Improving LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ cathode electrolyte interface under high voltage in lithium ion batteries

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Abstract
The demanding for high energy density as well as high safety is still an important threshold for battery commercialization. Next-generation layered LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ (NCM) cathodes will meet the specific energy required for driving range of at least 300 miles from a single charge to guarantee the success of electric vehicles. Extending operating voltage of NCM cathode materials is considered as an effective way to increase energy density of lithium ion batteries. However, unstable electrode electrolyte interface (CEI) limits the electrochemical performance of NCM cathodes when operating at high voltages (>4.3 V). In this review, underlying factors and mechanisms that result in the failure to form a robust CEI are analyzed, including surface phase reconstruction, stress-induced cracking, transition metal dissolution, electrolyte decomposition and oxygen redox reaction. Then, progress on how to improve and stabilize CEI is summarized. To bridge the gap between current and next generation automotive batteries, it is expected that the situation of NCM electrode materials at high voltage to be fine-tuned with available variables such as nickel content, packaging density and loading level. Moreover, more detailed work on designing and studying a reliable CEI can help the application of NCM cathodes under high voltage.

KEYWORDS
cathode electrolyte interface, high operating voltage, layered LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ cathode, lithium ion batteries

1 | INTRODUCTION

Since the commercialization in the early 1990s, rechargeable lithium-ion batteries (LIBs), as the most promising energy storage medium, have been widely used in portable electronic devices, electric vehicles (EVs), hybrid EVs, and smart grids.$^{[1-4]}$ Rapidly increasing energy demand in modern society has put forward requirements for the further development of LIBs in terms of capital cost, long-term cycling performance, durability and energy density.$^{[5,6]}$ Especially for EVs, “range anxiety” remains a major concern.$^{[6]}$ Generally, as the provider of lithium ion, cathode materials greatly limit the performance and capacity of LIBs on account of graphite is the most commercial anode.$^{[7]}$ Among current cathode materials, LiCoO$_2$ (LCO) suffers from low specific capacity of only $\approx$50% of
its theoretical capacity, structural degradation, and oxygen release at high de-lithiated states. Meanwhile, cobalt resources are scarce and expensive, which limits the large-scale application of LCO in EVs. LiFePO4 displays high safety characteristic, but operates at low voltage and has low volume specific energy. Due to Mn dissolution, high voltage spinel-like Li2MnO4 cathode materials suffer from accelerated capacity fading during prolonged cycling and storage. LiNi0.5Co0.2Mn0.3O2 (NCA) battery materials have high technical barriers. Moreover, because aluminum is amphoteric metal which is not easy to precipitate, NCA materials will suffer from thermal runaway at high temperatures, causing serious consequences. LiNi0.33Co0.33Mn0.33O2 (NCM), layered lithium transition metal oxide, is regarded as the most promising cathode material in the next generation of lithium ion batteries due to its large specific capacity, high operating voltage, good rate capability, and reasonable cost as the synergistic effects of transition metals. In order to satisfy the consumer-threshold of next generation of EVs to travel at least 300 miles on a single charge, namely, the cathode of a battery needs to provide an energy density of 800 Wh kg\textsuperscript{-1}. Therefore, it is crucial to further improve the energy density of NCM cathode.

At present, ternary NCM batteries (NCMs) containing more than 60% nickel have been fully commercialized, but they still cannot guarantee the success of EVs. To realize a high energy density NCM cathode LIB, the main strategy is to enhance the capacity and operating voltage according to the equation: energy density = capacity \times voltage. Running NCM electrode materials at high voltage is an effective way to increase the energy density of the corresponding batteries. It is deemed that the predominant oxidation states of Ni, Co, and Mn in the NCM compound are +2, +3, and +4, respectively with small content of Ni\textsuperscript{3+} and Mn\textsuperscript{3+} ions. LIBs achieve reversible capacity and provide energy by continuously de-intercalating lithium between anode and cathode. In general, different transition metals have different redox activities at different voltages due to crystal-field splitting and differences in electronegativity. The redox reactions of different transition metals play a crucial role in de-intercalation of lithium ion batteries. For layered NCM electrode, the Co\textsuperscript{3+}/Co\textsuperscript{4+} level is the lowest in energy and it will oxidize at the highest voltage, the next highest energy levels above those of Co are the Ni\textsuperscript{3+}/Ni\textsuperscript{4+} and Ni\textsuperscript{2+}/Ni\textsuperscript{3+} couples followed by that of Mn\textsuperscript{3+}/Mn\textsuperscript{4+} redox couple. Hence, the de-intercalation of a typical layered Ni-Co-Mn alloy via the oxidation of Ni\textsuperscript{2+} to Ni\textsuperscript{3+}, followed by the oxidation of Ni\textsuperscript{3+} to Ni\textsuperscript{4+}, and finally the oxidation of Co\textsuperscript{3+} to Co\textsuperscript{4+}.

Moreover, the Mn\textsuperscript{4+} maintain constant during the whole process. Enhancing the working voltage can promote the conversion of Co\textsuperscript{3+} to Co\textsuperscript{4+}, thus making NCM cathode materials release more capacity. Figure 1 shows a possible evolutionary roadmap of NCM- and NCA-based cells in terms of gravimetric (Wh kg\textsuperscript{-1}) and volumetric (Wh kL\textsuperscript{-1}) energy density. Ni-rich NCMs and particularly NCM811 (theoretical capacity of 280 mAh g\textsuperscript{-1}) is capable to reach energy density 700 kWh kL\textsuperscript{-1} and 300 Wh kg\textsuperscript{-1} at the cell level. This target is possible to achieve with adjustment in some key parameters, such as Ni concentration in the cathode active material (0.33–0.90 kmol%), anode material (graphite vs. Si–C anode with a capacity of 1000 kmAh kg\textsuperscript{-1}), cell upper cutoff voltage (4.2 V vs. 4.4 kV), and electrode density (15 mg cm\textsuperscript{-2}, 35% porosity, vs. 25 mg cm\textsuperscript{-2}, 20% porosity). Some novel materials and devices such as Li/S, Li/Se, Na-ion, and capacitors have been studied to meet energy storage requirements. For sodium ion batteries, the mass of Na is three times greater than that of Li, resulting in a lower theoretical capacity. Na electrodes tend to have lower average voltages (vs. Na/Na\textsuperscript{+}) than Li.
Intercalation in Na compounds generally occurs over a larger voltage window than in their Li analogues, which would reduce the practical energy density.\textsuperscript{[45]} Besides, as a consequence of larger ionic radius of Na\textsuperscript{+} (1.16 Å) compared to Li\textsuperscript{+} (0.76 Å), the strains associated with (de)intercalation of Na will be larger, phase transitions upon (de)intercalation are much more prevalent in Na compounds.\textsuperscript{[46]} Actually, the limited electrical conductivity and large volume variation of sulfur, as well as the formation of polysulfides during cycling, are yet to be addressed before lithium-sulfur batteries can become an actual reality.\textsuperscript{[47–49]} Particularly, when increasing the upper cutoff voltage above 4.5 V (≈220 mAh g\textsuperscript{−1}), and matching with lithium metal anodes, the gravimetric energy density of NCMs can approach that of lithium-sulfur batteries, and the volumetric energy density will exceed that of lithium-sulfur batteries. The areal capacity of the sulfur cathode must be controlled at 4–8 mAh cm\textsuperscript{−2} to compete with commercial LIBs, but it cannot be achieved at present.\textsuperscript{[50]} In addition, compared with NCMs, capacitors are inferior in energy density.\textsuperscript{[51]} Therefore, considering the comprehensive advantages of NCMs, it is necessary to study its performance under high operating voltage.

In NCM cathodes, it is widely accepted that Ni\textsuperscript{2+} migration has a tendency to occupy Li vacancy during the process of de-intercalation because of similar ionic sizes of Ni\textsuperscript{2+} (0.69 Å) and Li\textsuperscript{+} (0.76 Å), causing cationic mixing. High operating voltage will aggravate the mixing degree of ions, which will lead to anisotropic changes in crystal lattices of different transition metals, making NCM’s spherical secondary particle cracked and transition metal ions dissolved. The dissolved transition metal ions react with electrolyte resulting in the destruction of cathode material and the loss of electrolyte. The electrode material changes from layered phase to spinel phase and finally to irreversible rock salt phase,\textsuperscript{[52,53]} causing battery’s capacity loss and voltage attenuation, even gas generation and explosion accidents. Therefore, how to stabilize and optimize the CEI and reduce the occurrence of side reactions at interface are of great significance to stabilize the performance of NCMs at high operating voltage.

Herein, we review current problems of the CEI of NCMs under high voltages (>4.3 V), which plays an important role in controlling the degree of lithium-ion diffusion, charge transfer, and parasitic reactions. Degradation of cathode and corresponding effects on CEI will be discussed. Then, strategies will be postulated on how to improve and stabilize CEI, such as coating, doping, other surface treatments, structural modifications, electrolyte additives. Problems and countermeasures of NCM materials when operating at high voltages are shown in Figure 2. In the end, there will be conclusions on progress of improving the CEI of NCMs, meanwhile, remaining challenges and future development trends of NCMs are put forward.

\section{Remaining Challenges}

It needs to be aware that higher upper cut-off voltage, larger degree of lithium is utilized in NCM lithium ion batteries\textsuperscript{[6]} which results in a series of degradation problems. Unlike higher nickel incorporation (which also utilizes more lithium ions), electrolyte oxidation and anionic redox caused only by high operating voltage make the cathode - electrolyte interfacial side reactions extremely complicated, limiting cycle life and safety performance of NCMs. Understanding the surface structure evolution of NCM materials along with the interfacial side reactions under high working voltage is significant to design robust cathode electrolyte interface so as to improve electrochemical performance.
2.1 Surface phase reconstruction

As a layered cathode material, NCM have a prototype α-NaFeO$_2$ structure with R3m space group in which alternating layers are consisted of edge-sharing LiO$_6$ and MO$_6$ octahedra.$^{[54,55]}$ Figure 3A indicates the O3 structure of oxygen-lithium-oxygen-TM-oxygen along the rhombohedral[001] direction, with an AB CA BC stacking of oxygen, forming a rhombohedrally distorted fcc oxygen framework with three MO$_2$ sheets in the repeat unit.$^{[53]}$ In “O3,” the “O” indicates that the intercalants are octahedrally coordinated by anions, and the “3” indicates that the repeat unit is three MO$_2$ sheets.$^{[29]}$

Given the fact that Mn$^{3+}$ will spontaneously donate electrons to Ni$^{3+}$, yielding Mn$^{4+}$ and Ni$^{2+}$ according to crystal-field theory,$^{[56]}$ Ni$^{3+}$ is unstable because of the unpaired electron spin of the $e_g$ orbitals. As a consequence, when content of Mn is lower than Ni in the lithiated NCM, the predominant oxidation states of Ni, Co, and Mn are +2, +3, and +4 respectively.$^{[17,57,58]}$ Because the similarity of radius between Ni$^{2+}$ and Li$^+$,$^{[53]}$ Ni$^{2+}$ ions could occupy 3b lithium sites in the Li slab easily. Nevertheless, Doeff et al. reported that the cation mixing layer consisted of not only Ni$^{2+}$ but also other metal ions, like Mn$^{2+}$ and Co$^{2+}$ produced by reduction.$^{[52]}$ The mixing of cations between TM and Li layers will lead to structure reconstruction from layered to Fd3m disordered spinel and Fm3m rock-salt phase (Figure 3B)$^{[59,60]}$ Because the spinel and disordered rock-salt structures are crystallographically related to the O3 structure in that they all have an fcc oxygen framework, differing only in their arrangement of Li and TM cations over the octahedral and tetrahedral interstitial sites.$^{[29]}$

Theoretically, when one quarter of the metal ions migrate from the transition-metal layer to particular octahedral sites in the Li layer and metal ions ordering within the fcc oxygen framework and cubic symmetry, O3 will transform to spinel. Note that the spinel-like structure generated during phase reconstruction is far from well-ordered spinel.
In addition, the transformation from layered lithium-lack state $\text{MO}_2$ to rock-salt structure happen via densification and release of oxygen, with the Li and TM layers no longer exhibit long-range periodic order. This process is also supported by Hwang et al. with the discovery of a reduction of the Ni and an increase in the effective electron density of oxygen.[61]

The structure reconstruction phenomenon occurs most likely on the surface of NCM, especially cycling under high cut-off voltage. There are two main reasons behind: (1) the concentration of Li at the surface is lower than that in the bulk within a cathode material particle during charging process (Figure 3F) because the concentration gradient is needed as kinetic driving force for Li diffusion; (2) as mentioned before, in a high voltage charged state, extraction of Li from the material increase. As a result, the surface structure of NCM materials become so unstable that TM ions migrate from TM layer to Li layer easily. The transition-metal-ion migration has a tendency to occupy every second Li vacancy because the disordered cations repel each other (Figure 3C,D).

The relationship between high voltage Li extraction and structure reconstruction was supported by Doeff et al.[52] They found that the surface reconstruction layer is thicker after first cycle between 2.0-4.7 V than electrolyte exposure, and this layer consists of Fm$\bar{3}$m rock-salt structure with spinel structure from surface to inside (Figure 4). Even more noteworthy is that the surface reconstruction
Degradation mechanisms of LiNi0.5Co0.2Mn0.3O2 and phase transformation after cycle tests under high-voltage conditions. Reprinted with permission.\textsuperscript{[58]} Copyright 2013, Wiley

is orientation-dependent which occurs primarily along the lithium diffusion channels, suggesting that surface reconstruction is promoted by lithium removal during charging. Moreover, Jung et al. discovered that the formation of the rock-salt phase is more dominant under a higher voltage ($\approx 4.8$ V) than $4.5$ V (Figure 5), which is attributable to the highly oxidative environment that triggers the oxygen loss from the surface of the material.\textsuperscript{[61]}

The influence of surface phase reconstruction to electrochemical performance is probably poor due to the sluggish kinetics of electrochemical inactive rock-salt phase.\textsuperscript{[64]} Besides, the TM ions in Li layer acts as a barrier for Li
diffusion, causing high polarization and poor rate capability and deteriorating the capacity retention. Nevertheless, Cho et al. reported a thin cation disordered layer to improve cycling performance in which Ni$^{2+}$ ions were resided in Li slabs with “pillar effect,” because of Ni$^{2+}$ ions in the Li sites provide an electrostatic repulsion force to hinder further cation migration.\textsuperscript{65}

### 2.2 Stress-induced cracking

NCM layered cathode is often fabricated in the form of spherical secondary particles consisting of densely packed primary particles in order to meet the high volumetric energy density and alleviate interfacial side reactions. However, it brings a major problem of intergranular cracking induced by anisotropic volume change under electrochemical cycling, especially at high working voltage. Operando neutron diffraction is used by Goonetilleke et al. to elucidate the structural evolution of NCM electrodes.\textsuperscript{66}

As depicted by Figure 6A, the c lattice parameter initially increases until ∼4.0 V caused by increasing electrostatic repulsion between the transition-metal octahedra as the occupancy of the lithium layer is reduced. Beyond this voltage, the c lattice parameter decreases rapidly owing to cation mixing and phase transformation. This large amount of lattice contraction/expansion results in greater repeated mechanical stress on NCM material which also exhibits as changes in cell volume (Figure 6B) during charging/discharging. The structure collapse generated by

\[\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\]
lattice strains will lead to microcrack and pulverization of secondary particles. Li et al. demonstrated that the abrupt anisotropic lattice collapse of layered NCM at deep charge is a universal phenomenon critically dependent on Li utilization, and not Ni content as commonly believed, by combining in situ X-ray diffraction analysis and density functional theory (DFT) calculations. DFT predicts a similar extent of the c-axis lattice distortion up to 83 mol% Li extraction between LiNiO$_2$ and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (Figure 6C).

Besides intergranular cracks, intragranular cracks were also observed in several cathode materials after prolonged cycling. Yan et al. reported unexpected observations on the nucleation and growth of intragranular cracks in a commercial LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode and the density of intragranular cracks abruptly increases when cycled at a high cutoff voltage of 4.7 V (Figure 7A-C). Moreover, Lee et al. revisited the crystal structure of primary particles of NCM materials with transmission electron microscopy. They revealed that the so-called primary particles are in fact polycrystalline secondary particles. The low-angle grain boundaries between smaller true primary particles cause the development of nanocracks within the primary-like particles of NCM cathodes after repetitive electrochemical cycles.

Cracks can result in poor connections between grains of active materials and current collectors, leading to poor electrical conductivity and even loss of active materials due to fragmentation. In addition, cracks create fresh surfaces that will be exposed to electrolytes and generate new sites for surface phase transformation, corrosion and side reactions, consequently accelerating cell degradation. The correlation between TM dissolution and upper cutoff voltage was supposed by Gilbert et al. They found that continuous operation of full cells with NCM523 leads to dissolution of TM ions and their migration and incorporation into the SEI of the graphite-based negative electrode. These processes correlate with cell capacity fade and accelerate markedly as the upper cutoff voltage exceeds 4.3 V because the enhanced fracture creates new surfaces and causes increased solvent oxidation and TM dissolution. Among TMs, Mn content in the SEI shows a better relationship with cell capacity loss than Co and Ni contents. As Mn ions become incorporated into the SEI, the kinetics of lithium trapping change from power to linear at the higher voltage, indicating a large effect of these ions on SEI growth and implicating (electro)catalytic reactions. Likewise, Li et al. showed that the dissolved transition-metal ions cross the electrolyte to the anode and affect the SEI during cycling.

### 2.3 Transition metal dissolution

Lithium salts like LiPF$_6$ used in current electrolytes can react with the few ppm of H$_2$O present in all commercial formulations to form HF. The reaction is presented as follows:

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_5 \quad (1)
\]

\[
\text{PF}_5 + \text{H}_2\text{O} \leftrightarrow \text{POF}_3 + 2\text{HF} \quad (2)
\]

Then HF further corrodes the surface of NCM, leading to the dissolution of transition-metal species which can poison the anodic solid electrolyte interface (SEI) as well as form a CEI film on the cathode. The fracture of NCM particles with more surfaces exposed in electrolytes can accelerate this process.

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### 2.4 Electrolyte decomposition and CEI formation

One of the challenges for further development of NCM rechargeable batteries for EVs is safety, which essentially corresponds to electrolyte and interface stability. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is the electrochemical window of the electrolyte, within which the electrode potential needs to be controlled in order to maintain the thermodynamic stability of the electrolyte. Whereas HOMO and LUMO are derived from approximated electronic structure theory while investigating electronic properties of isolated molecules, their energy levels do not indicate species participating in redox reactions. Therefore Peljo et al. provided a correct thermodynamic representation for the electrochemical stability of the electrolyte based on redox potentials and Fermi level of the electron in solution. Due to the significance and widespread application of HOMO and LUMO in electrochemical stability, this representation will be adopted in the following parts.

Ideally, once the electrode potentials exceed the electrochemical window of electrolyte, the electrolyte will be oxidized on the cathode and reduced on the anode, with the generation of CEI and SEI respectively. The CEI and SEI can passivate the electrode hindering the transportation of electron, so as to stabilize the electrode and electrolyte. However, the reality is far more complicated about the electrolyte decomposition, parasite reaction and CEI formation under high cut-off voltage.

Recently, Zhang et al. developed an in situ Fourier transform infrared (FT-IR) method to study the reactivity of
FIGURE 7  A–C, Low magnification HAADF images of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ after 100 cycles at different high cutoff voltages. The red arrows indicate voids and the yellow arrows in g indicate intragranular cracks. Scale bars, 500 nm. Reprinted with permission.[66] Copyright 2017, Springer Nature. D, Cross-section of an embedded particle in a coin cell after one charge-discharge cycle. Cracking is observed throughout the particle and cracks in several locations are indicated by arrows; E, Cross-section of an embedded particle in a coin cell after 4500 charge-discharge cycles showing extensive cracking; F, Schematic of an idealized particle consisting of several grains indicated by dotted lines. Electrical contact to the shaded conducting medium surrounding the particle is represented by arrows; G, after cycling, separations at grain boundaries lead to the loss connectivity and electrical contact between grains. Reprinted with permission.[69] Copyright 2013, Wiley
the electrolyte on NCM surfaces as a function of voltage, finding unique evidence for dehydrogenation of ethylene carbonate (EC) on NCM811 surface at voltages as low as 3.8 V versus Li$^+$/Li. The electrolyte oxidation mechanism on NCM811 surface is described in Figure 8. [77] EMC and EC molecules can dissociate hydrogen and form de-H EMC and de-H EC respectively that adsorb on oxide surface through a C–O bond. The driving force becomes even greater during de-lithiation and decreasing of x in Li$_x$MO$_2$. Then one way of de-H EC is further dissociated a second hydrogen on the other carbon forming vinylene carbonate (VC), another is further oxidized to open the ring, or form oligomers with EC-like rings such as C$_6$H$_8$O$_6$, C$_9$H$_{14}$O$_8$, and C$_7$H$_{10}$O$_6$. The eventual products of solvent dehydrogenation may be CO$_2$ or CO. These Organic products form a passivating layer on the oxide surface with great impedance growth for Li$^+$ migration during charging of NCM811 measured by EIS. In addition, the dehydrogenation of EC and EMC generates protic species on the surface, which further trigger reactions with LiPF$_6$ to form HF and less-fluorine-coordinated species such as Li$_x$PF$_y$O$_z$, transition metal fluorides (MF) and PF$_3$O. The more specific electrolyte decomposition reactions and possible degradation pathways were investigated and postulated with $^{13}$C$_3$-labeled EC by Henschel et al.[78]

During delithiation, a charging potential leads to the further lowering Fermi Energy $E_F$ of the cathode material below the HOMO of the electrolyte, which is accompanied by a hole transfer from TM3d states to the HOMO of the electrolyte, promoting the decomposition of the oxide and reduction of the TM ions,[79] as well as oxygen release and oxidation of electrolytes.[80] A part of the lithium is chemically bound in the CEI, resulting in the formation of lithium oxides, fluorides, and carbonates (Figure 9). The observed reduction of the TM ions at the interface is inherently related to the formation of the CEI layer, which indicates that the highly oxidative Co$^{4+}$ and Ni$^{3+/4+}$ ions are involved in CEI layer formation. Aurbach et al. reported that the existence of nickel element in electrodes augmented the nucleophilicity of the surface oxygen.[81] Electrodes seem to reach passivation in LiPF$_6$/alkyl carbonate-based solutions, due to the formation of surface species such as LiF, MFx, ROCO$_2$Li, ROCO$_2$M, and Polycarbonates. Note that CEI components are not static during cycling. Li et al. described the dynamic behavior of the cathode interphase in the common non-aqueous electrolyte by conducting three-dimensional chemical and imaging analysis on LiNi$_{0.7}$Mn$_{0.15}$Co$_{0.15}$O$_2$, and drew a schematic diagram of the microstructure and chemical composition of CEI (Figure 10).[82] Studies shown that some substances in CEI will decompose in a high-oxidation environment of $\sim$4.5 V, but the CEI tends to stabilized during repeated cycles. Species like MF$_n$, LiF, RCFx, C$_2$HO$^-$. were detected on LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ surface after 100 cycles, proving that these components can withstand 4.5 V to a certain extent. Different from the SEI in anode, the components of CEI are more complicated due to the complex environment of cathode and conductive carbon may also affect the CEI components,[83] so the effective in situ characterizations of exploring the
different components during cycles are needed under high voltage.

In recent years, some researches have developed in situ characterization techniques to reveal the dynamic evolution of CEI during battery cycling. Identification of CEI chemistry and the dynamics changes serve as a basis for the hypothesis of CEI evolution mechanisms. In order to meet the high specificity and high sensitivity, Chen et al. designed operando surface-enhanced Raman spectroscopy (SERS) with strong SERS effect provided by the Au nanocube monolayer. They pointed out that initiated by the reduction of ester carbonates at the anode, small ester molecules undergo a series nucleophilic chain reaction steps and form polymer/oligomer chains containing ester and ether groups which adsorbed on NCM surfaces. As a result, CEI species containing ester and ether chains is more stable in the discharged state. Similarly, Li et al. used in situ shell-isolated nanoparticle-enhanced Raman spectroscopy to examine the changes in the interface between NCM and carbonate-based electrolyte. The protic species on the NCM811 surface resulted from dehydrogenation (De-H) reaction of EC could further
attack PF$_6^-$ anion to deposit lithium fluorides and oxyfluorides species in the surface layer at 3.8 V. Then these species would grow during charge. In addition Meng et al. developed operando attenuated total reflection-fourier transform infrared (FTIR) technique finding that the components of CEI basically generate in the first cycle owning to EC priority decomposition and the presence of tris(trimethylsilyl)borate (TMSB) can suppress the decompose of EC in part, and modify the stability of CEI film.\[86\]

### 2.5 Anionic redox reaction

Most studies of the anionic redox reactions have focused on Li-excess layered compounds. Nonetheless, Lee et al. showed unambiguous evidence of reversible anionic redox reactions in NCM111 with a detailed quantification on its reversibility upon electrochemical cycling.\[87\] There are two types of oxygen involvements: One is the typical involvement of O through hybridization with transition metals throughout the electrochemical operation which is enhanced upon charge; the other is the intrinsic O redox at high potentials when the de-lithiation rate above 65%, which contributes excess capacity but leads to irreversible O loss and associate surface reactions.

Although it is easier to think of these as separate phenomena, they in fact are deeply interconnected. During the battery cycling process, especially under the high working potential, a variety of problems exist at the same time. The emergence of one phenomenon will accompany or even aggravate the emergence of other problems, which brings great challenges to the research. The surface structure reconstruction increases the surface resistance of cathodes and the stress induced cracking exposures fresh cathode surfaces to electrolyte, leading to more severe side reactions and inefficient CEI generation. The products of electrolyte decomposition are considered to be the main components of CEI, with the part of dissolved transition metals participating in. The dissolution of transition metal and release of oxygen add to the sophistication of the interface reactions. The origination can be traced to a large number of Li extraction and the changes of electronic structure and crystal structure under high voltage. Fortunately, an improvement strategy may alleviate several problems at the same time and ultimately improve the cycling stability of NCM batteries under high cutoff voltage.

### 3 MODIFICATION

To solve the problems mentioned above, many methods have been proposed successively, such as coating, doping, other surface treatments, structural modification, electrolyte additives. It is generally believed that the coating layer not only can prevent the direct contact between cathode materials and electrolyte, it also influence interface performance.\[88,89\] Doping elements can reduce the rearrangement of ions to increase the structural stability of materials\[91\] and strengthen the TM-O bond energy to suppress the phase transition.\[92\] And structural design of cathode materials can also be used to stabilize CEI by reducing the variation in volume anisotropy.\[52,93–96\] In addition, the introduction of electrolyte additives can be regarded as an effective way to promote the formation of stable CEI.

### 3.1 Coating and other surface treatment

Coating the NCM cathode particles by metal oxides, phosphate, fluoride, lithium is an effective measure to provide a protection layer to suppress side reactions between electrode and electrolyte.\[86\] The surface coating layers are considered to improve the cycling stability, rate capability and thermal stability.\[97\] Metal oxides including TiO$_2$,\[63\] WO$_3$,\[98\] SnO$_2$,\[99\] ZrO$_2$,\[100\] La$_2$O$_3$,\[101\] V$_2$O$_5$\[102\] et al. have been used as coating substances to reduce the charge transfer resistance of material and improve electrochemical reversibility. Based on previous research, the materials are continuously improved. Wang et al. prepared an ultrathin Al$_2$O$_3$ film on NCM622, which facilitated ion diffusion dynamic characteristic and improved electrochemical stability.\[103\]

In addition to exploring the effects of different materials, new methods have also been developed. Cao et al. identified a green and simple coating way to dispersed Al$_2$O$_3$ on the cathode surface, the modified cathode materials has excellent high-voltage performance.\[104\] Jiang et al. explored a novel concept to modify primary particles of cathode materials by engineering their exposed surface with Na$_2$MoO$_4$ coating layer, the functionalized cathode shows superior cycling performance.\[105\] Since that covalent P-O bonds, phosphates such as AlPO$_4$\[106\] MnPO$_4$\[62\] exhibit high stability, and lithium-containing compounds Li$_3$PO$_4$\[107\] Li$_2$SiO$_3$\[108\] LiAlO$_2$\[109\] that with stable chemical properties are widely used as coating layers for fast Li$^+$ conduction. Fluorides suppressed oxidation decomposition of the electrolyte on the surface of cathode materials.\[110\] However, inorganic materials tend to deposited on cathode material surface and they always need complex and expensive processing steps. Therefore, Lee et al. modified NCM cathode with poly(tris(2-(acryloyloxy)ethyl) phosphate) (PTAEP) gel polymer electrolyte.\[111\] The coating layers serve as ion-conductive protective film that effectively improve...
electrochemical performance of the NCM111 at high-voltage. Neudeck et al. used organophosphates, specifically tris(4-nitrophenyl) phosphate (TNPP) and tris(trimethylsilyl) phosphate as surface modification for NCM622. The results show that molecular coating is a useful method for improving cathode materials.

Artificial CEI film with high ionic conductivity and electrochemical/thermal stability is suitable for Ni-rich NCM cathodes at high voltage to prevent the decomposition of electrolyte. To take advantage of that, some researchers make artificial CEI on the surface of NCM to achieve a high interfacial stability. Jang et al. achieved nanoscale-based artificial CEI layers through the reaction of lithium-tetra(trimethylsilyl)borate and cathode material. Chae et al. developed an amphiphilic sulfonate-based artificial CEI, which effectively reduces undesired parasite reactions, leading to high interfacial stability and cycling retention. On this basis, he further improved the synthesis method by utilizing an organic surfactant with a sulfate functional group to provide a sulfate-embedded CEI on the NCM811 surface. Results indicate that modified NCM811 showed better cycling performance and capacity retention. Most coating materials are detrimental to electronic and lithium ion conductivities, which is harmful to the electrochemical performances of NCMs.

### 3.2 Doping

Doping NCM with cations or anions is another way to modify cathode materials. Anion doping improves the thermal and structural stability of cathode electrode by partially replacing O\(^{2-}\), and stabilizes the discharge potential platform. Cation dopants can migrate into Ni, Co or Mn sites, but rarely in Li sites. It reported that substitution of Co sites generally enhances the charge transfer, while substitution of Mn sites hinders evolution of gas and mixing of cations. The metal ion may have a larger ionic radius and can be used as pillars for both lithium ion layer and transition mental layer, and it can also change the valence states of transition metals or oxygen. Jia et al. synthesized layered Nd-doped NCM523, confirmed that Nd\(^{3+}\) expanded Li-ion channels and strengthen bonding energy, results in improvement of structural stability and electron transfer. Mg also shows the same effect. Schipper et al. combined computation and experiment to explore the impact of Zr\(^{4+}\) on the electrochemical behavior of NCM622. Zhang et al. substituted oxygen ions of NCM622 with the boracic polyanion to suppress capacity degradation. To alleviate the structure degradation of NCM811, Yang introduced low-content Li\(_2\)MnO\(_3\) as structural stabilizer to suppress the phase transition and revealed the relationship between structure degradation and performance deterioration of NCM.

However, traditional doping elements are generally inactive under the operating voltage, and the first charge capacity of the battery decreases slightly with the increase of the doping amount. Hence, it is important to optimize a proper doping amount to balance capacity and stability.

In addition, anion doping has also been extensively studied. Compared with Li-O bond (341 kJ mol\(^{-1}\)), Li-F bond (577 kJ mol\(^{-1}\)) is stronger, and the stronger bond between TM and fluorine leads to more stable structure. In addition, the substitution of fluoride at oxygen site can reduce part of the trivalent nickel (0.56 Å) to divalent nickel (0.69 Å), thereby expanding lattice parameters. Yue et al. doped NCM811 with fluorine to protect the electrode from HF and maintain the structural stability of the electrode, thereby improving its cycle performance.

However, there are few studies on the impact of doping on CEI, and further development is needed in the future.

### 3.3 Synergetic modification of coating and doping

Considering advantages and disadvantages of doping and coating, researchers combined these two methods to modify NCM. Chen et al. covered cadmium oxide on the surface of NCM622 particles, at the same time, a part of cadmium oxides diffused into the crystal lattice with gradient distribution. Li et al. synthesized LiAlO\(_2\)-coated and Al-doped NCM523 via a facile coprecipitation method, electrochemical test results show that Al-modified sample shows better capacity retention and cycling performance than pristine NCM. Similar to this, Ran et al. applied gradient phosphate polyanion doping and in-suit coating of nano-scale Li\(_3\)PO\(_4\) layer to enhance the properties of NCM622.

The substitution of metal ion enlarges the inter-layer spacing and coating layer acts as a protective shell and suppresses various adverse effects during cycling, especially under high-voltage. The steps to achieve the co-modification of doping and coating are shown in Figure 11.

### 3.4 Structural modification

#### 3.4.1 Concentration gradient

Although it is possible to improve cycling performance of NCMs by coating and doping foreign elements, it is far from enough to meet the performance requirements of maintaining the battery at high operating voltage for a long time. To optimize the NCM electrode material
more rationally, we need to focus on elements that make up the material. The higher the Ni content, the larger the capacity of the battery. Co is usually added to improve layered ordering and electrical conductivity to enhance rate capability, while Mn is effective in inhibiting undesirable chemical and structural changes in the material at high voltage.\cite{7,53,131,132} Therefore, the NCM electrode material can be designed as Ni-enriched interior and Mn-enriched exterior to obtain both large capacity and high stable interface. This concept has been proposed since 2005\cite{133} and has developed a number of configurations involving core/shell\cite{133–137} core/compositionally graded shell,\cite{137,138} full concentration gradient (FCG)\cite{139–143} and two-sloped full-concentration gradient (TSFCG).\cite{141,142,144–147}

Core-shell structure means that two or more materials with different chemical structures are used as shell and core respectively in a certain way to construct a novel material, so as to achieve combination advantages of a variety of materials. By developing a core/shell NCM particle in which the surface is enriched Mn thin layer and Ni-rich core can combine effects of Ni and Mn, which will significantly improve the structure stability during cycling by partially reducing the Ni$^{3+}$ ions to more thermodynamically stable Ni$^{2+}$.\cite{147} On the basis of this idea, a fully functional microscale core/shell cathode was realized using a
coprecipitation method.\textsuperscript{[139]} Sun et al. proposed a spherical core/shell structure with a high capacity (delivered from the LiNi\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}O\textsubscript{2} core) and a good thermal stability (achieved from the LiNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} shell).\textsuperscript{[133]} This material delivered a reversible capacity of 188 mAh g\textsuperscript{−1} with the cutoff voltage of 3.0–4.3 V versus Li/Li\textsuperscript{+} and increased the onset temperature of the exothermic decomposition from 220 °C for conventional NCM811 material to 250°C. Moreover, the C/Li[Li\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1}][Li\textsubscript{0.5}Mn\textsubscript{0.5}]O\textsubscript{2} cell exhibited splendid cyclability with a capacity retention of 98% compared with the C/NCM811 cathode without LiNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} shell which only hold 81% capacity after 500 cycles. This core/shell structure can be regarded as an extension of surface coating, and active materials are often used as the shell, which can provide partial capacity while protecting bulk cathode materials. Cho et al. reported a LiNi\textsubscript{0.54}Co\textsubscript{0.12}Mn\textsubscript{0.34}O\textsubscript{2} cathode material which consists of a layered phase core and stable spinel phase shell possesses both high energy and safety on account of aforementioned two heterostructures.\textsuperscript{[136]} The material demonstrated a reversible capacity of 200 mAh g\textsuperscript{−1} when cycled between 3.0 and 4.5 V. It retained 95% capacity retention under the most severe test condition of 60°C and the amount of oxygen evolution from the lattice in the cathode is reduced by 70% as well. The eminent results of above two works are attributed to integration functions of Ni-rich core and Mn-rich shell materials. High nickel content ensures that the cathode material has a high capacity, and Mn-rich stable spinel phase shell suppresses the interface reaction at CEI, ensuring the stability and safety of battery under high voltage. However, after long-term cycling under high voltage, the disadvantage of this kind of combined cathode mate-

![Figure 12](image_url)

**FIGURE 12** A, Schematic diagram of positive-electrode particle with Ni-rich core surrounded by concentration-gradient outer layer. Reprinted with permission.\textsuperscript{[146]} Copyright 2009, Springer Nature. B, Schematic diagram of the FCG lithium transition-metal oxide particle with the nickel concentration decreasing from the center towards the outer layer and the concentration of manganese increasing accordingly. Reprinted with permission.\textsuperscript{[138]} Copyright 2012, Springer Nature
texture and c-axis of the unit cell aligned in the transverse direction radially aligned toward the particle center. Hence, the layered planes were oriented along the radial direction and formed a unique morphology, facilitating Li$^+$ transport, minimizing contact with electrolyte to have a stable CEI under high voltage charging.\cite{138,144,148} In order to further improve capacity and stability of NCMs under high voltage, a TSFCG Ni-rich cathode was developed to maximum the Ni concentration near the core and the Mn concentration at the surface. Sun et al. developed a high-performance LiNi$_{0.65}$Co$_{0.13}$Mn$_{0.22}$O$_2$ cathode material composed of layered lithium transition metal oxide with TSFCG within each particle.\cite{141} This material delivered a reversible capacity of 200 mAh g$^{-1}$ (4.3 V cutoff) compared with conventional electrode’s 187 mAh g$^{-1}$ and excellent capacity retention of 88% in contrast to 71% of conventional electrode after 1500 cycles at 1 C in full-cell configuration. Each TSFCG secondary particle consisted of rod-shaped primary particles that radially oriented from the particle center, further pushing the boundaries. Jaephil Cho et al. synthesized a highly stable transition-metal self-induced concentration gradient LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode exploiting polystyrene beads (PSBs) cluster incorporated coprecipitation method without the additional metal tank, decreasing the process time and capital cost (Figure 13).\cite{149} According to the reduction mechanism of Ni ions and changes of oxidation state of Ni element, other transition metal ions can form the concentration gradients in the primary particles from surface to core direction to balance charge neutrality. In addition, internal pore spaces which were generated by the thermal decomposition of PSBs during annealing process can be a buffer in the secondary particles to accommodate the strain generated during cycling as well as enhance the electrolyte wettability. Therefore, this unique structure of the PSB-NCM cathode showed superior structural stability at a high voltage cut-off of 4.45 V and high thermal stability at 60°C. The above research progresses on the concentration gradient of NCM materials provide references for us to reasonably design the material structure and improve thermodynamic stability. In the end, the CEI is stabilized to reduce parasitic reactions and optimize battery performance. However, due to the material preparation process is more complicated, the calcination temperatures of Ni-enriched core and Mn-enriched shell are different, and passivation method to suppress the surface Mn dissolution is also needed,\cite{150} the industrialization of this material requires more advanced equipment and higher costs, namely, the problem of cost performance needs to be considered. Therefore, more systematic analyses are needed on the road to commercialization.

### 3.4.2 Single crystalline

For the preparation of traditional polycrystalline NCM cathode materials, spherical secondary particles formed from randomly orientated primary particles. In the process of cycling, the volume of primary particles will change in anisotropy gradually along with Li$^+$ de-intercalation and charge compensation between transition metal elements, resulting in intergranular cracks, secondary particles’ rupture and the structure of cathode being destroyed. And high operating voltage and long-term cycling will aggravate rupture. At the same time, the electrolyte also penetrates into secondary particles along the crack, transition metals dissolve and react with electrolyte, which intensifies the phase transition of cathode material.
from layered structure to rock salt phase and hinders the diffusion of Li\(^+\). The impedance of CEI increases and the battery’s initial Coulomb efficiency is low which cause battery capacity decay. In addition, there is oxygen loss accompanied with undesired heat release, causing hidden trouble to safety. The working mechanism of monocrystalline materials as industrial cathodes’ materials is shown in Figure 14.\(^{[25]}\) There will be collapsed secondary particles for the polycrystalline cathode material and could give rise to the formation of resistant layer generated by interfacial side reactions during the electrode pressing process by high pressure. By contrast, the monocrystalline material maintains structural consistency and stable morphology, there is no anisotropic volume change in the cathode and void space between each primary particle during the pressing and battery cycling process. The morphological robustness could restrain the continuous formation of resistance layer, which effectively alleviates particle fracture and gas evolution, reducing impedance and battery performance degradation caused by unstable CEI.

The stability of single crystal structure ensures excellent electrochemical performance and safety of the battery under high operating voltage. Dahn et al. compared a single-crystal NCM523 (SC-523) material with grain size around 2~3 \(\mu\)m to conventional polycrystalline uncoated and Al\(_2\)O\(_3\)-coated NCM523 (AC-523) materials.\(^{[96]}\) It was shown that release of oxygen around 80°C from charged AC-532 and UC-532 materials whereas it was not detected for charged SC-532 samples. Moreover, SC-523 cells produce negligible compared with AC-523 cells’ substantial amounts of gas during potentiostatic holds at 4.4, 4.5, and 4.6 V for a total time of 300 hours at 40°C. In addition, SC-523 cells had a lower mean parasitic heat flow than that of AC-532 cells in all voltage ranges and exhibited a better capacity retention of \(\sim 92\%\) after 1600 cycles at 40°C between 3 and 4.4 V. It is the single crystal material’s superior stability and corresponding stable CEI that makes SC-523/graphite cells have outstanding performance at high voltage and high temperature. Yang et al. fabricated and investigated the integrated single crystalline Li\(_{0.83}\)Ni\(_{0.11}\)Co\(_{0.06}\)O\(_2\) (SC-NCM) with primary particles of 3~6 \(\mu\)m diameter, and the SiO-Cl\(_2\)-SC-NCM pouch-type full cell with a practical loading (8.7 mAh cm\(^{-2}\)) achieved a satisfied energy density of 225 Wh kg\(^{-1}\) and delivered a capacity retention of 84.8\% at 1°C after 600 cycles at 45°C.\(^{[151]}\) Additionally, SC-NCM coin cells exhibited higher discharge capacity of 162.6 mAh g\(^{-1}\) and maintained a capacity retention of 84.5\% compared with normal
LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2 cells’ 135.7 mAh g^{-1} and 68.3% after 150 cycles at 2.75~4.4 V. The improved electrochemical performance is mainly attributed to the fact that single crystal particles prevent interparticle rupture, avoid undesired interface contact between electrode and electrolyte, stabilize CEI and inhibit irreversible phase transition of electrode materials. To date, although single crystalline cathode materials of high purity have been successfully synthesized, its average particle size is still less than 1 μm, which indicates that the power tap/pellet density needs to be lowered. In addition, limited by intrinsic structure, single crystal materials cannot achieve reversible capacity comparable to those of polycrystalline materials. Moreover, some synthetic methods are not suitable for large-scale production because of the use of volatile and toxic solvents. More methods and resources are needed to solve the above problems in the process of industrialization of single crystalline cathode.

### 3.5 Electrolyte additives

In addition to the improvements in the NCM cathode materials, the interface problems under high voltage can also be effectively modified with the electrolyte additives. Adding a small amount of additives (typically 0.1~5.0% by mass or volume fraction) to current commercial electrolytes is more economical and facile compared with those strategies to design a new electrolyte formula or to coat on materials surface with annealing. Therefore, it is suitable for large-scale industrial production and practical application. Analogous to anode additives, these additives in high-voltage batteries mostly have higher HOMO level than the solvents, oxidizing prior to the electrolytes. Then a stable cathode-electrolyte interface (CEI) layer is formed in situ on the surface of the positive electrode, so as to prevent the side interface reactions by avoiding direct contact between electrode and electrolyte. In order to be easily decomposed and to generate robust CEI, the additives probably contain active functional groups or unsaturated bonds which can be divided into the flowing categories: (1) lithium salts like lithium dioxalate borate(LiBOB), (152) lithium difluoroxalate borate (LiDFOB) (153) and lithium difluorobis(oxalate) phosphate (LiDFBOP), (154) (2) boron-containing like tris(trimethylsilyl)borate (TMSB), (155) trimethoxy boroxine (TMOBX), (156) (3) phosphorous-containing like tris(trimethylsilyl)phosphite (TTPPi), (157) triphenylphosphine Oxide (TPPO), (158) and 2-(2,2,2-trifluoroethoxy) -1,3,2-dioxaphospholane 2-oxide (TFEOP). (159) (4) sulfur-containing like methylene methane disulfonate (MMDS), (160) 1,2,6-Oxadithiane 2,2,6,6-tetraoxide (ODTO), (161) and divinyl sulfone. (162) (5) carbonate like VC, methyl phenyl carbonate, and diphenyl carbonate. (163)

Ma et al. proposed that the functional coating at the positive electrode side may not be needed when appropriate additives are used. (161) They evaluated the ODTO as a novel electrolyte additive which has similar structure to MMDS in both uncoated and coated single crystal LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2/graphite pouch cells. Cells with uncoated NCM532 and additive blends containing 1% ODTO along with 1%LiPO_2F_2, 2% VC or 2%FEC showed virtually identical cycling performance to cells with coated NCM532 and the same electrolytes. This result illustrates that a coating layer is formed in situ on the surface of NCM cathode by these additives.

Owing to single additive cannot always satisfy the demands in practical application, the synergy effect between various additives is needed to improve the performance of the high-voltage NCM batteries. (165,166) In this regard, J.R. Dahn et al. did a series of work to evaluate the blended electrolyte additives in the past few years. (160,163,167,168) As shown in Figure 15, The charge end-point capacity slippage, capacity fade, coulombic efficiency, impedance change during cycling, gas evolution and voltage drop during “cycle-store” testing were compared to gain an understanding of the effects of these promising electrolyte additives or additive combinations on the different types of pouch cells. They found out that 2 wt% PES+ 1 wt% TTSPi+ 1 wt% MMDS (PES-211) can improve NCM111/graphite and NCM442/graphite cell performance up to 4.4 V and even to 4.5 V by controlling impedance growth and improving capacity retention during long-term cycling. Nevertheless, further studies suggested that PES-211 is not suitable for the high nickel NCM811 cathodes, indicating that there is a complex interaction between the additives and the cathode surface, thus the selection of additives should consider different positive electrode systems.

However, the effect mechanisms of these additives and blend additives are unknown, thus more efforts are needed to elucidate. It will be helpful to understand the mysteries if advanced characterization technologies like TOF-SIMS or operando liquid SIMS with theoretical calculation tools could be in use. Studying the mechanism of electrolyte additives with the relationship between their structures and functions will make the optimization and combination more efficiently.

Among the strategies mentioned above, they all have merits and demerits to NCMs under high voltage. Their comparison and main effects to CEI are summarized clearly in Table 1. It is known to all that coating is the direct way to construct the CEI artificially and controllably which would be promising to address the problems between cathodes and electrolytes.
FIGURE 15 Radar plots summarizing the effects of selected electrolyte additives (combinations) on A, NCM111/graphite, B, NCM532/graphite, and C, NCM622/graphite pouch cells studied using UHPC and the “cycle-store” procedure to 4.4 V. The axes are normalized to the worst value being equal to 100% and they consist of the average coulombic inefficiency (CIE) (from 11 to 15 cycles), the average charge end-point capacity slippage (from 11 to 15 cycles), the impedance (Rct) after UHPC cycling, the gas evolution during UHPC cycling, the capacity loss after 35 “cycle-store” cycles, the impedance after the whole “cycle-store” process, the voltage drop at 35 “cycle-store” cycle and the gas evolution during the whole “cycle-store” process. Values closest to the center of the radar plot are best. Reprinted with permission. [160] Copyright 2015 Elsevier

4 | CONCLUSIONS AND PROSPECTS

In this review, in order to pursue higher energy and more stable Li-based batteries, we analyzed the performance of NCMs which is currently considered to be the most promising of next generation of lithium ion batteries under high operating voltage. This review mainly discusses the decay mechanism of electrode materials, CEI, and solutions to key problems. Stable CEI is the premise that battery can circulate normally under high voltage. But under normal circumstances, in the process of cathode’s charging and discharging, cationic mixing and secondary particles rupture will occur, resulting in the irreversible phase transition of cathode material from layered phase to spinel phase and then to rock salt phase. The side reaction between electrolyte and electrode is intensified, the impedance and gas production are increased as well. Moreover, the effective components of electrolyte and electrode material are consumed, and finally the capacity is attenuated and the battery is damaged. Finding appropriate means to ensure stable CEI during battery cycling can reduce gas production, improve battery electrochemical and thermodynamic stability, and raise safety level. Some strategies have been proposed, including surface coating, element doping, structure design, utilizing electrolyte additives and so on. Surface coating refers to the artificial construction of a stable layer on the surface of cathode material to reinforce secondary particles. By acting as a physical barrier, the electrode material is separated from electrolyte, phase transition and transition metal dissolution are inhibited at high voltage, and interfacial side reactions are suppressed. However, the material type and thickness of coating layer need to be selected and controlled reasonably. The surface material
### TABLE 1 The comparison of different modification methods under high voltage

| Modification methods | Advantages | Disadvantages | Main effect to CEI |
|----------------------|------------|---------------|--------------------|
| Coating              | 1. Act as a physical barrier  
2. Suppress interfacial side reactions | 1. Material type selection  
2. Thickness controlling  
3. Capacity sacrifice | Artificial construction of CEI |
| Doping               | 1. Maintain a relatively stable structure  
2. Suppress the phase transition | 1. Reversible capacity sacrifice  
2. Doping content controlling | Reduce the volume anisotropy and CEI fracture |
| Concentration gradient | 1. Same trend lattice volume change  
2. Inhibit particle rupture | 1. High requirements for equipment and operating condition  
2. Not suitable for industry | Reduce the volume anisotropy and CEI fracture |
| Single crystalline   | 1. Good stability nature | 1. capacity release, preparation methods and tap density improvement | Form stable CEI |
| Electrolyte additives | 1. Economical and facile  
2. Easy to apply in industry | 1. Hard selection  
2. Decomposition during cycling | In situ formation of CEI |

with electron and ionic conductive characteristics and reasonable thickness can ensure sufficient protection for electrode material without lowering capacity and rate performance. Otherwise, there will be a capacity sacrifice as a consequence of impeding Li\(^+\) migration and electron conduction. At present, methods that can precisely control the coating thickness, such as atomic layer deposition (ALD) and chemical vapor deposition (CVD), need relatively high cost. Element doping refers to replacing the transition metal ions or lithium ions selectively according to the size of the foreign elements’ ion radius, and making the cathode material maintain a relatively stable structure under high operating voltage through the regulation of lattice parameters at the atomic level. However, due to the replacement of some active materials by chemically inactive foreign elements, the reversible capacity of some batteries will be reduced, and element doping content needs to be controlled. The synergistic effects of surface coating and element doping can stabilize material structure and CEI under high voltage simultaneously, but this will undoubtedly combine negative effects as well, it is worth considering how to reasonably select parameters. By constructing concentration gradient distribution of nickel and manganese elements in secondary particles, the lattice volume change of each primary particle has the same trend under high voltage, which inhibits particle rupture and stabilizes CEI. Whereas the method of concentration gradient design has high requirements for equipment and operating conditions, it is not suitable for large scale production. Particles in single crystalline morphology have very good stability nature, which is friendly for forming stable CEI and maintaining the stability of battery under high voltage. The capacity density, preparation methods and tap density of these particles still need to be improved. Many electrolyte additives have been reported to improve circulation performance under high voltage, and their mechanisms are different. All the above problems need to be solved by more accurate optimization of NCM cathode materials. It is believed that the most popular way to meet energy demand of EVs for industrial application should be economical, low requirements for equipment and production conditions, simple and easy to promote.\(^6\)

The interface layer is formed in situ by adding a small amount of electrolyte additives, and it only needs simple operation to realize this process, therefore, electrolyte additives are considered to be more facial and economic than other modifications and are more commonly used in industry.\(^7\) In order to realize the commercialization of high voltage NCMs, our future work will not only focus on electrode material and electrolyte, but also explore the CEI that can more safely match the solid electrolyte.

Next-generation layered NCM cathodes will enable a specific energy of 300∼350 or 350∼500 Wh kg\(^{-1}\) when they are matched with graphite-silicon or Li metal anode respectively, with a driving range of at least 300 miles from a single charge.\(^6\) Increasing the Ni fraction, optionally coupled with extended operating voltages of NCM cathode materials, which will further drive up energy output, are considered as effective means to increase the corresponding battery capacity. And high-nickel layered oxides under high operating voltage will occupy a major position in Li-based automobile batteries at least through the next decade. Range and safety requirements remain important threshold for battery commercialization. Using
NCMs to fill the gap between the present and next generation of automotive batteries requires fine-tuning of the available variables of nickel content, upper cutoff voltage, packing density, and loading level. The inherent structural instability of high-Ni cathode materials is higher than that of materials with low nickel content, and phase transition and gas generation are more likely to occur during cycling, which deteriorate batteries’ performance. In terms of the high nickel layered oxides cathode at high upper cutoff voltage, energy can be enhanced from high electrode density and loading. Ultrahigh electrode loading (e.g., 5~10 mAh cm^-2) has been demonstrated through non-conventional electrode fabrication \(^6,169\) and NCM811 is on track for full commercialization. Nevertheless, high electrode density is still a great challenge for high-Ni NCMs compared to LCO for high energy density. In addition, some other factors such as fast charge and element resource also have an effect on facilitating high voltage Ni-rich NCMs. In summary, the potential future research directions of NCM cathode mainly focused on: (1) high nickel content; (2) high upper cutoff voltage; (3) high packing density; (4) fast charge; (5) ultrahigh electrode loading.

Surface and interfacial chemical properties are important to determine the structure and electrochemical stability of NCMs at high voltage, especially those with high nickel content. At present, the research on the mechanism of CEI is not clear. In the future, more attention should be paid to the forming and mechanism of CEI. We expect more detailed work to study and reasonably design a reliable CEI to improve the electrochemical performance of NCMs at high voltage.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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