phase. Additionally, the strong, conductive SEI layer generated on the lithium surface prevents the corrosion of lithium metal, improving the stability of the Ni-rich layered NCM cathode material structure. Through the co-coating modification strategy of WO_3 and F elements (Z. Li et al., 2023e), this material can reduce surface damage and side reactions during electrochemical cycling, leading to the design of an effective CEI layer. This approach improves the performance of the NCM95 (nickel content is 95%) cathode material. However, using fluorine element alone as a coating for Ni-rich NCM cathode materials does not significantly improve cycle performance because of severe microcracks that occur during cycling (Jiang et al., 2021). Ryu's team doped the NCMA93 (nickel content is 93%) cathode material with antimony (Sb) and constructed a fluorine coating to form a robust CEI layer, suppressing surface degradation and improving battery cycle life. The residual lithium element reacts with the fluorine element in the Ni-rich NCM cathode material to form a lithium fluoride coating. The co-doping strategy with antimony effectively suppresses side reactions and the dissolution of transition metals with the electrolyte and hydrofluoric acid during cycling (H. Ryu, Lim, Kang, et al., 2023b).

1.3.3.2 Crystal facet engineering strategies

Crystal Facet Engineering is another common strategy for modifying Ni-rich layered NCM cathode materials. In NCM cathode materials, the (001) plane has the lowest surface energy, so it appears in the highest proportion. The atomic arrangement on the (001) plane is a layered structure in which transition metals (such as Ni, Co, Mn) and lithium alternate, so the lithium ion conduction rate of the (001) plane is relatively high. However, because of the high surface energy and low lithium ion conduction rate of the (010) plane, it has poor electrochemical cycle stability. Jiang's team used a solid-state reaction to synthesize NCM622 cathode materials with exposed (010) plane (Jiang et al., 2020). (010) plane is different from (001) plane. It has higher energy and exists in a smaller proportion in NCM cathode materials. Since the (010) plane is always exposed and has a high surface energy, it has better electrochemical activity. By doping with zirconium, the (010) plane of the NCM cathode material can be exposed. The (010) plane exposure can improve the reaction kinetics of the NCM cathode material (L. Cheng et al., 2023c). Uniform Zr element doping in the material significantly inhibits the anisotropic shrinkage of the *c*-axis during the phase transition process, effectively reducing the content of the H3 phase and inhibiting the dramatic lattice change during the H2→H3 phase transition. This maintains the complete R3m structure during long-term cycling, suppressing the accumulation of disordered phases (rock salt phase) and maintaining internal structural stability.

1.3.3.3 Controlling lithium excess

Controlling lithium excess is a common strategy for modifying NCM cathode materials. Excess lithium refers to the additional lithium source used relative to the theoretical stoichiometric ratio during the sintering process. Excess lithium can effectively compensate for the loss of lithium in the reaction. During the battery's initial charge and discharge process, part of the lithium ions will be irreversibly embedded into the NCM cathode material or consumed by the SEI layer (J. Liu et al., 2023e). By adding excess lithium in advance, these irreversible lithium losses can be compensated, and the battery's capacity can be increased. At the same time, excess lithium during the reaction can help stabilize the crystal structure of NCM materials and reduce lattice deformation and phase transformation during charge and discharge, thereby improving cycle life and capacity retention (Abebe et al., 2021b). Excess lithium can also reduce the degree of cation mixing of NCM cathode materials, thereby improving the electrochemical performance of NCM cathode materials (Liu et al., 2023d). Excess lithium can increase the specific capacity of the material, but excess lithium may increase the internal stress of the material and affect the structural stability. Excess lithium may also cause side reactions with the electrolyte on the surface of the NCM cathode material or be deposited on the Ni-rich layered NCM cathode material surface, thus affecting the electrochemical performance of NCM cathode materials (Cho et al., 2014).

Figure 8 uses XRD images to demonstrate that a moderate excess of lithium source can reduce the degree of cation mixing in NCM90 cathode materials, as evidenced by the higher $I_{(003)}/I_{(104)}$ in NCM90 cathode materials prepared with an excess lithium source. In addition, XPS analysis shows that excess lithium increases the proportion of Ni^{3+} ions in the structure, which positively impacts the performance of Ni-rich NCM cathode materials by improving electrochemical activity in lithium-ion batteries.

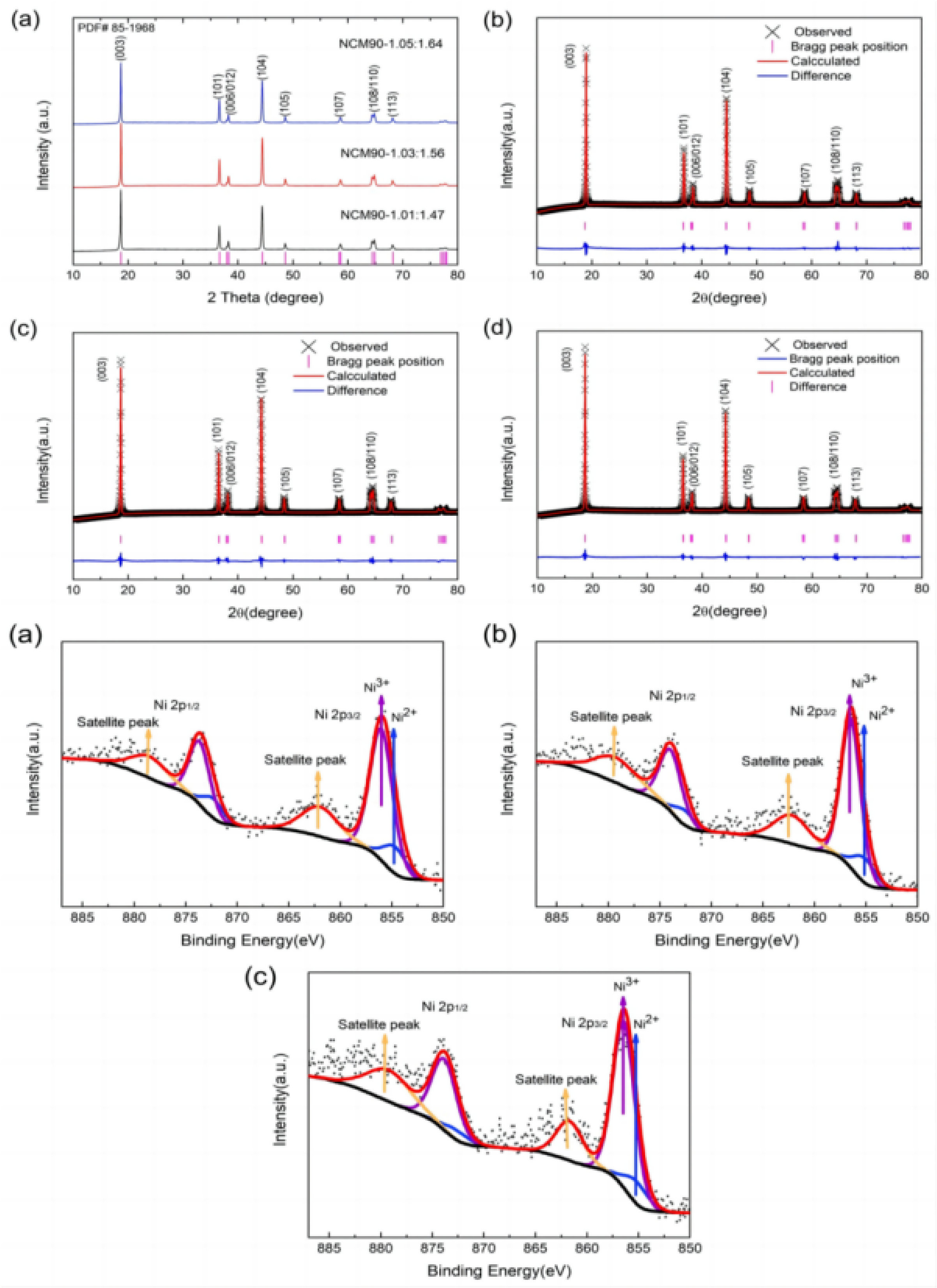


Fig. 8. XRD and XPS images of Modification strategy of NCM90 cathode material using excess lithium (J. Liu et al., 2023e).

1.3.3.4 Surface cleaning

There will be residual lithium on the surface of Ni-rich layered NCM cathode materials, and these residual lithium will undergo side reactions to reduce the electrochemical performance of Ni-rich layered NCM cathode materials (Su et al., 2020). Surface cleaning is a method for treating surface residues of NCM cathode materials. Through different cleaning methods, the surface residues can be removed, and some cleaning methods can generate a protective layer (Xiong et al., 2013), thereby achieving the purpose of improving the electrochemical performance of NCM cathode materials. Ryu's team employed various cleaning strategies to modify Ni-rich layered NCM cathode materials. Comparing the cleaning process with water and fluorine-containing liquids, they found that fluoride-containing liquids have advantages over standard cleaning processes. **Figure 9** shows that they found that using a mixed solution of fluoride ions and cobalt ions for surface cleaning effectively removed surface impurities, reduced the occurrence of surface side reactions, and improved the cycle performance of NCM cathode materials, especially during long cycling processes (H. Ryu, Lim, Lee, et al., 2023c). Different elements have different surface cleaning mechanisms. Anions, cations, and organic solvents all have their unique properties to affect the surface performance of NCM cathode materials. The balance between the construction of SEI film and the cleaning of residual alkaline substances on the surface has also become a very important part of surface cleaning.

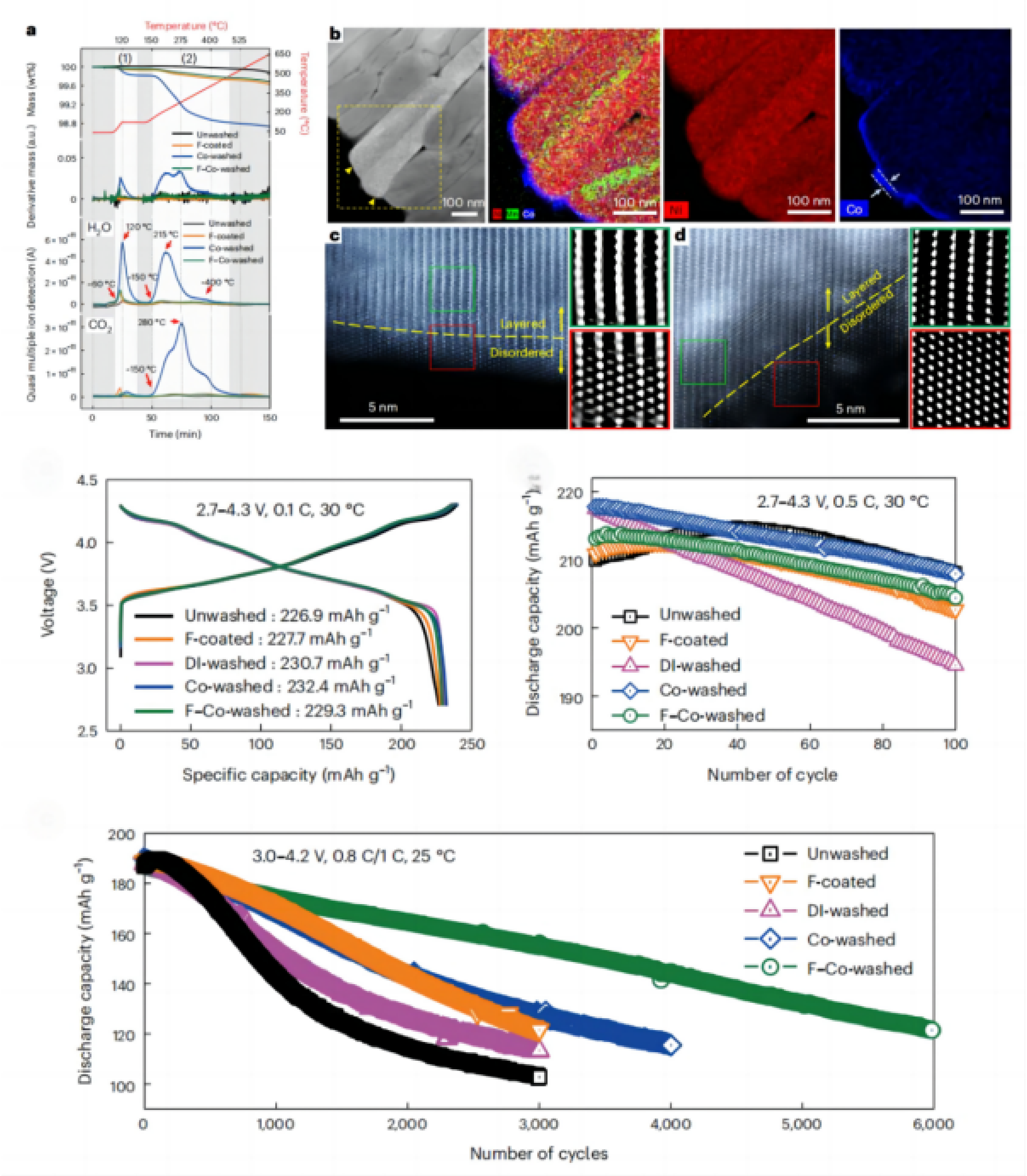


Fig. 9. Surface cleaning mechanism and electrochemical performance of NCM cathode materials (H. Ryu, Lim, Lee, et al., 2023c).

Impurities and unstable phases on the surface of Ni-rich layered NCM cathode materials can cause side reactions during battery cycling, leading to decreased electrochemical performance. After surface cleaning, NCM cathode materials can react with electrolytes to form better CEI films on the material surface, which can maintain the structure and cycling stability of lithium-ion batteries. Surface cleaning removes impurities, thereby improving the cycling performance of NCM cathode materials (H. et al., 2023b). Different types of detergents are used to remove residual lithium and induce structural surface reconstruction. The construction of a new CEI layer inhibits the direct contact between the surface of the Ni-rich layered NCM cathode material and the electrolyte, inhibits the interfacial side reactions between the electrolyte and the NCM cathode material, and inhibits structural collapse during the cycle. The washing process of aqueous solution which has cobalt reacts with the residual lithium on the Ni-rich layered NCM cathode material surface to form a uniform cobalt coating layer. Furthermore, the fluorine element is used to clean the Ni-rich layered NCM cathode material. Surface cleaning and multi-layer coating are achieved through different ion solubilities. The fluorine element is deposited on the NCM cathode material surface, and the residual lithium on the surface generates a stable lithium fluoride coating. The above coating strategies can reduce the direct contact between active transition metal ions and electrolytes, and improve the electrochemical performance of NCM cathode materials. Boric acid can also be used as a surface cleaner for NCM cathode materials. Su's team used an ethanol solution containing low concentration boric acid to perform a surface cleaning process on NCM90 cathode materials (Su, Chen et al., 2020). By cleaning the surface of NCM cathode material to remove residual lithium compounds, the electrochemical performance of NCM cathode material has been improved.

1.4 Summary and strategies of modification for Ni-rich NCM cathodes

As mentioned in the above review, NCM cathode materials have become one of the most important cathode materials in lithium-ion batteries because of their high specific capacity. Recent scientific research indicates that for Ni-rich NCM cathode materials, increasing the specific capacity requires increasing the nickel content. However, increasing the nickel content also enhances the instability of these materials. Therefore, using NCM cathode materials with higher nickel content while maintaining their high specific capacity has become a challenging problem and a key direction for future research. As NCM cathode materials become increasingly important, the operation of Ni-rich lithium compounds also presents a series of issues. The deepening of the H2→H3 phase transition leads to phase transition, where the surface phase of Ni-rich layered NCM cathode materials shifts from layered to spinel and rock salt phases, increasing the surface impedance of NCM cathode materials and negatively affecting their performance. To address the mentioned issues, the literature review has summarized various modification strategies for NCM cathode materials. Cation doping with rare earth metals, transition metals, and alkaline earth metals can effectively enhance the structural stability and overall electrochemical performance of NCM cathode materials. Surface engineering to form coatings of metal oxides or fluorides on NCM cathode materials helps protect them by reducing side reactions and increasing ion transport rates. Additionally, modification strategies involving excess lithium sources and surface cleaning have been employed to improve NCM cathode materials. Excess lithium ensures that during the high-temperature solid-state reaction, the chemical composition of the product remains stable and unaffected by lithium deficiency. This also prevents performance degradation in lithium-ion batteries because of low lithium content during electrochemical cycling. The cleaning process can reduce the surface alkalinity of NCM cathode materials, remove impurities, form a new CEI film, and further reduce side reactions, thus providing better protection for NCM cathode materials. These methods have been extensively studied and will continue to advance in the future, providing more benefits for the application of NCM cathode materials in industry production and daily life.

As mentioned above, rare earth oxides are used for doping and coating modification strategies for Ni-rich layered NCM cathode materials. rare earth oxides typically have high melting and boiling points, making them suitable for high-temperature environments. Many rare earth oxides also exhibit high hardness, making them useful as wear-resistant materials in industrial applications. In terms of electrical properties, rare earth oxides exhibit a wide range, with some showing good conductivity and others acting as insulators. Considering the release of lattice oxygen caused by highly active Ni^{4+} ions during redox reactions, the unique characteristics of rare earth elements with abundant high orbital valence electrons can spontaneously compensate for the unstable Ni^{4+} ions through electron transfer. This prevents lattice oxygen release caused by Ni^{4+} ions capturing electrons, thus avoiding surface instability of electrode materials (Ye et al., 2021). This modification strategy suppresses surface reactions of Ni-rich layered NCM cathode materials while inhibiting the phase transition process from layered structures to high-impedance spinel or rock salt phases, effectively addressing potential reductions in electrochemical performance during battery charge and discharge cycles.

This thesis uses representative CeO_2 rare earth oxides for coating and doping Ni-rich layered NCM cathode materials to overcome the drawbacks of pristine NCM90 cathode material ($LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$) during electrochemical cycling at high cut-off voltages. Cerium oxide (CeO_2) is an important rare earth metal oxide. The cerium element, with its unique outer electron orbitals $4f^15d^16s^2$, exhibits excellent redox performance, capable of reversible conversion between Ce^{3+} and Ce^{4+}. During this process, cerium oxide can release or absorb oxygen ions, facilitating conversion between different oxidation states. This reversible conversion of elemental valence states effectively provides electrons, allowing Ni^{2+} ions to lose electrons without causing lattice oxygen electron depletion and lattice oxygen release during electrochemical cycling. As a coating material, cerium oxide exhibits high chemical stability at room temperature and does not easily react with acids and bases, although it can react with strong acids at high temperatures to form soluble cerium salts. Pure cerium oxide is an electrical insulator, but doped cerium oxide can exhibit enhanced ionic conductivity. Cerium oxide is often used as a cathode material to promote oxygen reduction reactions (ORR) and enhance overall performance. Cerium oxide also has high thermal stability, maintaining good physical and chemical stability at high temperatures, with a low thermal expansion coefficient, making it suitable for high-temperature coating applications. Cerium oxide's electrochemical impedance characteristics at different temperatures and atmospheres significantly influence its application performance. During the sintering process, the Ce^{4+} ions formed by $Ce(OH)_4$ have strong oxidizing properties and can oxidize Ni^{2+} to Ni^{3+} ions. The proportion of Ni^{3+} ions plays an important role in the specific capacity and energy density of Ni-rich layered NCM cathode materials because it can increase the electrochemical activity of lithium-ion batteries. At high temperatures, cerium oxide exhibits low electrochemical impedance, conducive to ion conduction and electrochemical reactions. The results demonstrate that CeO_2 coating can enhance the performance of Ni-rich layered NCM90 cathode materials ($LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$).

Chapter 2 Experiments and methodology

2.1 The methodology of using cerium as a modification element for NCM cathode materials

The physicochemical properties and structure of the cerium-modified NCM90 cathode material need to be determined, and characterized by means such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), and compared with the pristine NCM90 cathode material. The electrochemical testing of CeO_2 modified NCM90 cathode material and original NCM90 cathode material includes galvanostatic charge/discharge (GCD), cyclic voltammetry (CV), differential capacity analysis (dQ/dV), rate performance, cycling performance, electrochemical impedance spectroscopy (EIS), and galvanostatic intermittent titration technique (GITT). The thesis analyze the CeO_2 modified NCM90 cathode material and the original NCM90 cathode material based on the above experimental results.

2.2 Materials synthesis

2.2.1 Synthesis of NCM90 precursor by co-precipitation method

Co-precipitation is commonly used in the synthesis of various composite materials. The reaction is simple and easy to control. The usual strategy of co-precipitation is to add different types of salt solutions to water and control precipitation conditions such as pH or temperature for precipitation. Precise control over the concentration and ratio of metal ions in the solution is essential. Moreover, the rate and amount of precipitant added, as well as the reaction temperature, need to be carefully regulated. After the precipitation reaction, washing the precipitated product is also crucial for influencing the final outcome. While the co-precipitation process is relatively simple and easy to control, achieving high purity of the precipitated products requires accurate regulation of the reaction conditions. In this study, the co-precipitation method is used to synthesize NCM90 precursor materials. By controlling the necessary conditions for precipitation, high-purity and high-tap-density NCM precursor materials can be obtained.

Based on the synthesis procedure of NCM90 cathode material precursor, we used a double-layer 2L steel reactor setup, which contained an overhead stirrer with controllable speed (maximum 1000 rpm), propeller blades (stainless steel), and Hot bath. An M300 pH meter and nitrogen gas were also connected to the reactor. In addition, transition metal solutions, including nickel sulfate, cobalt sulfate, manganese sulfate, ammonia solution, and NaOH solution pipes, are connected to the reactor, respectively. This study used hydrated sulfates as transition metal sources, including nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), and manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$). Alkali solution is prepared with sodium hydroxide (NaOH), and high-concentration ammonia ($NH_3 \cdot H_2O$, 25wt.%) is diluted to the required concentration before use (All chemicals were purchased from Chem Supply Australia and used as received without any further purification).

Deionized (DI) water was provided by the laboratory and was saturated with nitrogen before being used for solution preparation. The molar ratio of the mixed transition metal salt solution (S) :Ni:Co:Mn is controlled to 9:0.5:0.5. Prepare in advance a mixed salt solution with a concentration (based on the total amount of transition metals)Of 2mol/L and a volume of 0.5L. Dissolve 236.6 g $NiSO_4 \cdot 6H_2O$, 14.1 g $CoSO_4 \cdot 7H_2O$, and 8.5 g $MnSO_4 \cdot H_2O$ powder in an appropriate amount (0.4L) of nitrogen-saturated deionized water and stir well in a large beaker until the salts are almost dissolved at room temperature. Transfer the mixture to a 0.5L volumetric flask for volumetric manipulation. The obtained 0.5L mixed transition metal salt solution was further saturated with nitrogen and sealed in a jar for use. Alkaline solution (B) : Prepare a 4mol/L NaOH solution (1L) and use it as an alkaline solution. The process is similar to mixing transition metal salt solutions. Dissolve 160.0g NaOH powder in an appropriate amount (0.6L) of nitrogen-saturated deionized water and stir evenly in a large beaker until the salt is almost dissolved and the solution is completely cooled. Transfer the mixture to a 1L volumetric flask for volumetric manipulation. The obtained 1 L mixed transition metal salt solution was further saturated with nitrogen and sealed in a plastic jar for use. Ammonia solution (A) : To obtain 4 mol/L ammonia solution (1L), 0.3L ammonia solution (25wt.%) was dissolved in 0.7L nitrogen-saturated deionized water. Store the above solution in a sealed glass container and set aside. 0.6L of nitrogen-saturated deionized water was added to the reactor as substrate solution and stirred at 900 rpm. The pH was adjusted to 11.40 using a concentrated ammonia solution (25wt.%). The substrate solution was then heated to 50°C and held constant for approximately 0.5h. The mixed transition metal salt solution (S) was continuously added at a flow rate of 0.1 mL/min, and the ammonia solution (A) as a complexing buffer was added at a flow rate of 0.1 mL/min. Dynamically add alkali solution (B) as a precipitant (flow range 0-0.5mL/min) and adjust the pH value to 11.50±0.05. The entire reaction process was carried out under an N_2 atmosphere. Control the reactor temperature at 50°C, stir continuously for 72 hours, and stir at a speed of 900 rpm. After aging for 48 hours at 50°C and a stirring speed of 400 rpm, the resulting precipitate was recovered by filtration, washed twice with dilute ammonia water (0.6 mol/L), and then washed several times with deionized water until the pH value reached 8.0, and finally at 60°C in a vacuum drying chamber for 24 hours to obtain a yellow-brown precursor.

2.2.2 Synthesis of NCM90 cathode material by solid-state reactions

Solid-state reactions typically occur between solid materials and generally require high temperatures to facilitate contact, diffusion, and chemical reactions between the solids. High temperature plays a crucial role in the kinetics of these reactions, significantly accelerating the process. The rate of a solid-state reaction is influenced by the diffusion rate of the solid materials involved. Faster diffusion rates lead to quicker reaction speeds. At elevated temperatures, the crystal structures of the reactants may change, resulting in the formation of new solid compounds. Solid-state reactions are frequently employed in materials chemistry and catalyst preparation. High temperature solid-state reactions do not require solvents or reaction media, so the purity of the reaction products will be higher and suitable for large-scale industrial applications. However, high temperature solid-state reactions take a long time and require a continuous high temperature environment, so the process of solid-state reactions cannot be precisely controlled. In this thesis, high-temperature solid-state reactions are utilized to synthesize pristine NCM90 cathode materials as well as NCM90 cathode materials that have been doped or coated with Ce element modifications. This approach highlights the effectiveness of solid-state reactions in producing advanced battery materials while also demonstrating the inherent challenges and considerations involved in the process.

Cerium hydroxide ($Ce(OH)_4$), lithium hydroxide monohydrate ($LiOH\cdot H_2O$) were purchased from Sigma-Aldrich and used directly without any further purification. Lithium hydroxide monohydrate ($LiOH\cdot H_2O$) is the lithium source for sintering Ni-rich NCM90. The molar amount of $LiOH\cdot H_2O$ is equal to the total amount of mixed transition metals, with an excess of 3% to avoid the loss of lithium during mixing and sintering. When preparing a small amount of NCM products through the sintering process, the precursor NCM90 ($Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)_2$) is mixed with $LiOH\cdot H_2O$

powder and cerium hydroxide ($Ce(OH)_4$) are ground in a mortar, NCM90 precursor: $LiOH \cdot H_2O:Ce(OH)_4$ = 1:1.03:0.02, and transferred to a covered alumina crucible, and sintered at 750°C for 15h in an O_2 atmosphere at a heating rate of 2°C/min, the sintered products of 2%-CeO_2@NCM90 was obtained.

2.3 *Material characterization*

2.3.1 X-ray diffraction

X-ray diffraction (XRD) is an analytical method that leverages the diffraction phenomenon of X-rays in crystalline materials to determine their crystal structure. XRD can be used to ascertain the crystal structure of a substance and compare the XRD patterns of test samples and pristine samples to analyze and identify different phase compositions and the presence of different phases. This thesis uses a Bruker D8 Discovery X-ray diffraction system with Monochromatic Cu Kα radiation (λ=1.5418Å), a scan step of 0.04°/s, and a 2θ range of 10° to 80°. This thesis uses XRD test results to analyze the degree of cation mixing in the NCM cathode material, thereby analyzing the electrochemical properties of the NCM cathode material, and also confirming the elemental composition of the NCM cathode material after modification.

2.3.2 Scanning electron microscope

Scanning electron microscopy (SEM) is an electron beam scanning the surface of a sample. Signals are generated after the electron beam interacts with the sample. These signals are analyzed to obtain images and composition information of the sample. The resolution of SEM can reach the nanometer level. Energy dispersive X-ray spectroscopy (EDS) technology can analyze the elemental composition and distribution of samples. In this thesis, two SEM instruments, Zeiss Supra 55VP and EVO, were used to observe the pristine NCM90 cathode material and CeO_2 modified NCM90 cathode material, and SEM images and element distribution of the two materials were obtained.

2.3.3 Transmission electron microscope

Transmission electron microscopy (TEM) is an technique that uses high-energy electron beams to process samples. When the electron beam passes through the sample, the electron beam carries the structural information inside the sample. The amount of electrons transmitted through the dense parts of the sample is less, and the amount of electrons transmitted through the sparse parts is more. Therefore, the thickness and elemental composition of the sample will affect the imaging of TEM technology. The maximum magnification of TEM is one million times. At the highest magnification, TEM technology can display images of individual atoms. This article uses transmission electron microscopy (TEM, JEM-F200, JEOL, Japan) to photograph CeO_2 modified NCM90 cathode materials and study the crystal structure of NCM90 cathode materials.

2.3.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface chemical analysis technique that can be used to analyze the surface chemistry of metal materials in specific states or after some processing treatments. Not only does it provide information on molecular structure and atomic valence states for chemical research, but it also provides information on the elemental composition and content, chemical state, molecular structure, and chemical bonds of various compounds for electronic material research, enabling quantitative analysis of compounds. In this thesis, XPS is mainly used to test the number of oxidation states of nickel and cerium elements and the ratio of each oxidation state ion in the pristine NCM90 cathode material and the modified NCM90 cathode material. XPS analysis of the ratio of oxidation states of each element in the NCM cathode material can be used to analyze the reasons for the improvement of the performance of the NCM90 cathode material, and explain the reaction mechanism of the NCM cathode material modification strategy through the results of the XPS test.

2.4 Electrode preparation, cell assembly, and electrochemical testing

2.4.1 Electrode preparation

Cathode slurries were prepared by mixing active materials, conducting agents (carbon black), and binders [poly(vinylidene fluoride), PVDF] with a weight ratio of 8:1:1 using N-methyl pyrrolidone (NMP) as a solvent in a high-energy mixer. The obtained slurries were uniformly coated onto aluminum foils via a blade with an active material loading of 4 mg cm^{-2}. After vacuum drying at 120 °C overnight, the electrodes were roll-pressed and punched into discs with a diameter of 12 mm ready for use.

2.4.2 Battery assembly

The lithium-ion battery half-cell is assembled in a glove box filled with argon and the oxygen and water content is reduced to below 0.1 ppm to prevent the electrolyte and lithium metal from decomposing in the presence of water and oxygen. In the half-cell assembly, the lithium metal plate is used as the anode, and the lithium metal plate and Celgard 2400 membranes are the anode and separator in the half-cell. The electrolyte used for battery testing here is 1M $LiPF_6$ with a 1:1 volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC). All materials are assembled into a CR2032 coin cell, and stainless steel gaskets and springs are used to enhance the contact between the electrolyte and the electrode.

2.4.3 Cyclic voltammetry

Cyclic voltammetry (CV) is to scan the potential of the working electrode between two set values while measuring the current, and then analyze the redox properties of the material. The cyclic voltammetry test can draw different peaks corresponding to the material in the redox reaction. The image of each peak can correspond to a different redox process. Cyclic voltammetry images can display the reaction mechanism of electrochemical reactions, and can also compare images of different materials to discuss their electrochemical properties. This thesis used BioLogic VMP3 electrochemical workstation to obtain CV data and studied the CV images of CeO_2 modified NCM90 cathode and pristine NCM90 cathode materials. The reasons for the improved electrochemical performance of CeO_2 modified NCM90 cathode materials were analyzed.

2.4.4 Galvanostatic charge-discharge

Galvanostatic charge-discharge (GCD) is a very important method in studying the electrochemical properties of materials. GCD testing is a charge discharge test conducted at a constant current, recording the variation of its potential over time. It can observe the specific capacity of the material through images and analyze its cycle life and electrochemical performance. This article uses GCD method to study the electrochemical cycling process of the pristine NCM90 cathode material and CeO_2 modified NCM90 cathode material, and observes the advantages and disadvantages of CeO_2 modified NCM90 cathode material and pristine NCM90 cathode material in specific capacity and cycling stability.

2.4.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) testing is an electrochemical measurement method that uses small amplitude sine wave potentials (or currents) as disturbance signals. EIS first uses an AC signal and measures the resulting phase difference to provide an impedance spectrum. In addition, EIS testing can infer the equivalent circuit of materials to obtain the resistance value of the equivalent circuit, which can be used to analyze the dynamics and ion diffusion rate of materials. This thesis conducted EIS testing and analyzed the dynamic effects of pristine NCM90 cathode material and CeO_2 modified NCM90 cathode material in the frequency range of 100MHz to 10kHz with a test amplitude of 5mV.

Chapter 3 Results and discussion

3.1 Synthesis, morphology, and structural analysis

XRD testing can demonstrate the crystal structure and ion mixing degree of NCM cathode materials. **Figure 10** shows XRD image of pristine NCM90 cathode material and 2%-CeO_2@NCM90. All characteristic peaks of the materials can be attributed to the α-$NaFeO_2$ phase (PDF#09-0063), indicating that using CeO_2 did not alter the crystal structure of NCM90 cathode material. The CeO_2 diffraction peak indicates the formation of a composite of NCM90 cathode material and CeO_2. The appearance of the peak at approximately 28.5° has been confirmed to be associated with the presence of CeO_2, and diffraction peaks consistent with CeO_2 were found on the (111) and (200) planes, indicating that CeO_2 has successfully modified the NCM90 cathode material.The use of CeO_2 modification can lead to changes in lattice parameters, and the main CeO_2 diffraction peak may come from CeO_2 particles enriched on the surface of NCM90 cathode material (M. Wang et al., 2017). For NCM cathode materials, the (003) planes are predominantly occupied by transition metal ions, while the (104) planes have a mixed distribution of lithium ions and transition metal ions. The atomic scattering ability of transition metals is much stronger than that of lithium atoms. Therefore, if nickel ions migrate from the (003) planes to the (104) planes, it increases the overall atomic scattering ability of the (104) planes while weakening the response of the (003) planes to X-rays. The intensity of the X-ray diffraction peak is proportional to the scattering ability of the diffraction planes, so this results in an increase in the intensity of the (104) planes and a decrease in the intensity of the (003) planes, thus reducing the $I_{(003)}/I_{(104)}$ ratio. Therefore, the $I_{(003)}/I_{(104)}$ ratio is commonly used to measure the mixing degree of cations. In the experiment, the cation mixing degree of the 2%-CeO_2@NCM90 cathode material is lower. The $I_{(003)}/I_{(104)}$ ratio indicates that the CeO_2 coating decreases the mixing degree of Ni^{2+} and Li^{+} ions. Other metal elements such as lanthanum, zirconium, and aluminum were also subjected to solid phase reactions with the pristine NCM90 cathode material using the same method as cerium modification. XRD images showed that their cation mixing degree was higher than that of the original NCM90 cathode material. In addition, no peak of zirconium was found in the XRD images after zirconium modification strategy. Therefore, doping NCM cathode material with cerium is reasonable and effective.

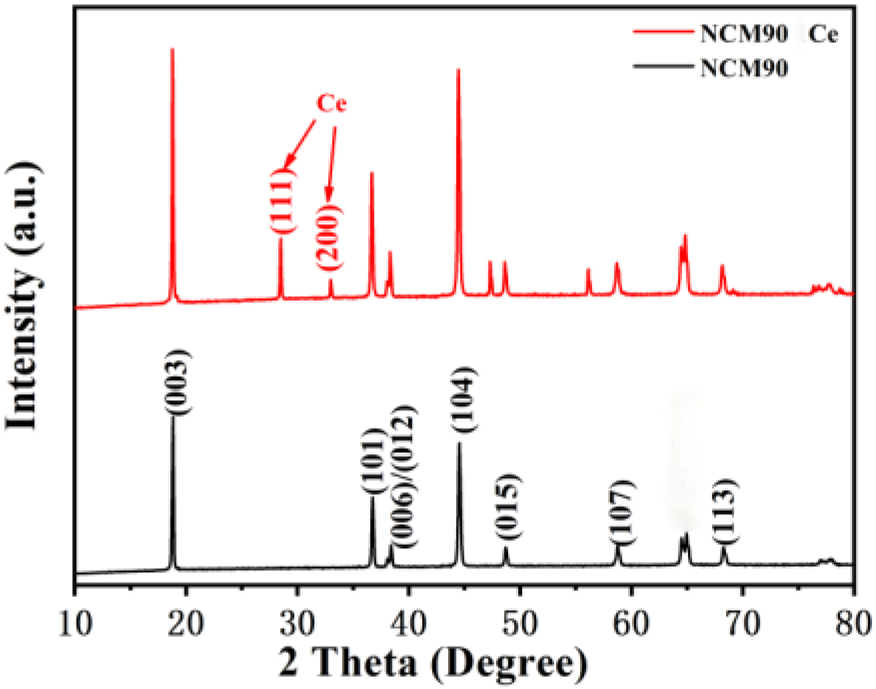


Fig. 10. XRD patterns of NCM cathode materials modified with Cerium oxides using the doping and coating modification strategy.

Figures 11a–11d show the SEM images of 2%-CeO_2@NCM90 cathode material and pristine NCM90 cathode material. Compared to the pristine NCM90 cathode material (**Figures 11a and 11b**), the morphology of the 2 mol% CeO_2-modified material (2%-CeO_2@NCM90) shows no obvious changes, the particle diameter and morphology are almost the same as those of the pristine NCM90 cathode material, only little CeO_2 aggregate particles appearing on the surface (**Figures 11c and 11d**).

In order to better observe the element distribution of 2%-CeO_2@NCM90 cathode material, EDS mapping was used for analysis (**Figure 11e**). **Figures 11e** shows that the 2%-CeO_2@NCM90 cathode material contains four elements: Ce, Ni, Co, and Mn. From **Figures 11e,** it is shown that cerium is barely detectable inside the structure but has significant signals on the particle surface, further indicating that most of the cerium element forms a surface coating with minimal internal lattice doping. The comparison of Ce with other metal oxides suggests that this large ratio of surface coating to internal doping is attributed to the relatively large ionic radius of Ce^{4+} ions. The ionic radius of Ce^{4+} ions is 0.87Å, which is larger than the radii of nickel ions, cobalt ions and manganese ions in the NCM cathode material, so it is not easy to enter the crystal lattice. Most of the cerium ions are concentrated on the surface of the NCM cathode material (Zhong et al., 2011). The enrichment of cerium elements on the NCM cathode material surface shown by EDS results is likely due to the large ionic radius of cerium ions, which cannot enter the lattice and can only be enriched on the surface of NCM90 cathode material. In order to better observe the structure of the 2%-CeO_2@NCM90 cathode material, TEM was used to test the 2%-CeO_2@NCM90 cathode material **(Figures 11f and 11g).** In **Figures 11f and 11g**, the (003) plane corresponding to the NCM cathode material is visible, with an interplanar spacing of 0.48 nm. Additionally, the (220) plane of CeO_2, with an interplanar spacing of 0.19 nm, can be identified in the CeO_2 coating on the surface of the Ni-rich layered NCM cathode material. There may also be amorphous CeO_2, which lacks long-range ordered crystal structures but retains the basic chemical composition of CeO_2 (P. Li et al., 2012). The images reveal diffraction patterns of both the NCM cathode material and CeO_2 oxide coating regions, indicating the presence of layered structures and cubic phases. The lattices in the figure correspond to the common lattices of CeO_2 and Ni-rich layered NCM cathode materials (Y. Zhang et al., 2019). The situation shown by TEM is consistent with the EDS mapping and XRD results, and CeO_2 is mainly modified by coating to form a coating layer on the NCM90 cathode material.

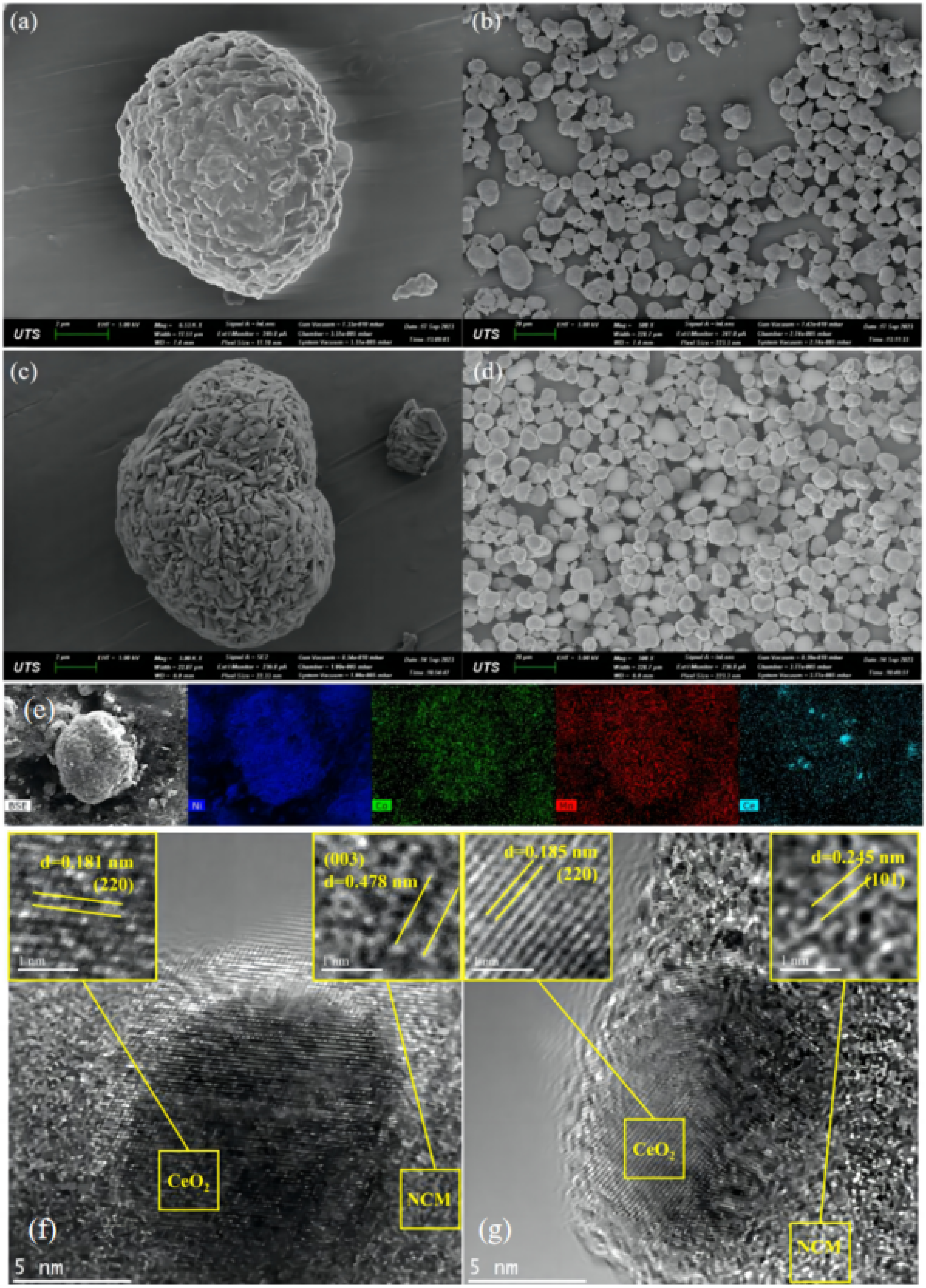


Fig. 11. (a,b) SEM images of NCM90; (c,d) SEM images of 2%-CeO$_2$@NCM90; (e) EDS mapping of 2%-CeO$_2$@NCM90 cathode material; (f,g) TEM images of

2%-CeO_2@NCM90 cathode material.

To further investigate the effect of Ce^{4+} ions on the NCM90 cathode material, XPS characterization of the 2%-CeO_2@NCM90 cathode material and pristine NCM90 cathode material was conducted to examine the elemental valence states (**Figure 12**).

Figure 12a displays the Ni 2p XPS spectra of these materials. In the spectra, the main peak of Ni $2p_{3/2}$ for all samples shifts to higher binding energy, indicating that more Ni^{2+} ions have been converted to Ni^{3+} ions after the co-sintering coating reaction. One of the key factors for the performance of Ni-rich layered NCM cathode materials, the proportion of Ni^{3+} ions, is only 21.23% in the 1%-CeO_2@NCM90 cathode material, compared to 33.01% in the pristine NCM90 cathode material, showing a decrease. In the 2%-CeO_2@NCM90 cathode material, the proportion of Ni^{3+} ions is 40.42%, indicating that the modification strategy with 2%-CeO_2 oxide successfully increased the proportion of Ni^{3+} ions in the Ni-rich layered NCM cathode material. Ni^{3+} ions have higher conductivity, which can effectively improve the migration rate of Li^+ ions and electrons, thereby enhancing the rate performance of the Ni-rich layered NCM cathode material. Additionally, Ni^{3+} ions can also stabilize the layered structure of the Ni-rich NCM cathode material, and because of the higher redox potential of Ni^{3+} ions, they can provide a higher voltage platform, ultimately improving the energy density of lithium-ion batteries. Moreover, Ni^{3+} ions can help form a more stable SEI film on the Ni-rich layered NCM cathode material, reducing the occurrence of side reactions. The activation effect of Ni^{3+} ions is very significant for NCM cathode materials.

Figure 12b shows the Ce 3d XPS spectra of 1%-CeO_2@NCM90 and 2%-CeO_2@NCM90 cathode materials. In the synthesis of 2%-CeO_2@NCM90 cathode material, the ratio of different valence states of cerium indicates that some Ce^{4+} ions were reduced to Ce^{3+} ions, while some Ni^{2+} ions in the NCM cathode material were converted to Ni^{3+} ions. Based on the XPS spectra data, the modification strategy of the pristine NCM90 cathode material with CeO_2 oxide shows that in the 1%-CeO_2@NCM90 cathode material, the proportion of Ce^{3+} ions is 42.03%, and Ce^{4+} ions is 57.97%. In the 2%-CeO_2@NCM90 cathode material, the proportion of Ce^{3+} ions is 29.36%, and Ce^{4+} ions is 70.64%, indicating that some of the Ce^{4+} ions were reduced during the modification process. Because the ionic radius of Ce^{3+} ions is larger than ionic radius of transition metal ions, Ce^{3+} ions cannot enter the lattice of the NCM cathode material. Ce^{3+} and Ce^{4+} ions exist on the surface of NCM cathode materials in the form of oxides. Additionally, the bond energy of Ce–O bonds, whether formed by Ce^{3+} or Ce^{4+} ions with oxygen atoms, is higher than that of Ni–O bonds, thus enhancing the structural stability of the NCM cathode material. The XPS images indicated a decrease in the proportion of Ni^{2+} ions in the Ni-rich layered NCM cathode material compared to the pristine NCM90 cathode material, while Ce^{3+} ions appeared in the XPS patterns, this indicates that redox reaction occurred during the CeO_2 modification process, part of the Ce^{4+} ions is converted into Ce^{3+} ions.

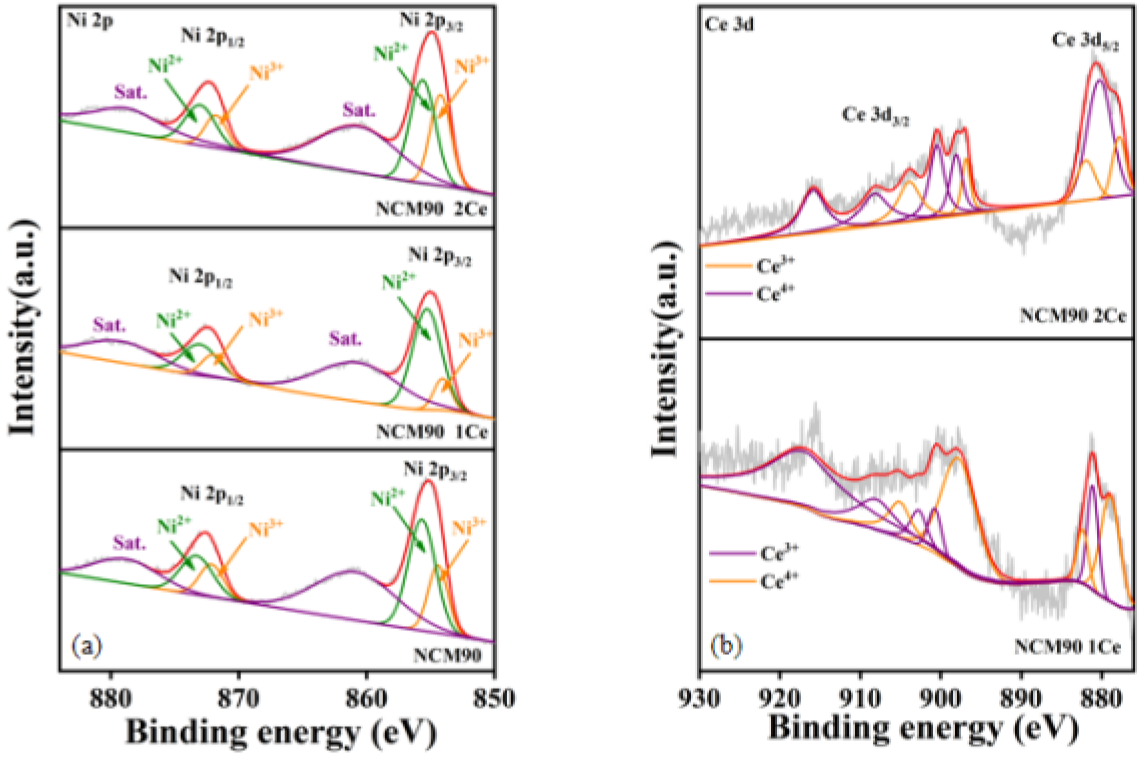


Fig. 12. (a) Ni 2p XPS spectra of NCM cathode materials; (b) 1%-CeO_2@NCM90 and 2%-CeO_2@NCM90 3d XPS spectra of NCM cathode material.

3.2 Electrochemical performance

Figure 13a shows the initial charge-discharge curves of 2%-CeO_2@NCM90 cathode material and pristine NCM90 cathode material. The discharge capacity of the 2%-CeO_2@NCM90 is 10 mAh·g^{-1} higher than that of the pristine NCM cathode material. Both the pristine NCM90 cathode material and 2%-CeO_2@NCM90 cathode material exhibit similar potential platforms at 3.75V, indicating similar chemical compositions, but the specific capacity of 2%-CeO_2@NCM90 material is slightly better than that of the pristine NCM90 cathode material. **Figure 13b** shows the cycling performance of 2%-CeO_2@NCM90 cathode material and pristine NCM90 cathode material at different current densities. After 200 cycles at 1C and between 2.7 and 4.3V, the pristine NCM90 cathode material had a discharge specific capacity of 139.12 mAh·g^{-1}, with a capacity retention rate of 80%.

However, the 2%-CeO_2@NCM90 cathode material had a discharge specific capacity of 163.33 mAh·g^{-1}, with a capacity retention rate of 86.9%. The CeO_2 coating inhibits the formation of surface SEI film and reduces the surface polarization of NCM90 cathode material, resulting in better cycling performance.

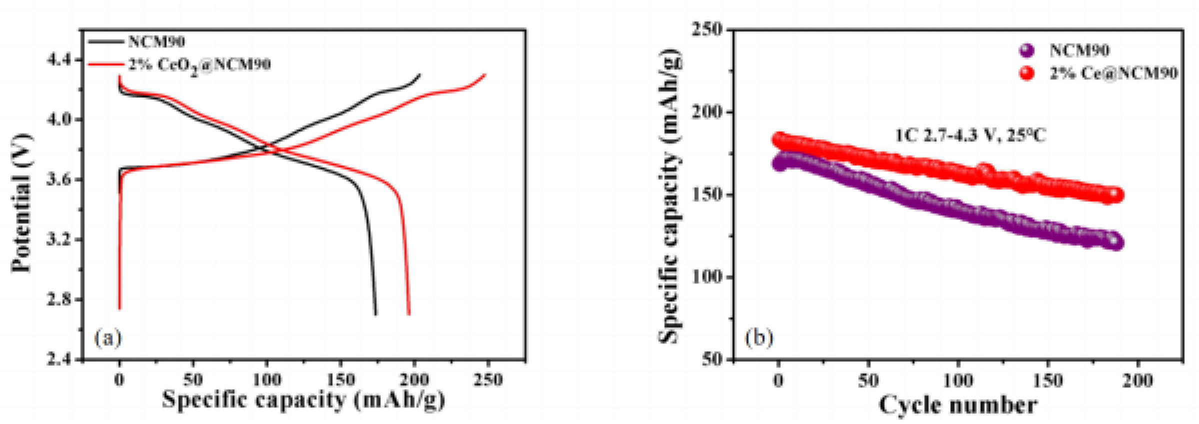


Fig. 13. (a) Initial charge-discharge curves of 2%-CeO_2@NCM90 cathode material and pristine NCM cathode material; (b) The cycle performance comparison between 2%-CeO_2@NCM90 cathode material and pristine NCM90 cathode material at 1.0C.

Figures 14a and 14b present the galvanostatic charge-discharge (GCD) curves from the 10th to the 100th cycle for the pristine NCM90 cathode material and 2%-CeO_2@NCM90 cathode material. GCD tests were conducted at 25°C with a voltage range of between 2.7 and 4.3V and a current density of 1C. The initial discharge specific capacity of the 2%-CeO_2@NCM90 cathode material is 187.94 mAh·g^{-1}, and after 100 electrochemical cycles, the discharge specific capacity is 173.47 mAh·g^{-1}, with a capacity retention rate of 92.3%. In contrast, the pristine NCM90 cathode material has an initial discharge specific capacity of 173.71 mAh·g^{-1}, and after 100 electrochemical cycles, the discharge specific capacity is 152.14 mAh·g^{-1}, with a capacity retention rate of 87.5%. The experimental results show that the 2%-CeO_2@NCM90 cathode material has better initial discharge specific capacity and capacity retention rate compared to the pristine NCM90 cathode material. Using CeO_2 oxide as a modification of Ni-rich layered NCM cathode materials can effectively reduce cation mixing and increase the lithium ion diffusion rate and make the redox reaction more complete. The decrease in capacity retention of the pristine NCM90 cathode material after 100 cycles at 1C and between 2.7 and 4.3V is due to the irreversible capacity loss caused by side reactions of the unprotected pristine NCM90 cathode material under high voltage. Side reactions of the unprotected pristine NCM90 cathode material destabilize the layered structure of the Ni-rich layered NCM cathode material, making it more prone to structural collapse, thereby reducing cycling performance.

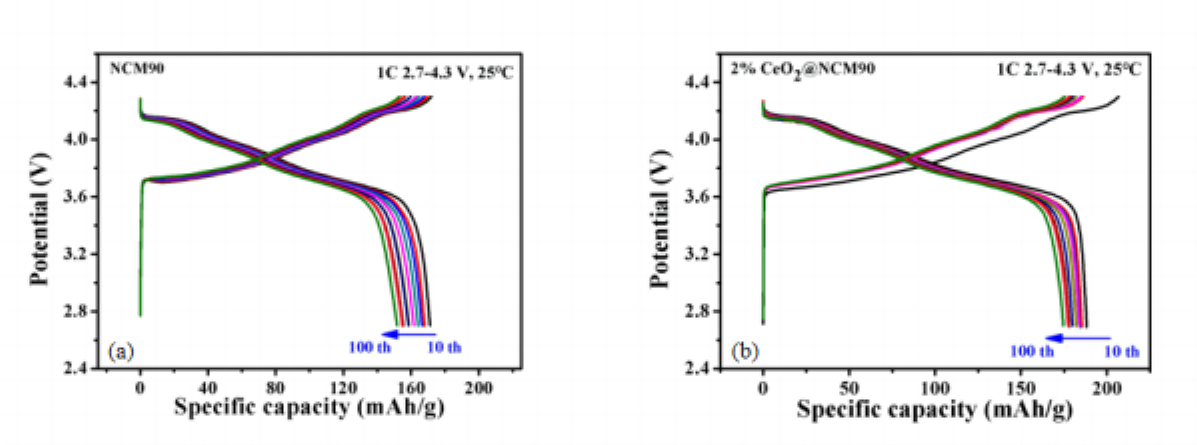


Fig. 14. (a) The charge/discharge curves of the pristine NCM90 cathode material at a voltage between 2.7 and 4.3V at 1C; (b) The corresponding charge/discharge curves of 2%-CeO_2@NCM90 cathode material at a voltage between 2.7 and 4.3V at 1C.

Figure 15 illustrates the rate performance of both the 2%-CeO_2@NCM90 cathode material and the pristine NCM90 cathode material. At a low current density of 0.2C, both materials exhibited nearly identical discharge specific capacities. However, as the current density increased to 0.5C, 1C, 2C, and 5C, the gap in discharge specific capacities between the different NCM cathode materials widened. When the current density reached 5C, the 2%-CeO_2@NCM90 cathode material maintained a discharge specific capacity of 147.85 mAh·g^{-1}, while the pristine NCM90 cathode material's capacity dropped to less than 115 mAh·g^{-1}. This is because the CeO_2 coating improves the structural stability of the NCM cathode material, reduces surface polarization during cycling, so rate performance is better than the pristine NCM cathode material under high current density and high voltage.

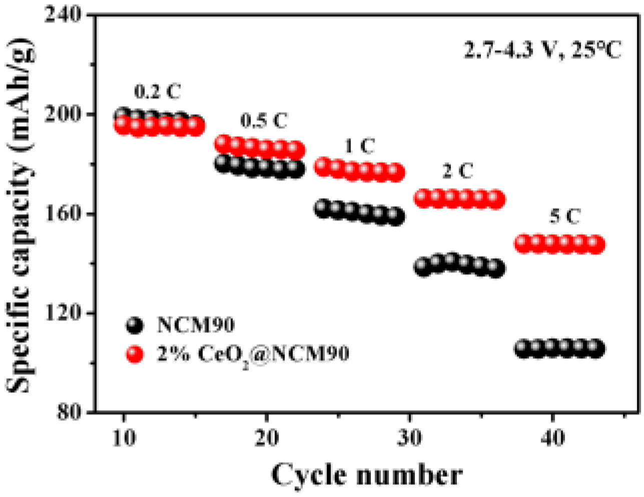


Fig. 15. Rate performance of the pristine NCM90 cathode material and 2%-CeO_2@NCM90 cathode material.

Figures 16a and 16b show the cyclic voltammetry (CV) curves of the first five cycles. **Figure 16a** displays the CV test of the 2%-CeO_2 modified NCM cathode material over the first five cycles, within a voltage range of between 2.7 and 4.3V and a scan rate of 0.1 mV/s. **Figure 16b** presents the CV test of the pristine NCM90 cathode material under the same conditions. During the first cycle, both types of NCM cathode materials undergo surface oxidation reactions with the electrolyte in the lithium-ion battery, forming SEI films (Yao et al., 2020b). From the second cycle onwards, although the oxidation peak shifts to a lower potential, the positions of the peaks in the subsequent four cycles are almost coincident. The degree of overlap is higher for the 2%-CeO_2@NCM90 cathode material compared to the pristine NCM90 cathode material, indicating that the irreversible capacity loss mainly occurs during the first cycle and that the 2%-CeO_2@NCM90 cathode material exhibits better cycling stability. Both the pristine NCM90 cathode material and the modified 2%-CeO_2@NCM90 cathode material exhibit symmetric peaks during the cycling process, indicating good reversibility for both materials, with the curves almost completely overlapping in subsequent cycles. The 2%-CeO_2@NCM90 cathode material shows better reversibility and higher peak intensity. All CV curves display three redox peaks corresponding to the processes of Ni^{2+} ions converting to Ni^{3+} ions, Ni^{3+} ions converting to Ni^{4+} ions, and Co^{3+} ions converting to Co^{4+} ions in the Ni-rich layered NCM cathode material. The oxidation peak at 3.75V and the reduction peak at 3.70V correspond to the redox process of Ni^{2+} and Ni^{4+} ions. During the entire charge-discharge process, the surface of the NCM cathode material undergoes the H1→M→H2→H3 phase transformation process. The 2%-CeO_2@NCM90 cathode material shows a smaller potential difference compared to the pristine NCM90 cathode material, indicating better cycling performance, this also suggests that CeO_2 modification improves the electrochemical performance of the Ni-rich layered NCM cathode material. It has been proven that CV images can show that modified NCM90 cathode materials have better cycling and reversible properties, which can improve the efficiency of NCM90 cathode material use.

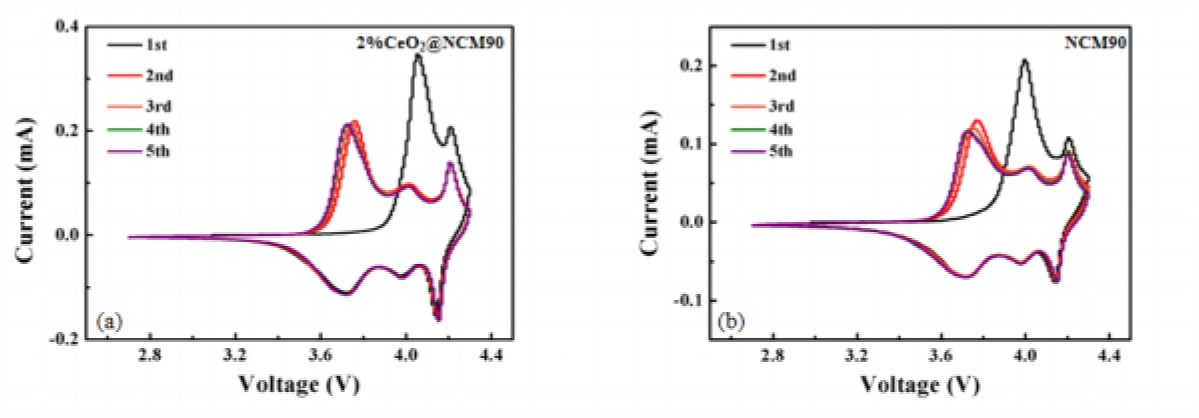


Fig. 16. (a) CV curve of 2%-CeO_2@NCM90 cathode material at a scan rate of 0.1 mV/s; (b) CV curves of pristine NCM90 cathode material at a scan rate of 0.1 mV/s.

Rate performance is generally closely related to impedance, so electrochemical impedance spectroscopy (EIS) tests were conducted on 2%-CeO_2@NCM90 cathode materials and pristine NCM90 cathode material after 10 cycles of electrochemical cycling. **Figure 17a** shows the EIS results for the 2%-CeO_2@NCM90 cathode materials, and **Figure 17b** shows the EIS results for the pristine NCM90 cathode material. From the EIS test results, the electrolyte resistance (R_s) shows no obvious difference under different conditions, indicating that the electrochemical reaction has little effect on the R_s value. The charge transfer resistance (R_{ct}) of the doped NCM cathode material is 1481Ω, which is lower than the 1790Ω of the pristine NCM90 cathode material, indicating that 2%-CeO_2@NCM90 cathode materials have faster charge transfer capabilities, facilitating easier electrochemical reactions. The CeO_2 coating effectively improved the diffusion and migration rate of lithium ions. In addition, the image shows the surface film resistance (R_f) of 2%-CeO_2@NCM90 cathode material is lower than that of the pristine NCM90 cathode material. the surface film resistance (R_f) of 2%-CeO_2@NCM90 cathode material is 67.64Ω, while R_f of the pristine NCM90 cathode material is 220.1Ω. The decrease of R_f may be due to the CeO_2 modification strategy, which reduces the interaction between the NCM90 cathode material and the electrolyte, thus inhibiting the formation of harmful SEI film.

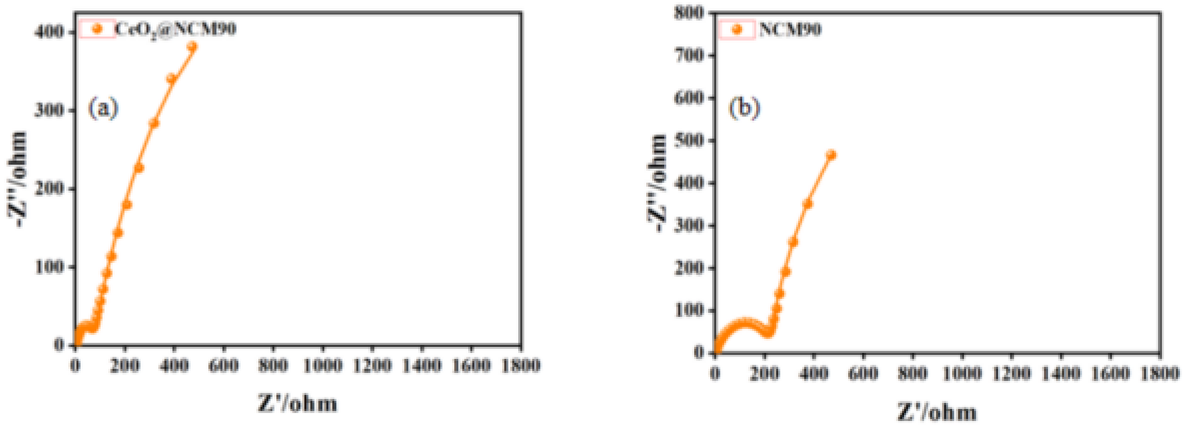


Fig. 17. (a) The EIS test of the 2%-CeO$_2$@NCM90 cathode materials; (b) The EIS test of the pristine NCM90 cathode material.

Figures 18a and 18b show the differential capacity analysis (*dQ/dV*) images of the 2%-CeO$_2$@NCM90 cathode material and the pristine NCM90 cathode material. The 2%-CeO$_2$@NCM90 cathode material exhibits four peaks during the charge and discharge process. From the lowest to the highest voltage, these peaks correspond to the transition from the hexagonal H1 phase to the monoclinic M phase, the transition from the monoclinic M phase to the hexagonal H2 phase, and the transition from the H2 phase to the H3 phase. From the image, it can be observed that 2%-CeO$_2$@NCM90 cathode material suppresses the phase transition process from hexagonal phase H1 to monoclinic phase M. The pristine NCM90 cathode material exhibits a narrow and strong peak during this transition process, indicating a severe phase transition process occurred (D. Wu et al., 2018). At a voltage of 4.18V, Both 2%-CeO$_2$@NCM90 cathode material and pristine NCM90 cathode material exhibited peaks related to redox reactions. This is the phase transition process of NCM cathode material from H2 phase to H3 phase, which is the most unstable part of the phase transition process of NCM cathode material. The phase transition process from H2 phase to H3 phase may lead to the transformation of layered structure into harmful rock salt or spinel phase, thereby releasing lattice oxygen and affecting the electrochemical performance of NCM cathode materials. The image of the 2%-CeO_2@NCM90 cathode material and the pristine NCM90 cathode material shows that 2%-CeO_2@NCM90 cathode material has narrow oxidation-reduction peak of the cathode material which indicates a faster kinetic process. In addition, The peak of 2%-CeO_2@NCM90 cathode material during the phase transition from H2 to H3 is more symmetrical than that of the pristine NCM90 cathode material, and the peak lateral distance during charge and discharge is smaller, indicating a lower degree of polarization. This is attributed to the protective effect provided by CeO_2. The more symmetrical peak of 2%-CeO_2@NCM90 cathode material also reflects that the proportion of irreversible phase transition in CeO_2 modified NCM cathode materials is lower. In the pristine NCM90 cathode material, the peak symmetry during the phase transition from H2 phase to H3 phase is bad, and more irreversible phase transition processes occur, which also proves that the modification strategy of CeO_2 on NCM90 cathode material is successful (S. S. Zhang, 2020d).

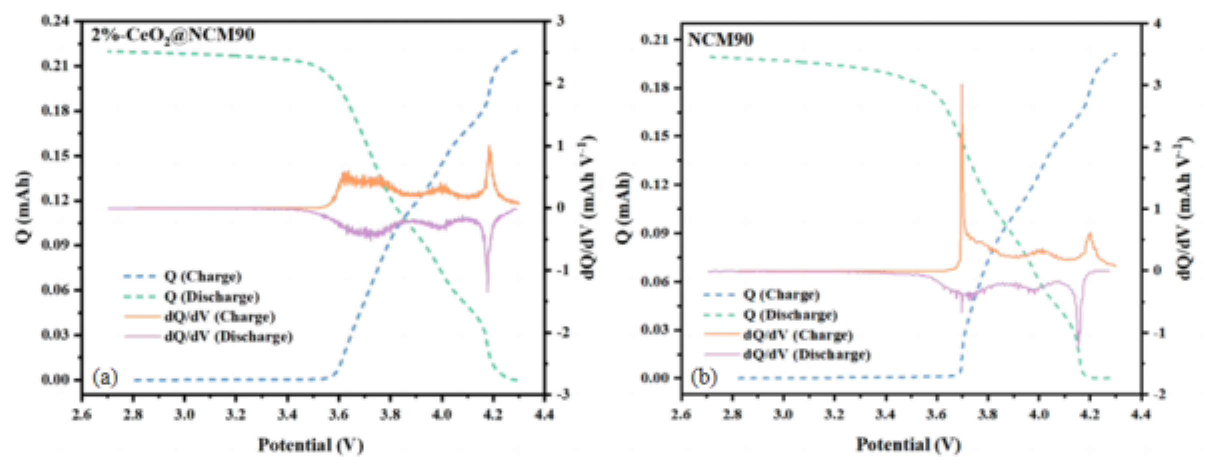


Fig. 18. (a) The *dQ/dV* image of the 2%-CeO_2@NCM90 cathode material; (b) The *dQ/dV* image of the pristine NCM90 cathode material.

3.3. The reaction mechanism of Ni-rich NCM cathodes modified by CeO_2

Figure 19 is EDS mapping pattern of 2%-CeO_2@NCM90 cathode material after 100 electrochemical cycles at 1C, between 2.7 and 4.3V. Observing the image reveals that after 100 electrochemical cycles, cerium element is enriched on the surface of the NCM90 cathode material. This indicates that there has been a surface reaction between CeO_2 and NCM90 cathode material, and it also suggests that cerium dioxide is mainly modified through coating, and the vast majority of Ce^{4+} ions have not entered the lattice of NCM90 cathode material. This is also consistent with the XPS results that many Ce^{4+} ions convert to Ce^{3+} ions and Ce^{3+} ions have larger diameter than transition metal ions and lithium ions. The enrichment of cerium element on the surface of NCM90 cathode material can enhance its electrochemical performance, as the formed CeO_2 coating can effectively inhibit the direct contact between NCM cathode material and organic electrolyte.

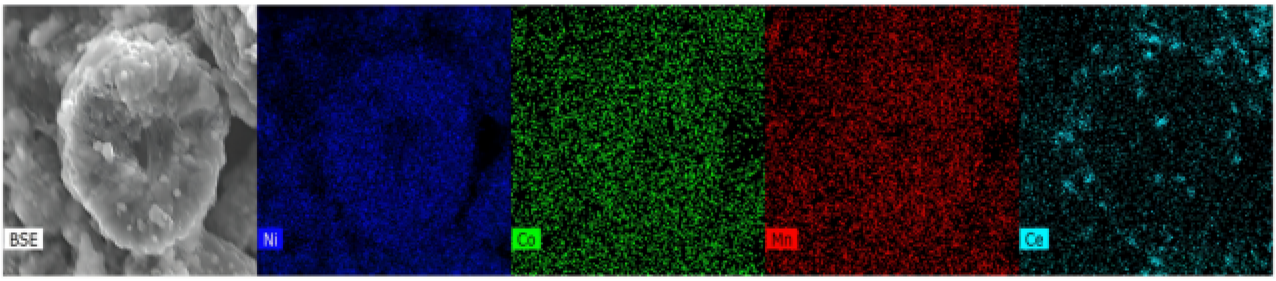


Fig. 19. EDS mapping of 2%-CeO_2@NCM90 cathode material in the cathode of lithium ions battery after 100 cycle at 1C, between 2.7 and 4.3V.

To observe the detailed structural evolution of the pristine NCM90, 1%-CeO_2@NCM90, and 2%-CeO_2@NCM90 cathode materials, in-situ XRD tests were conducted. **Figures 20, 21, and 22** shows the XRD patterns of (113), (018), (101), (110), (012), and (104) reflections between the pristine NCM90, 1%-CeO_2@NCM90, and 2%-CeO_2@NCM90 cathode materials. **Figures 20-22** show that the pristine NCM90, 1%-CeO_2@NCM90, and 2%-CeO_2@NCM90 cathode materials all undergo similar phase transitions: from H1 to M, from M to H2, and from H2 to H3. The strategy of modifying NCM90 cathode material with CeO_2 suppressed the side reactions during the H1→M→H2 phase transition process, reduced internal stress, and enhanced the crystal structure of NCM cathode material (Huang et al., 2020). (Y. Liu et al., 2019). Compared to the pristine NCM90 cathode material, 2%-CeO_2@NCM90 cathode material inhibits the irreversible phase transformation from the hexagonal H1 phase to the monoclinic M phase, and then from the monoclinic M phase to the hexagonal H2 phase. During the phase transition from H2 to H3, the *c*-axis contraction amplitude of 2%-CeO_2@NCM90 cathode material is smaller than other cathode materials, so CeO_2 coating may suppress the occurrence of irreversible phase transition from H2 to H3 and reduce the release of lattice oxygen, thereby improving the structural stability of NCM cathode materials. It can be seen that the peak of NCM cathode material modified with cerium element has a significant shift, this shift indicates an improvement in the cyclic reversibility of the modified NCM cathode material.

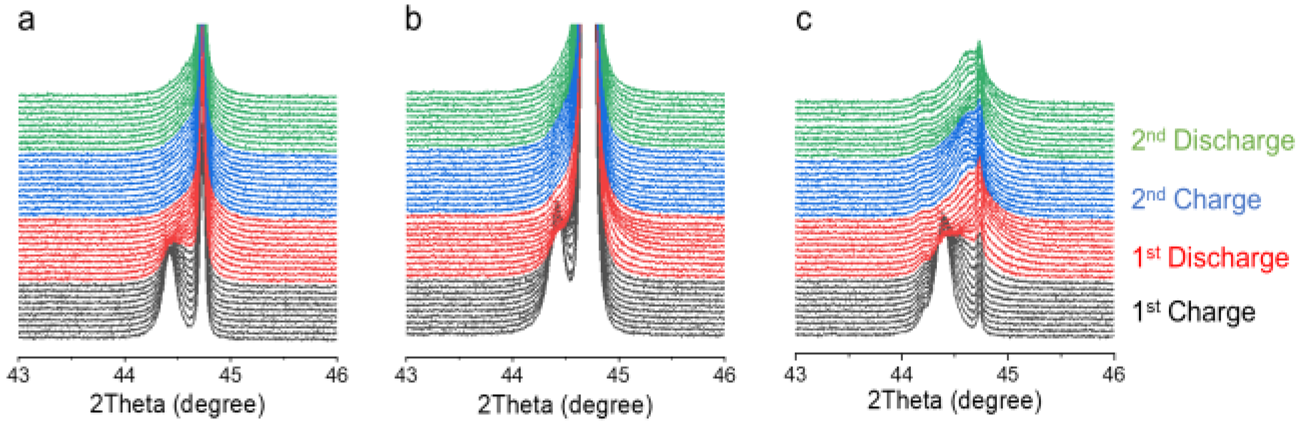


Fig. 20. In-situ XRD patterns of pristine NCM90 cathode material (a), 1%-CeO_2@NCM90 cathode material (b) and 2%-CeO_2@NCM90 cathode material (c) during the first and second charge-discharge process (between 2.7 and 4.3V) and their corresponding shifts in (104) reflection at 44.3°.

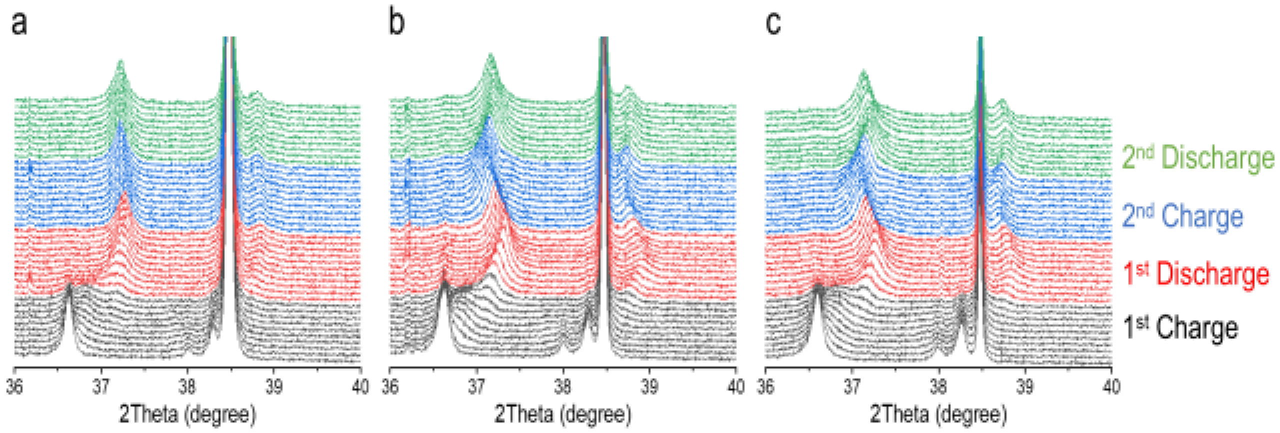


Fig. 21. In-situ XRD patterns of pristine NCM90 cathode material (a), 1%-CeO_2@NCM90 cathode material (b) and 2%-CeO_2@NCM90 cathode material (c) during the first and second charge-discharge process (between 2.7 and 4.3V) and their corresponding shifts in (101) reflections at 36.6° and (012) reflection at 38.3°.

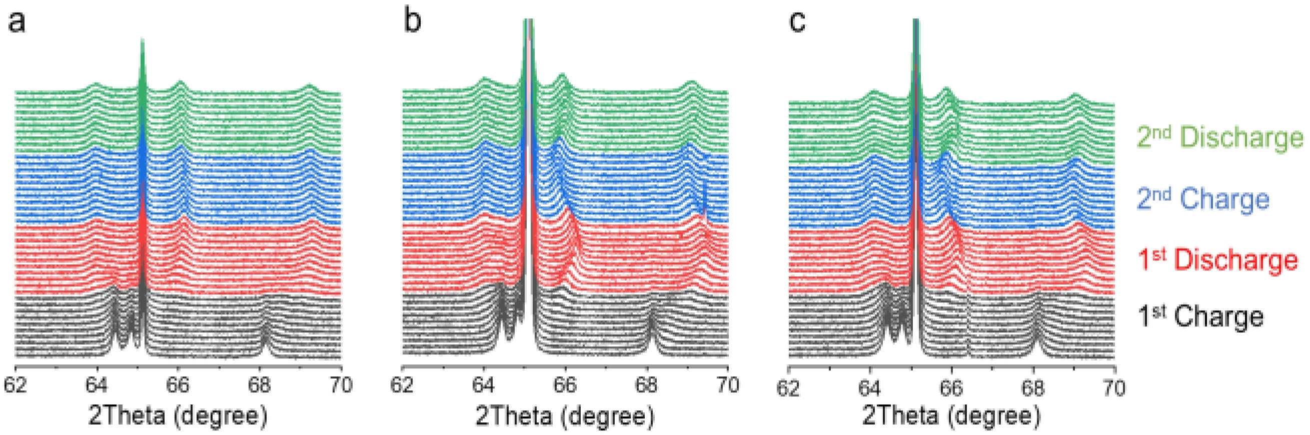


Fig. 22. In-situ XRD patterns of pristine NCM90 cathode material (a), 1%-CeO_2@NCM90 cathode material (b) and 2%-CeO_2@NCM90 cathode material (c) cathodes during the first and second charge-discharge process (between 2.7 and 4.3V) and their corresponding shifts in (018) reflections at 64.2°, (110) reflection at 64.8° and (113) reflection at 68.1°.

Chapter 4 Conclusion

In conclusion, This thesis first summarizes various modification strategies for Ni-rich NCM cathode materials, including cation doping, surface coating, control of lithium content, surface cleaning, CEI film construction, and crystal surface engineering. The above methods can enhance the structural stability and electrochemical performance of Ni-rich NCM cathode materials. Based on the modification strategy of cation doping and surface coating, this thesis used cerium hydroxide as the raw material, which was co-sintered with NCM90 precursor material at high temperature. Through solid-state reaction the thesis designed a CeO_2 oxide to modify NCM90 cathode material. Modification of Ni-rich layered NCM cathode materials with CeO_2 oxide improved their electrochemical performance and structural stability. The CeO_2 oxide-modified NCM90 cathode material demonstrated that a small portion of the cerium element entered the crystal structure, while most formed a CeO_2 surface coating. This surface coating acts as a physical barrier, improving interfacial structural stability and reducing the degradation rate of the crystal structure during electrochemical cycling. The CeO_2 coating prevents corrosion of the electrolyte and inhibits the formation of SEI film. The conversion between Ce^{4+} and Ce^{3+} ions can oxidize Ni^{2+} ions in Ni-rich layered NCM cathode materials to Ni^{3+} ions during high-voltage electrochemical cycling. Ni^{3+} ion is one of the important factors affecting the electrochemical activity of Ni-rich layered NCM cathode materials. A higher proportion of Ni^{3+} ions indicates that the modified NCM cathode material has better electrochemical performance. The results show that the 2%-CeO_2@NCM90 cathode material exhibits superior cycle and rate performance compared to pristine NCM90 cathode material. This thesis provides a new idea for using rare earth oxides to improve the electrochemical performance of Ni-rich layered NCM cathode materials under high voltage environment.

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