

Study on the interface of high specific energy High stability

Shuhan Yin

Shandong University (Weihai), Weihai, China

202100700215@mail.sdu.edu.cn

Abstract. High nickel ternary oxide, with high specific capacity and low cost advantages, is the preferred positive electrode for high specific energy lithium-ion power batteries at present. However, the high nickel ternary cathode material is easy to have side reactions with the electrolyte in the high delithium state, which can not only lead to the dissolution of transition metal ions and the formation of the surface salt phase, but also cause the lattice oxygen loss and surface interface side reactions, resulting in rapid attenuation of electrode capacity. In this paper, the development history and structural characteristics of high nickel ternary cathode materials are introduced, and the surface interface problems leading to capacity attenuation and structural degradation are comprehensively analyzed. From this perspective, three effective strategies for improving electrochemical performance of high nickel ternary cathode materials are summarized. Finally, by describing the advantages and disadvantages of these layered cathode materials, the challenges faced by these layered cathode materials are discussed, and it is pointed out that in the future, composite modification strategies should be adopted to optimize their structures and improve their properties.

Keywords: lithium-ion battery, high energy density, high nickel layer oxide, surface interface, modification strategy.

1. Introduction

In 2020, China solemnly promises to the world to achieve the "double carbon" goals of "carbon peak" and "carbon neutrality" by the middle of this century, that is, the level of carbon dioxide emissions goes from fast to slow, until the artificial source of emissions and absorption sink offset. In recent years, with the increasingly prominent energy crisis and environmental pollution problems, the development of sustainable new energy materials has become one of the most important problems. Chemical power supply (i. e., battery), as a stable device that can provide electricity, is easy to carry, and can be prepared into different shapes to meet the requirements of different devices. In the field of secondary batteries, lithium-ion batteries are widely used because of their high energy density and power density, as well as the lack of "memory effect".

As an important part of lithium-ion batteries, cathode materials can be divided into LiCoO_2 (LCO), LiMn_2O_4 (LMO), LiFePO_4 (LFP), $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM). Different cathode materials have different advantages and are applied in different fields. For example, LCO has high energy density and high working voltage; LMO has abundant raw materials, low price and good safety; LFP has low raw material price, high cycle performance, high safety performance and environmental protection. Ternary material is a polycrystalline composite oxide represented by NCM, which can set all the advantages of three materials. At the same time, ternary material becomes one of the main cathode materials of lithium ion batteries because of its high energy density. With the increase of nickel content in ternary materials, its capacity also increases. High nickel ternary materials also has many disadvantages, such as synthesis easily deviate from the measurement ratio, cycle to spinel structure transformation, etc., lead to high nickel ternary material cycle performance, safety performance and storage performance is poor, hindered the ternary materials in the field of power battery, especially the surface structure of lithium lead to unstable, high surface alkali content interface problems affect the preparation of the battery and electrical performance. To solve the above problems, this paper summarizes the oxygen vacancy structure (surface structure regulation), surface coating, and in-situ CEI construction.

2. Development process of NCM ternary cathode materials

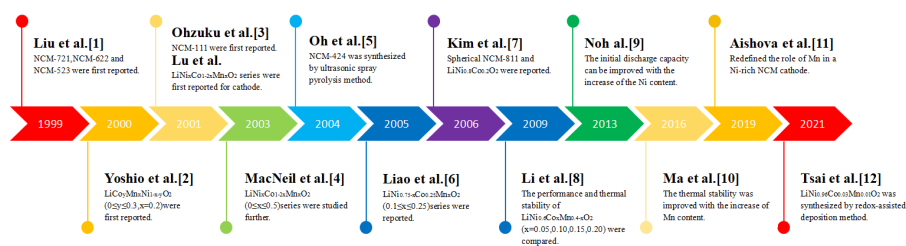


Figure 1: Structure of multi-scale supervision model

Liu et al.^[1] Nickel-rich NCM materials, such as $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ (NCM-721), $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM-622) and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM-523) as a cathode material for lithium-ion batteries, and later Yoshio et al.^[2] Report the $\text{LiCo}_y\text{Mn}_x\text{Ni}_{1-x-y}\text{O}_2$ ($0 < y < 0.3$, $x = 0.2$) for the cathode material. Studies have found that Co, in $\text{LiMn}_{0.2}\text{Ni}_{0.8}\text{O}_2$ Presence in can inhibit the mixing of some cation, $\text{LiCo}_y\text{Mn}_{0.2}\text{Ni}_{0.8-y}\text{O}_2$ The cathode material has more than 155 mAhg^{-1} The high specific capacity of the. But the NCM positive pole does not seem to receive as much attention, especially the nickel-rich NCM. Until 2001, the Ohzuku and Makimura^[3] Reported layered NCM materials with the same proportions of Ni, Co and Mn, and researchers began to gradually recognize the importance of NCM. take part in LiCoO_2 In contrast to the NCA, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM-111) with 160 mAhg^{-1} Reversible capacity and higher safety of. Open the new time of NCM cathode material, the door of generation, low nickel NCM cathode into the rapid development period of lithium ion battery. After that, LiNi was successively reported, $\text{LiNi}_{1-x}\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ series ($\text{LiNi}_{0.25}\text{Co}_{0.5}\text{Mn}_{0.25}\text{O}_2$ And $\text{LiNi}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}\text{O}_2$), $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ ($0 \leq x \leq 0.5$), $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NCM-424). These low nickel NCM, material than LiCoO_2 With a higher energy density and thermal stability, but its specific capacity is still limited ($< 200 \text{ mAhg}^{-1}$)^[4,5].

Due to the high specific capacity ($> 200 \text{ mAh g}^{-1}$), Low toxicity and low cost, high nickel NCM cathode materials have become the mainstream of research in recent years, especially in the field of electric vehicles. In 2005, Liao et al.^[6] Reported for the $\text{LiNi}_{0.75-x}\text{Co}_{0.25}\text{Mn}_x\text{O}_2$ ($0.1 < x < 0.25$) The cathode material, in which $\text{LiNi}_{0.6}\text{Co}_{0.25}\text{Mn}_{0.15}\text{O}_2$ Optimbest electrochemical performance (initial discharge capacity 167 mAh g^{-1}). The following year, Kim et al.^[7] Reported the synthesis of spherical LiNi by cop-precipitation $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM-811) and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, The discharge ratio capacity ranged from 197 to 202 mAhg^{-1} . NCM-811 exhibited more than $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Better thermal stability, due to the enhanced structural stability achieved by the addition of small amounts of Mn elements. This finding was subsequently validated by Lee et al. In 2009, Li et al.^[8] Was compared between the $\text{LiNi}_{0.6}\text{Co}_x\text{Mn}_{0.4-x}\text{O}_2$ ($x = 0.05, 0.10, 0.15, 0.2$) Electrochemical properties and thermal stability of the cathode materials. They found that the discharge capacity of these cathode materials increased with the increasing Co content, but the cycle performance and thermal stability simultaneously deteriorated with the decrease of the Mn content, where $\text{LiNi}_{0.6}\text{Co}_{0.05}\text{Mn}_{0.35}\text{O}_2$ Best thermal stability due to the high Mn content., 2013, Noh et al.^[9] It is proved that the initial discharge capacity of the NCM cathode material increases with the increasing Ni content. In 2016, Ma et al.^[10] We show that thermal stability improves with increasing Mn content, but Mn doping may lead to a decreased discharge capacity. In the past five years, researchers have been increasingly concerned with the construction of high-nickel NCM cathode materials. In today's development, with the decrease of Co and Mn, the proportion of nickel in NCM is increasing (over 90%)., 2019, Aishova et al.^[11] LiNi was synthesized and compared $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ (NCM90), $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$ (NM 90) and $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ Physical and chemical properties of (NC90). NM 90 showed good cyclic stability, showing rate performance close to NCM 90 at temperatures up to 60°C . The study may redefine the role of Mn in the positive pole of the nickel-rich NCM., 2021, Tsai et al.^[12] LiNi was prepared using a new redox-assisted deposition method $\text{LiNi}_{0.96}\text{Co}_{0.03}\text{Mn}_{0.01}\text{O}_2$ (NCM 96) cathode material. We have shown that the high crystallinity of NCM 96 positive crystallinity benefits from low cation mixing and ordered surface structure.

3. Crystal structure of the NCM ternary cathode material

Ternary material (NCM) is an integrated LiNiO_2 , LiCoO_2 and LiMnO_2 developed on the basis of the electrochemical properties, it can be regarded as a solid solution of the three. Its microstructure is similar to the LiCoO_2 of the α - NaF layered salt structure (Figure 2a)^[13]. The space group belongs to the $R\bar{3}m$, hexagonal system. In the ternary material, Li is located at the 3a position of the crystal, the transition metal M (M is Ni, Co, Mn) is disordered in the 3b position of the crystal, and O is located in the 6c position of the crystal, and is arranged in a hexagonal close packing form in ABCABC mode. Six oxygen atoms combine with one of the nickel, cobalt, and manganese elements to form the MO_6 octahedron, and then stack with each other to form the MO_2 layer, while lithium is embedded in the layered structure of oxygen and transition metal (Figure 2b)^[14].

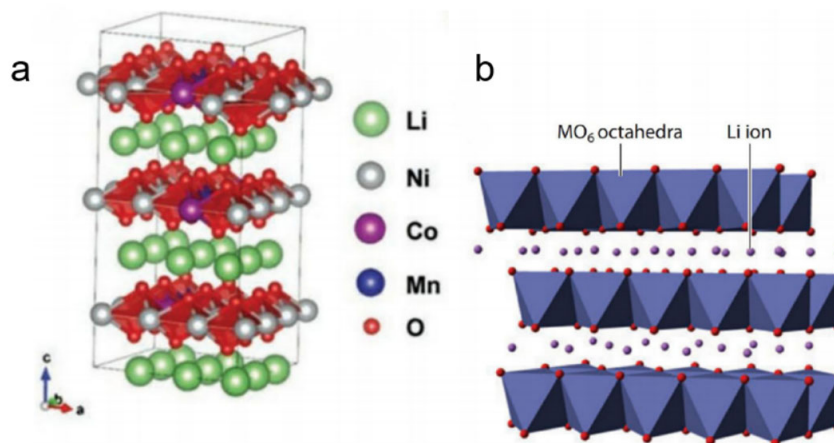


Figure 2.(a)Structure Model of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$;(b)Layered structure model of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ cathode material.

4. Advantages of NCM ternary cathode materials

Ternary NCM material is another very typical layered cathode material besides lithium cobalt oxide in the cathode material. LiCoO_2 with a single transition metal component, LiNiO_2 , LiMnO_2 . In contrast, ternary materials have the advantages of low cost, high discharge capacity, good cycle performance and good thermal stability. The fusion of the three transition metals makes ternary materials have LiCoO_2 high-rate performance, LiNiO_2 high discharge capacity, LiMnO_2 structural stability energy, and the ratio of the three transition metals is flexible and controllable, can be balanced by designing different proportions^[15], Hyung-Jo Noh et al.^[9] The properties of NCM cathode materials are studied in detail. Figure 3a shows the relationship between the main properties of the ternary materials. With the increase of Ni content, the discharge capacity of NCM cathode materials increases, but the thermal stability and capacity retention rate decrease.

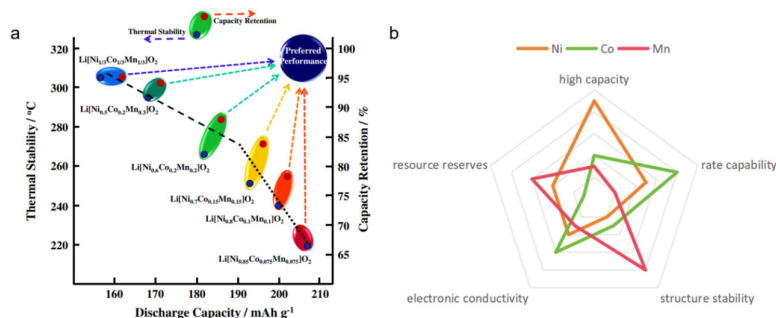


Figure 3.(a)A map of relationship between discharge capacity, and thermal stability and capacity retention of $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x=1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85). (b) The role of Ni, Co, and Mn in NCM ternary cathode materials and the elemental resources reserves respectively.

For the layered ternary NCM materials, the transition metal elements play different roles in the energy storage contribution and show better complementary effects, as shown in Figure 3b. Specifically, high concentrations of Ni ions can provide high capacity and rate capacity, thereby improving bulk energy density and mass energy density^[15]. Increasing the content of Co ions can improve the electronic conductivity of the cathode material and inhibit the cation mixing arrangement, thus improving the ratio performance and discharge ratio capacity^[16]. However, the Co element is an expensive and scarce metal, which greatly increases the cost of making lithium-ion batteries. Although inactive Mn ions do not participate in electrochemical reactions during lithification / sulfur removal, they can stabilize the layered structure by inhibiting the multistep phase transition of high-nickel cathode materials^[17]. $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$ ^[18] And $\text{LiNi}_{0.72}\text{Co}_{0.1}\text{Mn}_{0.18}\text{O}_2$ ^[19] The layered ternary materials have high cyclic performance and high capacity retention with increasing stable Mn elements.

5. Interface problems existing in the high-nickel NCM ternary cathode materials

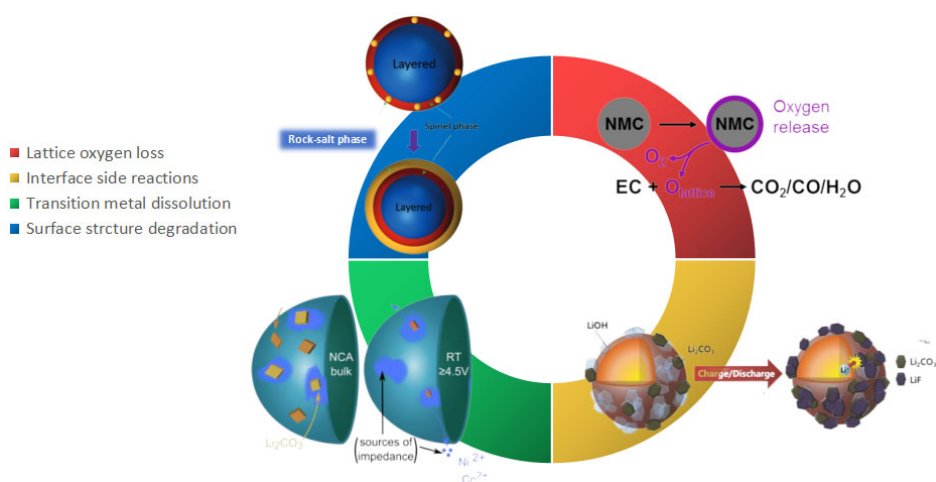


Figure 4. Interface problems of high nickel ternary materials.

5.1 Surface structure degradation

In the high lithium degradation state, the overlapping band of Ni, Co and O will trigger the redox activity of lattice oxygen to generate reactive oxygen or direct surface oxygen loss. Oxyloss is accompanied by the migration of transition metals and the reconstruction of the surface structure. As shown in Figure 6^[21], The migration of nickel along the diffusion direction of lithium ions is the main reason of its structural transition. Due to the low diffusion barrier, Ni ions can migrate easily in the lattice and dissolve in the electrolyte, resulting in a capacity decrease of the cycling sample and a Ni concentration gradient. Therefore, nickel ions continuously transfer from the whole to the surface in the form of irreversible reduction (Figure 5a), resulting in atomic rearrangement to form the SRL (surface reconstruction layer), including disordered layered zone, defective rock salt zone and rock salt zone. As Ni ions migrate throughout the cycle, the SRL extends from the surface to the whole (Figure 5b), and the performance continues to decay due to the poor electrochemical activity of the rock salt phase.

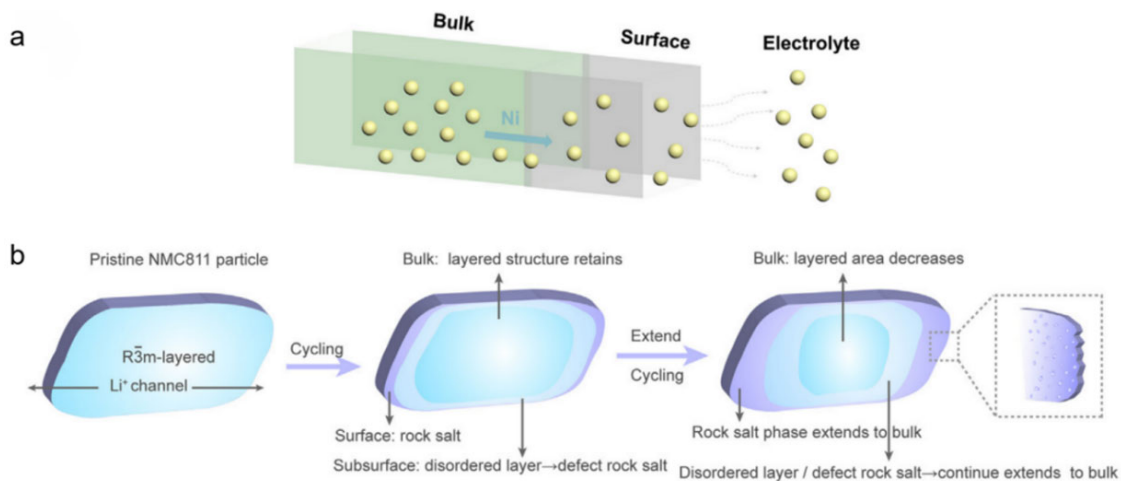


Figure 5. Schematic illustrations of (a) the Ni ions migration process and (b) the structural evolution from surface to bulk during the battery cycling. The enlarged schematic image shows the detailed surface morphology.

5.2 Interface side reaction

The side reaction at the electrode surface interface usually refers to the reaction of the surface active residual lithium of the ternary material with water or carbon dioxide in the air, and the reaction of the electrode surface active ternary NCM with the electrolyte, as shown in Figure 6. Excessive lithium salt reactants are required for the synthesis of layered and ordered high nickel ternary NCM, and the high nickel ternary NCM particles will have active lithium (such as Li_2O and Li_2O_2). The reactive lithium side reacts with water and carbon dioxide in the air to form LiOH and Li_2CO_3 . Lithium compounds (LiOH and Li_2CO_3) The composed insulation layer will cause irreversible loss of capacity in the first week, and will hinder Li in the charging and discharging process. The spread of. The high nickel ternary NCM particle surface (or surface crack) has direct contact with the electrolyte, and the highly reactive Ni is found at the interface. It can promote the decomposition of the electrolyte to generate a series of organic / inorganic miscellaneous phases (such as LiF , Li_2O , Li_2CO_3 , ROCO_2Li class). Due to the nucleophilic and chemical properties of these miscellaneous phases, the complex are attached to the surface of high nickel ternary NCM particles, forming an insulating solid electrolyte interface membrane (SEI membrane), which hinders the diffusion of lithium ions and reduces the electrochemical properties of the electrode.

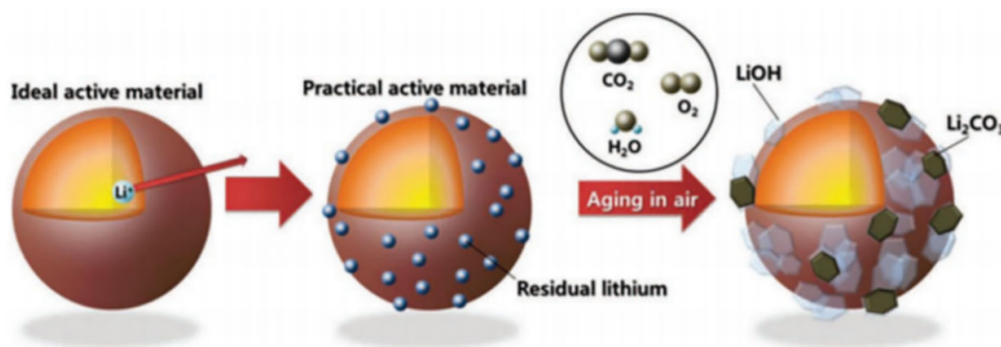


Figure 6. Schematic representation of surface change of $\text{Li}[\text{Ni}_{0.7}\text{Mn}_{0.3}]\text{O}_2$ materials after exposure in air.[22]

5.3 Transition metal dissolution

The dissolution of transition metals is also one of the interfacial problems faced by high-nickel layered ternary cathode materials. In the actual production process, there will inevitably be traces of water in the electrode material, electrolyte, diaphragm and battery structure, which will be combined with the lithium ion carrier LiPF_6 in the electrolyte. Of the decomposition product of PF_5 Reactions to

generate the HF. The emergence of HF in the battery has great harm to the system. On the one hand, HF will interact with the transition metal oxide M_xO_y ($M = Ni, Co, Mn$) reacts to provide a fluoride ion to leach the transition metal ion into the electrolyte and deposit it to the negative electrode^[23-24]. On the other hand, the reaction of HF with the transition metal oxides would produce water, which would be associated with PF_5 . The reaction produces more HF, forming a vicious cycle, according to the principle of chemical reaction balance, will cause the lithium ion carrier $LiPF_6$. The battery performance will gradually deteriorate. The dissolution of transition metal ions causes the local collapse of the crystal structure of ternary materials, which is not conducive to the unembedding of lithium ions. Meanwhile, the reduction of transition metal ions with redox activity directly leads to the reduction of material capacity. Although the HF in the electrolyte is initially small, the above reactions accelerate as the upper cutoff potential increases, so the operating voltage is an important factor in determining the dissolution rate of metal ions. Surface degradation in the high charge state dissolves transition metals and significantly increases the cathode impedance, resulting in a rapid decrease in electrochemical properties (Figure 7)^[25]. Moreover, the dissolved metal elements can be reached to the anode through the electrolyte and deposited on the graphite surface, causing a sharp rise in the anode impedance. Rising impedance is one of the important reasons for battery cycle failure at high charging voltage.

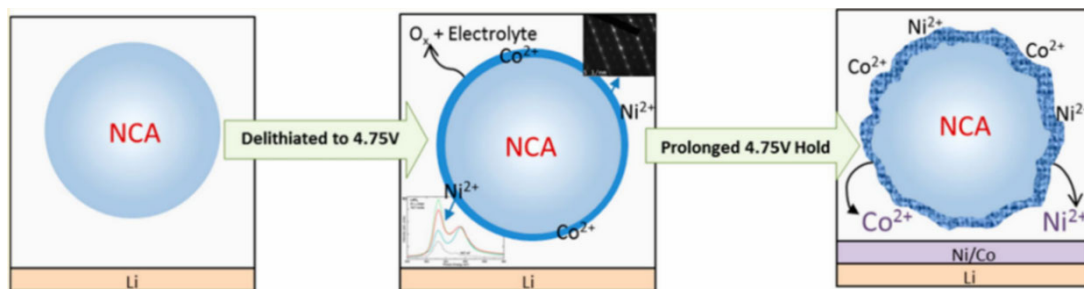


Figure 7. NCA surface degradation at a high voltage of 4.75V.

5.4 Lattice deoxygenation

The safety hazard caused by the lattice oxygen loss of high nickel ternary materials is an urgent problem to be solved. With the removal of lithium ions from the ternary material during charging, Ni^{2+}/Ni^{3+} -electron oxidation occurs to form Ni^{4+} . Ni^{4+} The high price state leads to Ni^{4+} -O bonded electrons are withdrawn, in O_{2p} hole states are formed in the orbit, causing bond disintegration. And the NiO caused by the preferential oxidation of Co and Mn during the synthesis of ternary materials. The distortion of the octahedral unit enhances the movement ability of O in the octahedral unit, and the detachment of lithium ions during the charging process breaks Li-O, which leads to the strong mobility of the reactive oxygen anion on the surface of the high nickel ternary material. Li et al. showed by neutron diffraction and mass spectrometry analysis linked with temperature that with the release of lithium ions, the oxygen species in the ternary material is removed from the lattice oxygen (O^{2-}). Gradually evolved into the chemisorbed oxygen ($2O^-$, O_2^{2-} , O^{2-}), Physical adsorption of oxygen (O_2). And the oxygen, (O_2) (graph 8)^[28]. When the amount of lithium removal is less than 50%, the oxygen species inside the ternary material are mainly lattice oxygen and chemical adsorbed oxygen, chemical adsorbed oxygen exists in the form of negative ions, the charge is lower than lattice oxygen, more active than lattice oxygen and not easy to leave the lattice position. With the continuous increase of lithium removal, in order to balance the charge, part of the chemical adsorption oxygen continues to lose electrons, forming oxygen molecules to leave the lattice position, and fixed on the surface of the ternary material through physical adsorption to form physical adsorption oxygen. Due to the weak van der Waals force, physical adsorption oxygen is easily released from the material surface^[26]. Li was explored by in-situ temperature-resolved X-ray diffraction by Bak et al. $Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ In the gas production and phase transition of the cathode material in different charge states, as the lithium ion emerges from the crystal structure of the ternary

material, the oxygen release temperature gradually decreases, and the highly active oxygen released reacts with conductive carbon black, binder, and dimethyl carbonate (DMC) and vinyl carbonate (EC) in the electrolyte to produce additional CO₂^[27]. The gas produced will cause the battery to swell, bulge and even explode.

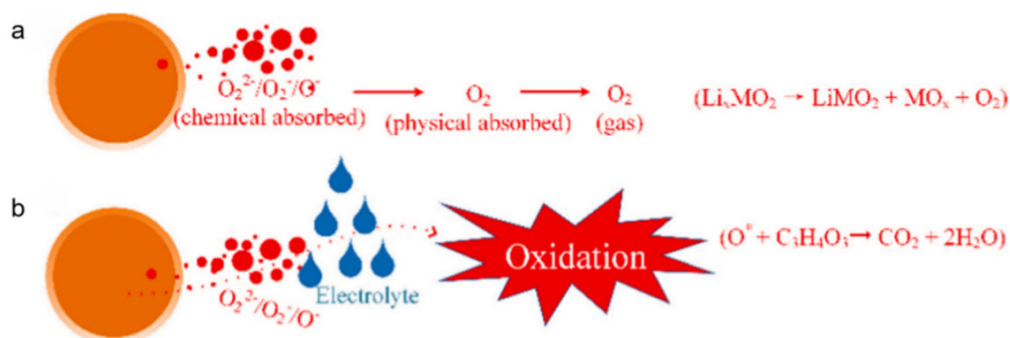


Figure 8. Gas generation process of NCM materials ((a) shows the process of oxygen species in ternary materials changing into oxygen, and (b) shows the process of oxygen species in ternary materials reacting with electrolyte to generate carbon dioxide).

6. Solution

6.1 Surface structure to regulate the construction of — oxygen vacancies (OVs)

OVs are closely related to the electronic and ion transport properties of lithium-ion cathode materials. The introduction of OVs is an effective strategy to improve the electrochemical properties of cathode materials in lithium-ion batteries. OVs can improve the capacity and rate performance, accelerate lithium-ion transport, prevent unnecessary phase transitions, and reduce the energy barrier for the diffusion of transition metal cations. However, stabilizing OVs remains a partially resolved challenge, especially in oxidative (oxygen-rich) conditions, where OVs are very active and difficult to enforce or maintain. Limited stabilization strategies are currently available, including a hypoxic atmosphere, heteroatomic doping, interface engineering, and specific crystal planes.

Chemically-assisted heat treatment is often used to generate OVs in layered NCM cathode materials. For example, with the HNO₃^[29], octadecanoic acid^[30,31], CaH₂/LiH^[32], NaBH₄^[33] and carbon black (Super P)^[34] and Na₂S₂O₈^[35] heat the Li [Ni, Co, Mn] O₂. The cathode material can get the hypoxia cathode material. Cheng et al. found that, through OV / Mg²⁺ charge compensation mechanism, LiCoO₂OVs can be formed during Mg doping, keeping the system in an overall electroneutral state^[36]. Qiu et al. successfully produced OVs on the particle surface through the gas-solid interface reaction of lithium-rich layered oxide and carbon dioxide^[37]. The gas-solid interface reaction can achieve precise control of oxygen activity by uniform generation of OVs without affecting the structural integrity of lithium-rich layered cathode materials. Chen et al. reported that under the interaction of plasma bombardment and mechanical milling, the OVs in LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂-SnO₂ effective distribution of the cathode material surface^[38].

Liu, prepared surface Se-doped NCM cathode material (Se-NCM) by chemical vapor deposition (Figure 9a)^[39]. Rich in the surface oxygen defect LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (OD-NCM) cathode material is a mechanism at the interface between Se and NCM (i. e., the reaction of Se with NCM surface oxygen to form SeO₂, Volatized from the NCM surface above 400°C) as obtained by the deoxygenation process. During the lithium storage of NCM by cyclic voltammetry (CV) at 3.0-4.5 V scan rate of 0.1 mV s⁻¹, the initial two cycles of OD-NCM were less different from the NCM compared to the original NCM (Figure 9b), only the position of the first oxidation peak moved to the low potential and the peak intensity was unchanged (Figure 9c), indicating better electrochemical reversibility of OD-NCM. By comparing the initial CV curves of the original NCM and OD-NCM, Figure 9d shows that the difference in the redox potential increased significantly (3.5 to 3.9 V from 61 mV to 102 mV, and 4.0 to 4.3 V from 56 mV to 137 mV), which was related to the increase of OD-NCM polarization. It is

noteworthy that for the original NCM, the first oxidation peak is divided into two peaks at the low voltage (3.5-3.9 V) (Figure 9e). This indicates that the NCM underwent a severe phase transition, leading to the occurrence of a heterogeneous phase transition. Although the polarization of OD-NCM is increased, the occurrence of the heterogeneous phase transition is inhibited. It still has good reversibility in the subsequent cycles 2 and 3, corresponding to a high degree of CV curve overlap, which also verifies the good stability of the reconstructed layer. The oxygen-rich surface interface is electrochemically reconstructed to form a stable and dense spinel-like interface; This interface significantly enhances the stability of the cathode material and suppresses the formation of the inactive NiO salt phase.

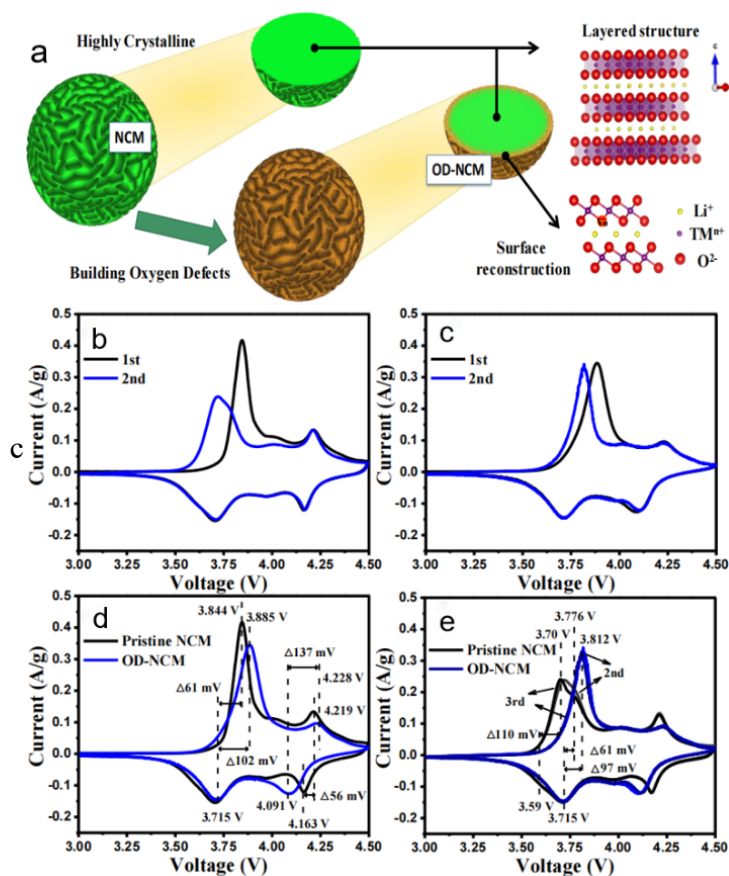


Figure 9.(a) Diagrams of the pristine $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (Pristine NCM) and the oxygen-defects $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (OD-NCM). CV curves of (b) Pristine NCM and (c) OD-NCM at a sweep rate of 0.1 mV s^{-1} during the 1st and 2nd cycle. Comparison of CV curves between Pristine NCM and OD-NCM for (d) initial cycle and (e) the next two cycles.

6.2 Surface modification

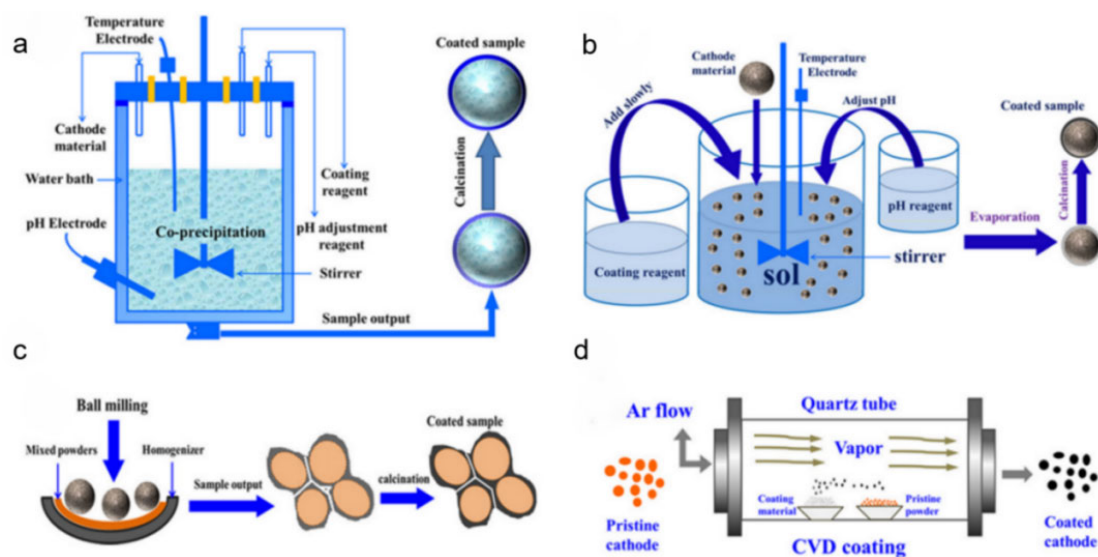


Figure 10. Schematic diagram for the coating process of (a) Co-precipitation, (b) Sol-gel, (c) Dry coating and (d) Chemical vapor deposition (CVD)^[40].

6.2.1 Inert coating layer

Electrochemically inert substances, such as oxides (Al_2O_3 ^[41], TiO_2 ^[42], ZrO_2 ^[43], SiO_2 ^[44], Nd_2O_3 ^[45] Etc.), metal fluoride (LiF ^[46], AlF_3 ^[47] Etc.) and the metal phosphate ($\text{Mn}_3(\text{PO}_4)_2$ ^[48], AlPO_4 ^[49] etc.), has high electrochemical stability and thermal stability, as a modified layer can isolate the direct contact between the material and the electrolyte, inhibit the occurrence of side reactions, so as to improve the cycle stability of the material, and can also improve the thermal stability of high nickel layered oxide cathode material to a certain extent. As described in Liang et al^[44] A layer of 10 – 30 nm SiO_2 was modified on the NCM811 surface using the carbonate neutralization method₂, Increasing the capacity retention rate of NCM811 from 69.8.8% to 8% after 300 weeks (Figure 11a), the modified NCM811 cycle after 100 weeks is 93.5%, while the capacity retention rate of unmodified NCM811 is only 79.1% (Figure 11b). This comparison shows that SiO_2 The modified layer can significantly improve the cycle stability and thermal stability of the high nickel layered oxide cathode.

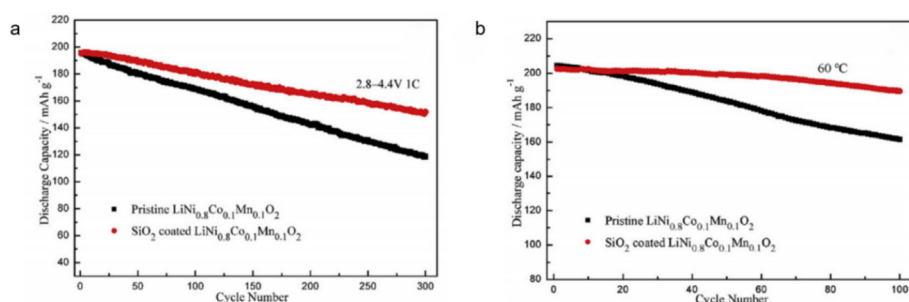


Figure 11. The Cycle performance (a) at 1 C rate between 2.8 and 4.4 V; The Cycle performance (b) at 60°C, 1 C rate between 2.8 and 4.3 V of pristine and SiO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ sample^[44].

6.2.2 Ion-conductor coating layer

Lithium-ion conductor, due to the ability to provide a three-dimensional Li^+ transmission channel, while acting as a physical isolation layer, can also effectively improve the ratio performance of the material, and thus it is considered as an ideal modification material for the high nickel layered oxide cathode. Gan et al^[50] exploitation $(\text{NH}_4)_3\text{PO}_4$ Reacting with residual lithium compounds on the material surface, a layer of Li was modified on the NCM811 surface by the solvent-free method₃ PO_4 , And using HRTEM, analytically investigated the detailed structural properties of NCM811 and NCM811 @ LPO. Compared to NCM811 (Figure 12a), NCM811 @ LPO particles (Figure 12c) have

a distinct heterostructure, consisting of a highly ordered core and amorphous coating with a uniform thickness of 4 to 5 nm. As shown in Figure Figure 12a-d, (003) the internal isometric stripe of the crystal plane is clear, and the inter-plane distance is 0.472 nm, proving that NCM811 can maintain the layered structure after coating LPO. The capacity retention of the modified NCM811 increased by 25.3% after 200 weeks of cycling and remained at 160 mAhg at the 5C multiplier⁻¹The discharge ratio capacity of. Non-situ soft X-ray absorption spectroscopy (SXAS) and in situ Raman (Raman) tests show that Li₃PO₄The (LPO) modified layer can effectively inhibit the irreversible phase transition and the release of oxygen on the material surface, which is why the stability of the material cycle is improved. Besides this, the LiFePO₄^[51], LiAlO₂^[52], Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃^[53], LiAlF₄^[54], Li₂ZrO₃^[55]Lithium ion conductor has also been used as the modification layer of high nickel layered oxide cathode material, and has played a certain effect on improving the electrochemical properties of the material.

6.2.3 Electronic conductor coating layer

Conductive polymers with the advantages of high electronic conductivity, good environmental stability and low cost are also often used as the surface modification layer of the positive electrode of high nickel layered oxide. Lu et al^[56]Using the bonding effect between the surfactant polyvinyl pyrrolidone (PVP) and polyaniline (PANI), a uniform PANI-PVP modification layer was formed on the NCM811 surface (Figure 13).

The XRD spectra of NCM811, NCM811 @ PANI and NCM811 @ PANIPVP cathode materials and their Rietveld refinement are shown in Figure 14. The XRD profile in Figure 14a shows that the well-developed layered NCM811 structure corresponds to the well-developed diamond R-3m structure (α -NaFeO₂ structure). The Rietveld refined lattice parameters and unit cell volume of the three sample XRD maps (Figure 14b-d) are shown in Table 1. As shown in the figure, there are only minor differences in the lattice parameters of the three positive poles, indicating that the structure of NCM811 is well maintained after surface modification. Furthermore, no additional diffraction from the PANI polymer was observed in the XRD plots of the NCM811 @ PANI and NCM811 @ PANI VP samples due to the amorphous and / or low content of the PANI coating. This phenomenon shows that the surface modification of PVP and PANI on NCM811 cathode material did not change its structure and crystallinity. The results show that the modified layer can effectively inhibit the side reaction between electrode material and electrolyte and the production of secondary particle micro cracks, and improve the kinetic characteristics of CEI, thus improving the cycle stability and multiplier performance of NCM811.

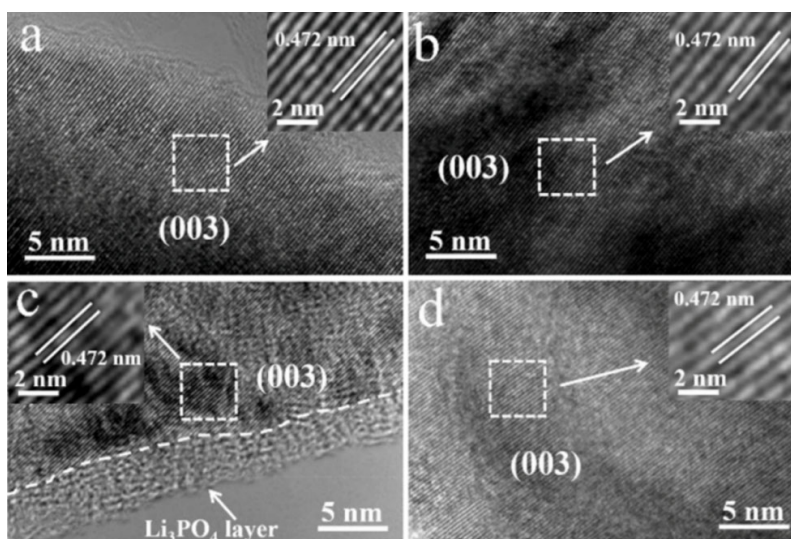


Figure 12. HRTEM images showing the surface of (a) pristine NCM811 and (c) NCM811@LPO. HRTEM images showing the bulk part of (b) pristine NCM811 and (d) NCM811@LPO.

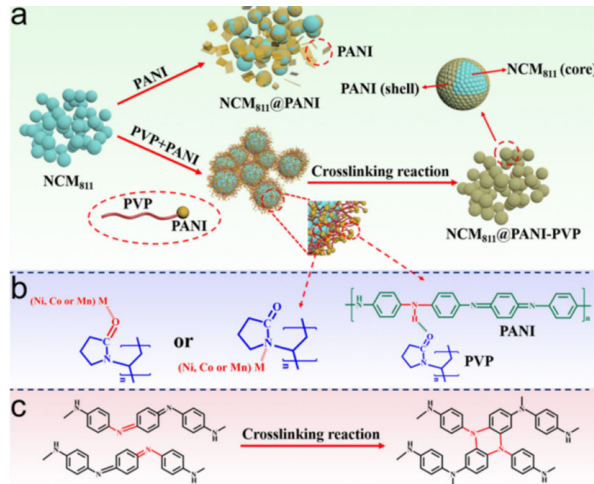


Figure 13.(a) Schematic illustration of the preparation of NCM811@PANI-PVP, (b) possible reaction among NCM811,PVP,and PANI, and(c)cross-linking reaction for PANI polymers.

Table 1.Lattice Parameters of the NCM811,NCM811@PAN and NCM811@PAN-PVP Cathodes.

materials	a-axis[Å]	b-axis[Å]	c-axis[Å]	V[Å ³]	Ni _L (%)
NCM811	2.87212	2.87212	14.19477	101.41	2.6
NCM811@PANI	2.87312	2.87312	14.19964	101.51	2.4
NCM811@PANI-PVP	2.87087	2.87087	14.18555	101.25	2.3

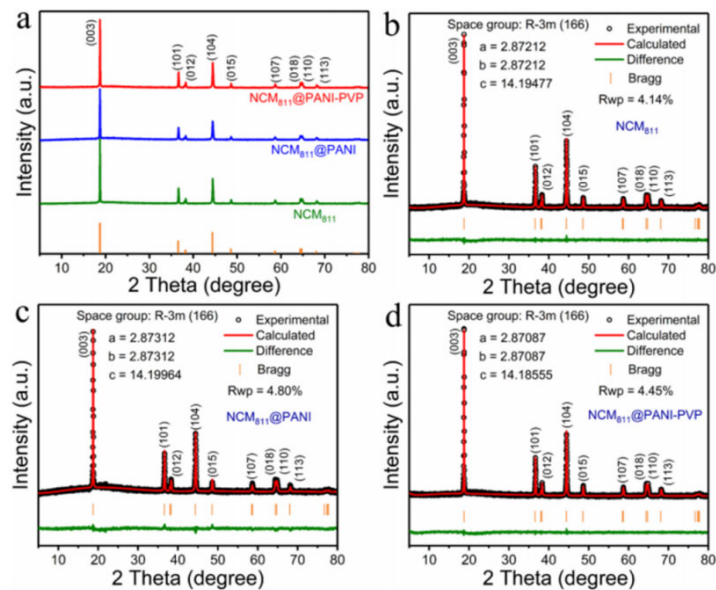


Figure 14.(a) XRD patterns of the NCM811 cathodes with and without coating. Rietveld refinements of the XRD patters of(b)NCM811, (c)NCM811@PANI, and (d)NCM811@PANI-PVP.

Xu et al^[57]Using oxidation chemical vapor deposition (o CVD), in high nickel layered oxide cathode material $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$ A poly (3,4-ethylene dioxythiophene) (PEDOT) modified layer was formed on the surface of the secondary particles and between the primary particles. This modified layer can be coordinated with HF, thus inhibiting the erosion of the electrode material by HF, reducing the dissolution of the transition metal, and improving the cyclic stability of the material. 37% by 100 weeks compared to the unmodified material.

6.3 In-situ CEI construction

The problem of the high nickel layered oxide cathode mainly appears on the material surface in contact with the electrolyte, therefore, improving the stability of CEI is the key to improve the electrochemical properties and thermal stability of the material. Because the electrolyte plays an important role in the formation of CEI, the electrolyte composition can also be optimized to improve the stability of CEI.

Pham et al^[58] Use propylene carbonate (PC) and linear fluorocarbon by replacing vinyl carbonate (EC) and methyl ethyl carbonate (EMC) as the electrolyte solvent for the NCM811 battery. The electrolyte, unable to burn, and can effectively inhibit the growth of interfacial impedance, improve the electrochemical stability, making the NCM811 battery at 2.7-4.5 V (vs.Li/Li⁺) 95% capacity retention after 100 weeks.

Compared with solvent optimization, optimizing the composition of CEI by adding small amounts of additives to the conventional carbonate electrolyte is considered as a more efficient method. In order to improve the stability and electrochemical properties of lithium metal anode and high voltage cathode, various electrolyte additives were developed, such as ethylene fluorocarbon, ethylene carbonate, subethylene, borate, sulfonate, phosphate, etc. As in the Beltrop^[59] et al found that in the carbonate electrolyte 1 M LiPF₆/EC/EMC (3:7, vol.) With 0.5 wt% triphenyloxyphosine (TPPO), NCM811 surface alkyl carbonate) and LiPO_xF_y And both components contribute to the stability of CEI. Moreover, TPPO also participates in the formation of the anode-electrolyte interface (AEI). The electrochemical test results showed that the cycle life of the graphite / NCM811 whole cell was increased by 77% when the health of the additive reached 80%.

Numerous studies have shown that in fluorine electrolyte solutions (including F salt, solvent and additives), the lithium metal anode surface can form LiF, phase, and the LiF-rich SEI membrane can achieve uniform lithium ion flux and inhibit the growth of lithium dendrites (Figure 15)^[60-63]. Similarly, the introduction of preferential oxidation molecules can form a stable CEI membrane on the positive electrode surface.

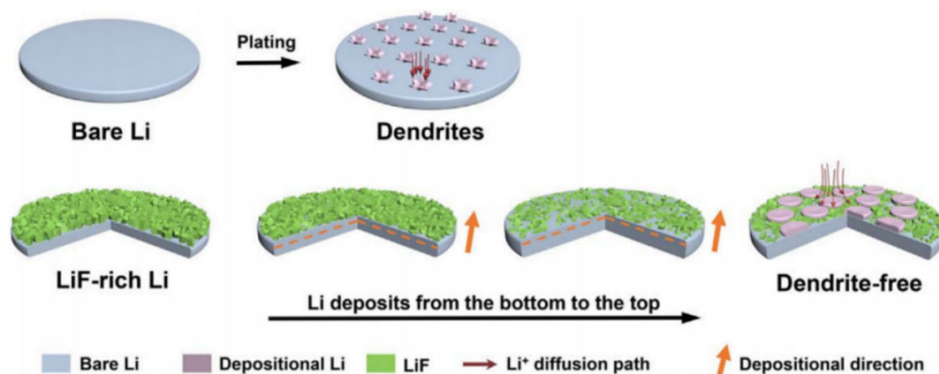


Figure 15. The inferred electrodeposition mechanism: Lithium diffusion near the surface of electrodes represented by kermesinus arrows. LiF host is shown in green. Due to lower diffusion barrier on LiF, wafer-like Li deposition is expected, while in usual SEI, needle-like Li plating is formed.

Recently, silicon-based additives have received much attention as functional additives of high pressure positive electrode. Choi et al^[64] 3-(trimethylsilyl)-2-oxazolidinone (TMS-ON) was proposed as an electrolyte additive to improve graphite / LiNi_{0.7}Co_{0.15}Mn_{0.15}O₂ Battery, the base of TMS-ON promotes LiPF₆ through coordination with lithium ions. Of the dissociation, stabilizing the PF₅, Clear the HF (Figure 16b). The results show that the phase transition of the NCM positive pole occurs from the surface to the bulk. After 400 cycles at 45°C, the NCM positive electrode cycling with the baseline electrolyte has a mixed phase of the rock salt combined with the layered structure (Figure 16c). The FFT diagram shows that the surface of point A is rock salt phase, B is mixed phase, and C is the original layered structure, and the phase transition thickness is about 24.6 nm. In the electrolyte containing 0.5 wt% TMS-ON, the phase transition thickness of the NCM positive

electrode was significantly reduced to 7.5 nm. The FFT diagram confirmed that point D is rock salt phase, point E is mixed phase, and point F is layered structure (Figure 16d). It is clear that the stable ON-derived SEI at the NCM positive pole, inhibiting the NCM active surface to electrolyte exposure, effectively slows down the highly active Ni^{4+} in the reduction to a lower oxidation state ($\text{Ni}^{3+}, \text{Ni}^{2+}$) the process of. Size with Li^+ -like Ni^{2+} The mixing arrangement of Li / Ni cation is easily aggravated in the NCM positive electrode. Scanning transmission electron microscopy (STEM) provides further evidence for the formation of the rock-salt phase at the atomic scale. Because the transition metal replaces the Li in the lithium plate⁺, The eline electrolyte caused the formation of a thick rock salt phase ($> 11 \text{ nm}$) at the NCM cathode, while electrolytes containing 0.5 wt% TMS-ON resulted in a relatively thin rock salt phase (4 nm) (Figure 16e, f).

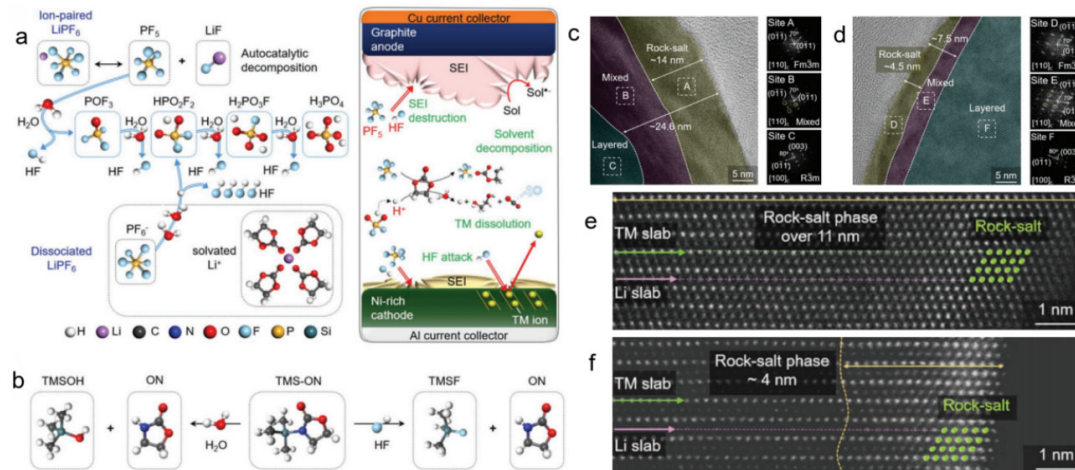


figure 16.(a) Schematic illustration of the hydrolysis of LiPF_6 , to generate acidic compounds in the electrolyte and reactive species (HF and PF_5)-derived problems in batteries.(b) HF and H_2O scavenging mechanisms of TMS-ON.Microstructure and nanostructure of the NCM cathodes retrieved from NCM/graphite full cells after 400 cycles at 45°C (charge and discharge rates:0.5 C).TEM and FFT images of NCM cathodes cycled with the (c) baseline electrolyte and (d)0.5 w% TMS-ON electrolyte. Magnified STEM images of the surfaces of NCM cathodes cycled with the (e) baseline electrolyte and (f) 0.5 wt%TMS-ON electrolyte.

In addition, Li et al^[65]Dual (trimethylsilyl) -carbon diimine (BTMSC) electrolyte additive on high voltage $\text{Li}_{1.2}\text{Mn}_{0.55}\text{Ni}_{0.15}\text{Co}_{0.1}\text{O}_2$ Stability of the positive electrode, it is found that BTMSC can form a stable and uniform silica nitrogen-containing CEI layer on the positive electrode surface. Yu et al^[66]A synergistic "anchoring and pouring" strategy is proposed with the use of 1,3,6-hexane triitriole and three (TMS) phosphate electrolyte additives to construct the CEI layer to stabilize $\text{Li}_{1.13}\text{Mn}_{0.517}\text{Ni}_{0.256}\text{Co}_{0.097}\text{O}_2$ positive pole.

7. Outlook

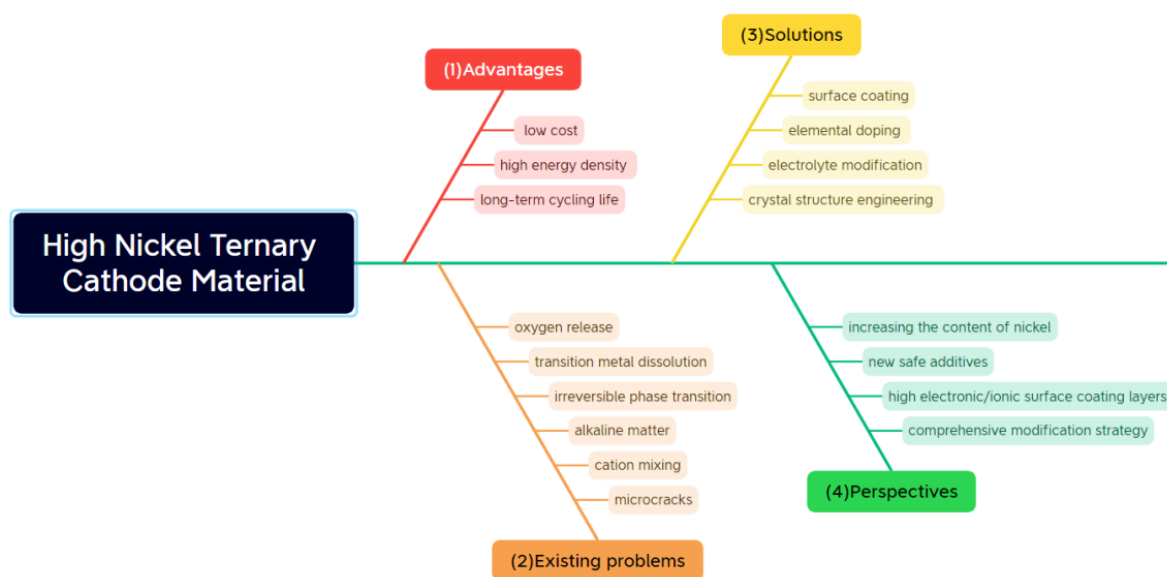


Figure 17. Modification strategies and development goals of high nickel ternary cathode materials in the future.

High-nickel ternary layered oxide is the most potential cathode material for lithium-ion batteries because of its high energy density, low cost and long cycle life. However, the further optimization of these cathode materials still faces some important unsolved problems, such as cation mixing, intercrystalline microcracks, and surface interface problems such as residual lithium compounds and irreversible phase transition.

In order to solve the above problems, various strategies such as surface coating (coating), constructing in situ CEI and oxygen vacancy have been adopted to improve the performance of high nickel layered cathode materials. Among them, adopting the surface coating strategy can effectively inhibit the corrosion of HF and slow the dissolution of transition metals. But in the charge and discharge process, the protective layer will be gradually destroyed. In addition, although the use of additives to optimize the composition of the electrolyte helps to form a high-quality CEI membrane, but the additive boiling point and flash point are low, there are safety risks. In addition, the engineering crystal structure and morphology of high-nickel cathode materials can only reduce the production of microcracks to a certain extent and inhibit the decomposition of electrolyte solvent.

In conclusion, a single modification strategy for high-nickel layered cathode materials is still difficult to meet the requirements of long-cycle stability and battery safety. Therefore, comprehensive modification strategies become hot spots nowadays, such as combining surface coatings with elemental doping strategies, or elemental doping with electrolyte modification strategies. For example, PPy PAA can be used for coating materials, and doping materials can be used for $\text{Rb}^+\text{Ca}^{2+}\text{Mn}^{2+}\text{Al}^{3+}$ class. Different doping elements are selected according to the different doping sites. This can not only prevent micro-cracks, transition metal dissolution, irreversible phase transition, but also prevent cation mixing row. To improve the electrochemical properties and safety of high nickel electrode materials, developing high electron ion surface coatings and new safety additives are needed. In addition, a further increase in the nickel content ($> 90\%$) or the introduction of cheaper elements can optimize the high-nickel material system in the manufacturing process. Therefore, high nickel-layered cathode materials can achieve future goals of high energy density, long-term stability, good safety and low cost.

References

- [1] Liu Z., Yu A., Lee J.Y. Synthesis and Characterization of $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ as the Cathode Materials of Secondary Lithium Batteries [J]. Journal of Power Sources, 1999, 81-82: 416-419.

- [2] Yoshio M.,Noguchi H.,Itoh J.-i.,et al.Preparation and Properties of $\text{LiCo}_y\text{Mn}_x\text{Ni}_{1-x-y}\text{O}_2$ as a Cathode for Lithium Ion Batteries [J].*Journal of Power Sources*,2000,90(2):176-181.
- [3] Ohzuku T., Makimura Y.Layered Lithium Insertion Material of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for Lithium-ion Batteries [J].*Chemistry Letters*,2001,30(7):642-643.
- [4] MacNail D.D.,Lu Z.,Dahn J.R.Structure and Electrochemistry of $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2(0 \leq x \leq 1/2)$ [J].*Journal of the Electrochemical Society*,2002,149(10):A1332
- [5] Oh S.W.,Park S.H.,Park C.-W.,et al.Structural and Electrochemical Properties of Layered $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]_{1-x}\text{Co}_x\text{O}_2$ Positive Materials Synthesized by Ultrasonic Spray Pyrolysis Method [J].*Solid State Ionics*,2004,171(3):167-172.
- [6] Liao P.Y.,Duh J.G.,Sheen S.R.Effect of Mn Content on the Microstructure and Electrochemical Performance of $\text{LiNi}_{0.75-x}\text{Co}_{0.25}\text{Mn}_x\text{O}_2$ Cathode Materials[J]. *Journal of The Electrochemical Society*,2005,152(9):A1695.
- [7] Kim M.-H.,Shin H.-S.,Shin D.,et al.Synthesis and Electrochemical Properties of $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$ and $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.2}]\text{O}_2$ via Co-precipitation[J].*Journal of Power Sources*, 2006,159(2):1328-1333.
- [8] Li J.,Wang L.,Zhang Q., et al.Synthesis and Characterization of $\text{LiNi}_{0.6}\text{Mn}_{0.4-x}\text{Co}_x\text{O}_2$ as Cathode Materials for Lithium Ion Batteries [J].*Journal of Power Sources*,2009,189(1):28-33.
- [9] Noh H.-J.,Youn S.,Yoon C.S.,et al.Comparison of the Structural and Electrochemical Properties of Layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2(x=1/3,0.5,0.6,0.7,0.8 \text{ and } 0.85)$ Cathode Material for Lithium-ion Batteries[J].*Journal of Power Sources*, 2013,233:121-130.
- [10] Ma L.,Nie M.,Xia J.,et al.A Systematic Study on the Reactivity of Different Grades of Charged $\text{Li}[\text{Ni}_x\text{Mn}_y\text{Co}_z]\text{O}_2$ with Electrolyte at Elevated Temperatures Using Accelerating Rate Calorimetry [J].*Journal of Power Sources*,2016,327:145-150.
- [11] Aishova A.,Park G.-T.,Yoon C.S.,et al.Cobalt-Free High-Capacity Ni-Rich Layered $\text{Li}[\text{Ni}_{0.9}\text{Mn}_{0.1}]\text{O}_2$ Cathode [J].*Advanced Energy Materials*,2020,10(4): 1903179.
- [12] U.-H. Kim, L.-Y. Kuo, P. Kaghazchi, C.S. Yoon, Y.-K. Sun, Quaternary Layered Ni-Rich NCMA Cathode for Lithium-Ion Batteries, *ACS Energy Lett.* 4 (2) (2019) 576–582.
- [13] Xiao G, Chen P, Ren W, et al. Recent development of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as cathode material of lithium ion battery. *Modern Chem Ind.* 2014;34(5):53-57.
- [14] Hayner CM, Zhao X, Kung H. Materials for rechargeable lithium-ion batteries. *Annu Rev Chem Biomol Eng.* 2012;3:445-471.
- [15] A. Manthiram, B. Song, W. Li, A perspective on nickel-rich layered oxide cathodes for lithium-ion batteries, *Energy Storage Mater.* 6 (2017) 125–139.
- [16] B. Chu, Y.J. Guo, J.L. Shi, Y.X. Yin, T. Huang, H. Su, A. Yu, Y.G. Guo, Y. Li, Cobalt in high-energy-density layered cathode materials for lithium ion batteries, *J. Power Sources.* 544 (2022), 231873.
- [17] B. Chu, Y.J. Guo, J.L. Shi, Y.X. Yin, T. Huang, H. Su, A. Yu, Y.G. Guo, Y. Li, Cobalt in high-energy-density layered cathode materials for lithium ion batteries, *J. Power Sources.* 544 (2022), 231873.
- [18] J. Zheng, W.H. Kan, A. Manthiram, Role of Mn content on the electrochemical properties of Nickel-Rich layered $\text{LiNi}_{0.8-x}\text{Co}_{0.1}\text{Mn}_{0.1+x}\text{O}_2$ ($0.0 \leq x \leq 0.08$) cathodes for lithium-ion batteries, *ACS Appl. Mater. Interfaces.* 7 (12) (2015) 6926–6934.
- [19] M. Jeong, H. Kim, W. Lee, S.J. Ahn, E. Lee, W.S. Yoon, Stabilizing effects of Aldoping on Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ cathode for Li rechargeable batteries, *J. Power Sources.* 474 (2020), 228592.
- [20] Seok Hyun Song, Moses Cho, Inchul Park, et al. High-voltage-driven surface structuring and electrochemical stabilization of Ni-rich layered cathode materials for Li rechargeable batteries [J]. *Advanced Energy Materials*, 2020, 10(23): 2000521.
- [21] Qingyun Lin, Wenhao Guan, Jie Meng, Wei Huang, et al. A new insight into continuous performance decay mechanism of Ni-rich layered oxide cathode for high energy lithium ion batteries. *Nano Energy* 54 (2018) 313–321
- [22] Cho D.-H.,Jo C.-H.,Cho W.,et al.Effect of Residual Lithium Compounds on Layer Ni-Rich $\text{Li}[\text{Ni}_{0.7}\text{Mn}_{0.3}]\text{O}_2$ [J].*Journal of The Electrochemical Society*,2014, 161(6):A920-A926.
- [23] Zhang S S. Problems and their origins of Ni-rich layered oxide cathode materials[J]. *Energy Storage Mater.*, 2020,24: 247-254.
- [24] Jung R, Metzger M, Maglia F, et al. Chemical versus Electrochemical Electrolyte Oxidation on NMC111, NMC622, NMC811, LNMO, and Conductive Carbon[J]. *Phys. Chem. Lett.*. 20178(19):4820-4825.
- [25] Xiaodan Wang, Ying Bai, Xinran Wang, and Chuan Wu. High-Voltage Layered Ternary Oxide Cathode Materials: Failure Mechanisms and Modification Methods. *Chin. J. Chem.* 2020, 38, 1847—1869
- [26] Li J, Zhang Z, Guo X, et al. The studies on structural and thermal properties of delithiated $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($0 < x \leq 1$) as a cathode material in lithium ion batteries[J]. *Solid State Ionics*, 2006, 177(17-18): 1509-1516.

- [27] Bak S M, Nam K W, Chang W, et al. Correlating structural changes and gas evolution during the thermal decomposition of charged $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode materials[J]. *Chemistry of Materials*, 2013, 25(3): 337-351.
- [28] Li Y, Liu X, Wang L, et al. Thermal runaway mechanism of lithium-ion battery with $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode materials[J]. *Nano Energy*, 2021, 85.
- [29] S.-H. Kang, C. S. Johnson, J. T. Vaughey, K. Amine and M. M. Thackeray, *J. Electrochem. Soc.*, 2006, 153, A1186–A1192.
- [30] Y. Sun, H. Cong, L. Zan and Y. Zhang, *ACS Appl. Mater. Interfaces*, 2017, 9, 38545–38555.
- [31] Y. Sun, L. Zan and Y. Zhang, *Appl. Surf. Sci.*, 2019, 483, 270–277.
- [32] K. Kubota, T. Kaneko, M. Hirayama, M. Yonemura, Y. Imanari, K. Nakane and R. Kanno, *J. Power Sources*, 2012, 216, 249–255.
- [33] X. Tan, R. Liu, C. Xie and Q. Shen, *J. Power Sources*, 2018, 374, 134–141.
- [34] B. Song, H. Liu, Z. Liu, P. Xiao, M. O. Lai and L. Lu, *Sci. Rep.*, 2013, 3, 3094.
- [35] S. Han, B. Qiu, Z. Wei, Y. Xia and Z. Liu, *J. Power Sources*, 2014, 268, 683–691.
- [36] J. H. Cheng, C. J. Pan, C. Nithya, R. Thirunakaran, S. Gopukumar, C. H. Chen, J. F. Lee, J. M. Chen, A. Sivashanmugam and B. J. Hwang, *J. Power Sources*, 2014, 252, 292–297.
- [37] B. Qiu, M. Zhang, L. Wu, J. Wang, Y. Xia, D. Qian, H. Liu, S. Hy, Y. Chen, K. An, Y. Zhu, Z. Liu and Y. S. Meng, *Nat. Commun.*, 2016, 7, 12108.
- [38] Z. Chen, Y. Liu, Z. Lu, R. Hu, J. Cui, H. Xu, Y. Ouyang, Y. Zhang and M. Zhu, *J. Alloys Compd.*, 2019, 803, 71–79.
- [39] Liu. Study on interface optimization and lithium storage performance of high nickel ternary $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials. (C) China Academic Journal Electronic Publishing House. <http://www.cnki.net>
- [40] Lim J M, Hwang T, Kim D, et al. Intrinsic Origins of Crack Generation in Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ Layered Oxide Cathode Material[J]. *Sci. Rep.*, 2017, 7: 39669.
- [41] Wang X, Cai J, Liu Y, et al. Atomic-scale Constituting Stable Interface for Improved $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ Cathodes of Lithium-ion Batteries[J]. *Nanotechnology*, 2021, 32: 115401.
- [42] Chen Y, Zhang Y, Chen B, et al. An approach to application for $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material at high cutoff voltage by TiO_2 coating[J]. *J. Power Sources*, 2014, 256: 20-27.
- [43] Yao L, Liang F, Jin J, et al. Improved electrochemical property of Ni-rich $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode via in-situ ZrO_2 coating for high energy density lithium ion batteries[J]. *Chem. Eng. J.*, 2020, 389: 124403.
- [44] Liang L, Hu G, Jiang F, et al. Electrochemical behaviours of SiO_2 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials by a novel modification method[J]. *J. Alloy. Compd.*, 2016, 657: 570-581.
- [45] Zhu J, Cao G, Li Y, et al. Nd_2O_3 encapsulation-assisted surface passivation of Ni-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ active material and its electrochemical performance[J]. *Electrochim. Acta*, 2019, 325: 134889.
- [46] Xiong X, Wang Z, Yin X, et al. A modified LiF coating process to enhance the electrochemical performance characteristics of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials[J]. *Mater. Lett.*, 2013, 110: 4-9.
- [47] Lee S-H, Yoon C S, Amine K, et al. Improvement of long-term cycling performance of $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}]\text{O}_2$ by AlF_3 coating[J]. *J. Power Sources*, 2013, 234: 201-207.
- [48] Cho W, Kim S-M, Lee K-W, et al. Investigation of new manganese orthophosphate $\text{Mn}_3(\text{PO}_4)_2$ coating for nickel-rich $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode and improvement of its thermal properties[J]. *Electrochim. Acta*, 2016, 198: 77-83.
- [49] Tang W, Peng Z, Shi Y, et al. Enhanced cyclability and safety performance of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ at elevated temperature by AlPO_4 modification[J]. *J. Alloy. Compd.*, 2019, 810: 151834.
- [50] Gan Q, Qin N, Wang Z, et al. Revealing Mechanism of Li_3PO_4 Coating Suppressed Surface Oxygen Release for Commercial Ni-Rich Layered Cathodes[J]. *ACS Appl. Energ. Mater.*, 2020, 3(8): 7445-7455.
- [51] Zhong Z, Chen L, Zhu C, et al. Nano LiFePO_4 coated Ni rich composite as cathode for lithium ion batteries with high thermal ability and excellent cycling performance[J]. *J. Power Sources*, 2020, 464: 228235.
- [52] Huang B, Zhao Z, Sun Y, et al. Lithium-ion conductor LiAlO_2 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ as cathode material for lithium-ion batteries[J]. *Solid State Ion.*, 2019, 338: 31-38.
- [53] Cheng Z, Lv F, Xu N, et al. Enhanced rate performance and cycle stability of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ at high cut-off voltage by $\text{Li}_6\text{La}_3\text{Al}_0.3\text{Zr}_2\text{O}_{12}$ surface modification[J]. *Appl. Surf. Sci.*, 2020, 524: 146556.
- [54] Xie J, Sendek A D, Cubuk E D, et al. Atomic Layer Deposition of Stable LiAlF_4 Lithium Ion Conductive Interfacial Layer for Stable Cathode Cycling[J]. *ACS Nano*, 2017, 11(7): 7019-7027.
- [55] Liang H, Wang Z, Guo H, et al. Improvement in the electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode material by Li_2ZrO_3 coating[J]. *Appl. Surf. Sci.*, 2017, 423: 1045-1053.

- [56] Gan Q, Qin N, Zhu Y, et al. Polyvinylpyrrolidone-Induced Uniform Surface-Conductive Polymer Coating Endows Ni-Rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with Enhanced Cyclability for Lithium-Ion Batteries[J]. *ACS Appl. Mater. Interfaces*, 2019, 11(13): 12594-12604.
- [57] Xu G-L, Liu Q, Lau K K S, et al. Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes[J]. *Nat. Energy*, 2019, 4(6): 484-494.
- [58] Pham H Q, Hwang E H, Kwon Y G, et al. Approaching the maximum capacity of nickel-rich $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathodes by charging to high-voltage in a non-flammable electrolyte of propylene carbonate and fluorinated linear carbonates[J]. *Chem. Comm.*, 2019, 55(9): 1256-1258.
- [59] Beltrop K, Klein S, Nölle R, et al. Triphenylphosphine Oxide as Highly Effective Electrolyte Additive for Graphite/NMC811 Lithium Ion Cells[J]. *Chem. Mater.*, 2018, 30(8): 2726-2741.
- [60] Yuan, Y.; Wu, F.; Bai, Y.; Li, Y.; Chen, G.; Wang, Z.; Wu, C. Regulating Li deposition by constructing LiF-rich host for dendrite-free lithium metal anode. *Energy Storage Mater.* 2019, 16, 411–418.
- [61] Chen, J.; Fan, X.; Li, Q.; Yang, H.; Khoshi, M. R.; Xu, Y.; Hwang, S.; Chen, L.; Ji, X.; Yang, C.; He, H.; Wang, C.; Garfunkel, E.; Su, D.; Borodin, O.; Wang, C. Electrolyte design for LiF-rich solid electrolyte interfaces to enable high-performance micro-sized alloy anodes for batteries. *Nat. Energy* 2020, 5, 386–397.
- [62] Tan, J.; Matz, J.; Dong, P.; Shen, J.; Ye, M. A Growing Appreciation for the Role of LiF in the Solid Electrolyte Interphase. *Adv. Energy Mater.* 2021, 11, 2100046–2100070.
- [63] Jiang, R.; Hong, L.; Liu, Y.; Wang, Y.; Patel, S.; Feng, X.; Xiang, H. An acetamide additive stabilizing ultra-low concentration electrolyte for long-cycling and high-rate sodium metal battery. *Energy Storage Mater.* 2021, 42, 370–379.
- [64] Kim, K.; Hwang, D.; Kim, S.; Park, S. O.; Cha, H.; Lee, Y. S.; Cho, J.; Kwak, S. K.; Choi, N. S. Cyclic Aminosilane-Based Additive Ensuring Stable Electrode–Electrolyte Interfaces in Li-Ion Batteries. *Adv. Energy Mater.* 2020, 10, 2000012–2000023.
- [65] Lan, J.; Zheng, Q.; Zhou, H.; Li, J.; Xing, L.; Xu, K.; Fan, W.; Yu, L.; Li, W. Stabilizing a High-Voltage Lithium-Rich Layered Oxide Cathode with a Novel Electrolyte Additive. *ACS Appl. Mater. Interfaces* 2019, 11, 28841–28850.
- [66] Zhao, J.; Liang, Y.; Zhang, X.; Zhang, Z.; Wang, E.; He, S.; Wang, B.; Han, Z.; Lu, J.; Amine, K.; Yu, H. In Situ Construction of Uniform and Robust Cathode–Electrolyte Interphase for Li-Rich Layered Oxides. *Adv. Funct. Mater.* 2020, 31, 2009192–2009202.