Topical Review

Recent progress in synthesis and surface modification of nickel-rich layered oxide cathode materials for lithium-ion batteries

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Abstract
Nickel-rich layered oxides have been identified as the most promising commercial cathode materials for lithium-ion batteries (LIBs) for their high theoretical specific capacity. However, the poor cycling stability of nickel-rich cathode materials is one of the major barriers for the large-scale usage of LIBs. The existing obstructions that suppress the capacity degradation of nickel-rich cathode materials are as a result of phase transition, mechanical instability, intergranular cracks, side reaction, oxygen loss, and thermal instability during cycling. Core–shell structures, oxidating precursors, electrolyte additives, doping/coating and synthesizing single crystals have been identified as effective methods to improve cycling stability of nickel-rich cathode materials. Herein, recent progress of surface modification, e.g. coating and doping, in nickel-rich cathode materials are summarized based on Periodic table to provide a clear understanding. Electrochemical performances and mechanisms of modified structure are discussed in detail. It is hoped that an overview of synthesis and surface modification can be presented and a perspective of nickel-rich materials in LIBs can be given.

Keywords: nickel-rich layered oxides, capacity degradation, surface modification, single-crystal cathode

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1. Introduction

Lithium-ion batteries (LIBs) are closely related with our convenient life, because it is an engine of our daily power tools ranging from the cellphones and laptops to bikes and electric vehicles [1, 2]. Cathodes determine the energy-density and cost of LIBs; therefore, it is significant to develop alternative cathodes [3, 4]. Recently, layered LiNiO$_2$ cathode materials have attracted many interests, as nickel is natural abundance in contrast to cobalt in the earth crust, and a LiNiO$_2$ cathode shows higher capacity than LiCoO$_2$ [5, 6]. Nevertheless, it is revealed that the LiNiO$_2$ based electrode delivers very poor cycling stability and potential safety hazards in LIBs, suggesting that pristine LiNiO$_2$ is not desirable for LIBs [7]. The cubic-hexagonal transition is driven by lithium–nickel mixing in the nickel-rich materials that hinders Li$^+$ transport and accelerates composition degradation [8, 9]. Thus, selecting a suitable stabilization strategy is vital for the commercial usage of LiNiO$_2$ [10–12]. Until now, single dopants, such as LiNi$_{1-x}$M$_{1-x}$O$_2$ ($M = Co$ [13–16], Mn [17–19], Fe [18], Ti [19, 20], Mg [21, 22], Cu [23], B [24], Ce [25], Ga [26], Y [27], Sb [28, 29], Zn [30], Ca, Nb [7], In and Ti [31], LiNiO$_2$ $\times$F$_2$O$_2$ [32] and LiNiO$_{1.7}$S$_{0.3}$ [33] have been studied and have achieved a proper stability and energy density. But their electrochemical performance still needs to be further improved. For example, although Li–Ni mixing is hindered by Co$^{3+}$ substitute in LiNi$_{1.25}$Co$_{0.75}$O$_2$ ($y > 0.25$), rock-salt phase can still be observed during the charge/discharge process, accompanied by oxygen evolution [13–16]. Thermal stability of LiNiO$_2$ can be enhanced through Mn-doping, and excessive Li may contributed to the formation of a stable Li$_2$MnO$_3$ layered phase [17, 34–36]. Al$^{3+}$ substitute can decrease cationic disorder of LiNiO$_2$, because of $\alpha$-LiAlO$_2$ has a high value of $\alpha_{ela}$ = 5.08 compared to those of LiNiO$_2$ ($\alpha_{ela}$ = 4.93), however, Al$^{3+}$ is redox-inactive [37, 38]. LiNi$_{0.8}$Fe$_{0.2}$O$_2$ delivers an initial specific capacity of 191 mA h g$^{-1}$, due to Fe$^{2+}$/Fe$^{3+}$ cation almost matching the size of Ni$^{2+}$, but Fe$^{3+}$/Fe$^{2+}$ oxidation is often hard to achieve [18]. LiNi$_{0.975}$Ti$_{0.025}$O$_2$ delivers initial capacity of 154.8 and 235 mA h g$^{-1}$ at 19.3 $\mu$A cm$^{-2}$ [19, 20] and 0.2 mA cm$^{-2}$ [39], respectively. It is observed that specific capacity decreases accompanied with an increase in the amount of Ti doping. It is illustrated that cycling stability of LiNiO$_2$ can be greatly improved through doping low amounts of W [40] and Zr [41, 42].

Double-metal co-doping is also investigated to improve stability of LiNiO$_2$. Enlightened by improvement performance of LiNi$_{0.3}$Fe$_{0.7}$Al$_{0.1}$O$_2$ ($x \leq 0.2$) [43, 44], LiNi$_{0.89}$Co$_{0.09}$Mg$_{0.02}$O$_2$ [45], Li[Ni$_{0.9}$Co$_{0.09}$W$_{0.01}$]O$_2$ [46] and LiNi$_{0.92}$Co$_{0.08}$O$_2$–Zr$_{2}$O$_2$ [47], the Li[Ni$_{0.9}$Co$_{0.1}$Mn$_{0.1}$]O$_2$ (NCM) and Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ (NCA) were developed, and they are easy synthesis and high-energy density [5, 6]. There is high initial discharge capacity with increasing Ni content in nickel-rich cathodes, however, its mechanical stability, thermal stability and air stability are substantially reduced during cycling. To realize their full potential, strategies including control of the particle and crystallite microstructures, intuitive bulk and surface stabilization are often applied [48–50]. Among them, core–shell structure has been considered as ideal method for suppressing the lattice instability of NCM/NCA during cycling [51, 52]. Otherwise, the doping of foreign element endows the NCM/NCA a reasonable electronic transport pathway [53, 54]. Huang et al prepared LiNi$_{0.8}$Co$_{0.2}$O$_2$ microspheres through rapid co-precipitation and spray drying method. Benefiting from the optimized particle structure, the 94.7% of its initial capacity was achieved after 200 cycles at 1.0 $^\circ$C in a NCM811/graphite full cell [55]. A core–shell structured Li[Ni$_{0.886}$Co$_{0.06}$Mn$_{0.05}$Al$_{0.035}$]O$_2$ material was fabricated by Kim et al, it can deliver an initial capacity of $\sim$222 mA h g$^{-1}$ at 4.5 V and 100 mA g$^{-1}$ with a retention rate of 88.3% after 100 cycles [56]. Park et al demonstrated borodoped LiNi$_{0.06}$Co$_{0.05}$Mn$_{0.9}$O$_2$ ($B_{1.0}$–NCM90) in the primary particles, the $B_{1.0}$–NCM90 maintained 91% of its initial capacity after 100 cycles at 90.0 mA g$^{-1}$ and 55 $^\circ$C [57]. Otherwise, many nickel-rich cathode materials also suffer from severe lattice change induced by the surface phase transition and side reactions with electrolyte, and many efforts have been initiated to restrain them. For instance, Zhang et al constructed LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.0}$O$_2$ primary particles agglomerated with tight grain boundaries by a hydrothermal method [60]. At 18.0 mA g$^{-1}$ rate, NCM-750 $^\circ$C delivered an initial discharge capacity of 203.7 mA h g$^{-1}$, 93.25% and 86.19% retention were retained after 100th and 200th cycles at 180 mA g$^{-1}$, respectively. Yan et al constituted Li$_3$PO$_4$-infused LiNi$_{0.7}$Co$_{0.14}$Mn$_{0.16}$O$_2$ within the surface and grain boundaries of secondary particles [61]. When cycled at 200/3 mA g$^{-1}$ and three formation cycles 20.0 mA g$^{-1}$, the composite maintained 91.6% retention after 200 cycles. In one word, increasing attentions have been committed to improve performance of nickel-rich cathodes for LIBs and promising materials have been developed.

Many review articles focus on the particles structure optimizing, capacity fading mechanisms [62, 63], and stabilization techniques for their development prospects [3, 64, 65]. In this review, recent remarkable research of nickel-rich cathode materials in the synthesis, surface modification, characteristics, degeneration mechanisms, strategies to enhance their stability for commercialization [66–68], as well as particles optimizing, e.g. the fabrication of single crystals [69] are introduced in details. Specifically for the surface modification methods and mechanisms for improving the nickel rich cathode materials performance, including doping or/and coating strategies et al, are summarized based on Periodic table. This review not only presents clear discussion about previous studies, but mirrors future development of nickel-rich cathode materials.
2. Mechanisms and challenges of nickel-rich cathode materials for LIBs

Electrochemical reaction mechanisms of nickel-rich layered oxides (Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2}/Li[Ni_{1/6}Al_{2/3}O_{2}]) are similar with LiNiO_{2}. Generally, for NCM/NCA, the delithiation process might be associated with process of deintercalation, transition metal oxidized reactions (e.g. LiNi^{III}O_{2}→Ni^{IV}O_{2}+Li^{+}+e^{-}), reversible O redox, and irreversible oxygen release (e.g. LiNi^{III}O_{2}→Ni^{II}O+1/2O_{2}) [70, 71]. Oxygen on a NCM/NCA particle surface has more charge compensation or higher reactivity than in the bulk. The different electronic configurations of Ni^{3+}/Ni^{2+} and Co^{3+} make the charge compensation, especially oxygen activity, even more elusive. Compared with Ni^{3+} based cathode materials, Co^{3+} based cathode materials with empty $e_g$ orbitals can trigger oxygen oxidation at even lower voltages, thus, layered oxides with varied Ni/Co content have the different spectrum of redox chemistry [70]. The nickel-rich electrode materials (Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2}, LiNi_{0,5}Co_{0,2}Mn_{0,3}O_{2}) deliver 200, 177, 173.1, 205 mA h g$^{-1}$ initial discharge capacity at a constant 20 mA g$^{-1}$ within 2.5–4.6, 2.8–4.5, 2.8–4.4, 3.0–4.6 V, respectively [72-75]. Additionally, LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} exhibits discharge capacities of 170 and 146 mA h g$^{-1}$ at a constant 20 and 200 mA g$^{-1}$, capacity retentions of 98.2 and 94.6 after 30 and 100 cycles, respectively [76-78]. Generally, these NCMs with optimized structure could form a stable solid electrolyte interphas (SEI) layer based on electrolyte additives, and improve their cycling stability compared to pristine LiNiO_{2}. While, LiNi_{0.5}Co_{0.2}Mn_{0.3}O_{2} and LiNi_{0.5}Co_{0.2}Al_{0.15}Mn_{0.85}O_{2} with $x \geq 0.8$ enable a high energy density (greater than 200 mA h g$^{-1}$).

Although nickel-rich cathode materials possess a series of outstanding properties, their challenges must be addressed. Firstly, anisotropic volume variations caused by phase transition destabilize the internal microcracks, and these microcracks propagate to the surface that provided channels for electrolyte penetration and subsequent degradation [79-83]. A large number of Ni$^{2+}$ ions are occupied at Li$^+$ during the discharge process which contributes to the large Li$^+/Ni^{2+}$ mixing [84–86], anisotropic volume change and subsequent phase transition on the particle surface as well as microcrack propagation in the bulk [87]. Capacity retention is closely related to the extent of microcracking within the secondary particles; primary particles within the secondary particles are exposed to electrolyte attack and the structural damage is accelerated [88]. Especially the mechanical integrity of the secondary particles is undermined with increasing cut-off voltage [89, 90], and the range and limit of the depth of discharge (DOD) [91, 92]. A kinetic barrier will be established with rapid degradation of the internal exposed surfaces and increased surface impedance on the primary particle level [93, 94]. For this issue, doping external elements is also a critical method to hinder the Li$^+/Ni^{2+}$ mixing of nickel-rich materials, such as Al doping [95, 96]. Second, side reactions between electrode and electrolyte induce transition metal dissolution, originating from the hydrogen fluoride (HF) initially presented in decomposition of the LiPF$_6$ salt during the charging/discharging process [97–99]. The dissolved transition metal ions are deposited on the anode side forming the organic and inorganic solid electrolyte interphase (SEI) layer [100–102], and consequently deteriorating both cathode and anode integrity [103, 104]. To overcome this challenge, many studies have shown that precise treatment of the surface with a robust coating layer can effectively suppress side reactions against continuous cathode degradation [105, 106]. Investigations reveal that TiO$_2$ [107, 108], Li$_2$PO$_3$, and a pyrazine-linked 2D sheet [109], etc., as a protective layer can prevent the nickel-rich materials from direct contact with the electrolyte, and thus suppress unwanted side reactions [47]. Additionally, electrolyte additive such as diethyl phenylphosphonite can improve cycling stability of nickel-rich cathode through shielding HF and constructing a protective interphase [99, 110]. Third, unwished side reactions are often exothermal, causing complicated electro-chemo-mechanical effect at specific temperatures [111]. Thermal behavior of NMC-811 during charging was performed by in-situ heating x-ray diffraction (XRD), surface-sensitive x-ray absorption spectra (XAS) and bulk sensitive x-ray Raman spectroscopy (XRS) data [112]. The results indicate that bulk phase transition occurs at temperatures above 150 °C for 75% Li$^+$-deintercalation samples or 250 °C for 50% Li$^+$-deintercalation samples, subtle changes involving evolution of oxygen and metal redox can occur at temperatures well below the detectable point of phase transition, and thermal decomposition starts at particles surface and diffuses into the bulk, as well as small particles have much less thermal stability than large particles. Surface reaction and structural transition (e.g. oxygen loss, reconstruction, metalldissolution) occur quickly and deeply at high temperatures. Even at lower temperatures, the degradation occurs rapidly and eventually matches the degradation at high temperatures [113]. Thermal stability of LiNi$_{0.5}$Mn$_{0.2}$Co$_{0.3}$O$_2$ (NMC433, 532, 622, 811) during charging was investigated by in-situ XRD and mass spectroscopy techniques [114]. The results reveal that there is more oxygen release and lower initial temperature of phase transition with increasing of Ni contents. The effect between Li$^+$ vacancies and Ni$^{2+}$ raised Ni$^{3+}$ during Li$^+$-deintercalation process can intensify oxygen loss, and form more NiO compounds in local coordination structure unit [115]. It has been reported that the alloying effect of surface reactivity is effective in improving thermal stability, such as sophisticated synthesis methods that reduce the amount of Ni on particle surfaces [6]. Suitable surface modification is an effective method to form strong metal–oxygen bonding. Development of these strategies require deep understanding of the mechanism about metal–oxygen interaction. Finally, gas generation caused by parasitic side effects is one of the fundamental problems of the most advanced LIBs, because bubbles can block parts of the electrode surface, blocking the transport of lithium ion and resulting in uneven distribution of current. During the production, storage, and application of nickel-rich cathode materials, Li$_2$CO$_3$ decomposition was induced by the electrochemical oxidation of the, resulting in the increase in the Li$^+/Ni^{2+}$ disorder and polarization resistance [116–118]. In addition, Li$_2$CO$_3$ decomposition contributed to CO$_2$ evolution, especially during the first charging

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are washed for several times and dried in an oven overnight. The mixture solution is stirred at a speed of 1000 rpm. The reaction temperature is controlled at 50 °C, providing significant evidence for the reaction between singlet oxygen and electrolyte to be a chemical reaction [121].

3. Synthetic methods and characterizations

3.1. Synthetic methods

3.1.1. Co-precipitation. Co-precipitation is the most frequently used method for nickel-rich layered oxide cathode materials. As shown in figure 1(A), reaction process is conducted in an environmental of an Ar, aqueous solutions of NiSO4 · 6H2O, CoSO4 · 7H2O, MnSO4 · H2O (molar ratio = 8:1:1) are pumped into the reactor together with definite concentration of NaOH and NH3 · H2O solutions. The mixture solution is stirred at a speed of 1000 rpm and the reaction temperature is controlled at 50 °C, the pH value is carefully monitored at 11 ± 0.2. After reaction for about 12 h, the obtained Ni0.85Co0.10Mn0.10(OH)2 precursors are washed for several times and dried in an oven overnight [55, 124, 125]. As shown in figure 1(B), scanning electron microscopy (SEM) images show that Ni0.85Co0.10Mn0.10(OH)2 primary particles stack inside the denser surface of spherical secondary particles with diameter of ~8 µm [124]. Porous Ni0.8Co0.2Mn0.1O2 secondary particles (10 µm) are also obtained through controlling the flow speed of argon at 300 ml min⁻¹ [126]. Whereafter, the resulted precursors and LiOH · H2O are mixed, the mixture is pre-heated first and subsequently annealed at 750 °C in a pure O2 condition to obtain the spherical LiNi0.8Co0.2Mn0.1O2 (NCM811) powders [125]. By comparison of the aqueous solutions used in the co-precipitation process, e.g. sulfate, acetate and nitrate, it is found that sulfate materials formed the best layered LiNi0.8Co0.2Mn0.1O2 structure, showing the best cycling performance [127].

Gradual variation of pH value from 12.0 to 10.6 during the traditional co-precipitation has been performed to a prepared hollow microsphere of Ni0.8Co0.2Mn0.1O2 [128]. The self-organization process in the hollow LiNi0.8Co0.2Mn0.1O2 is induced by the Kirkendall effect, resulting in the 4 µm sized spherical precursors with a core–shell structure (nanoplate-like surface and fine nano-seed core region). Regulating the reaction time of LiOH and Ni0.55Co0.25Mn0.17(OH)2 is beneficial for enhancing electrochemical performance of nickel-rich cathodes [129]. The samples are collected at three different reaction times (3, 13 and 32 h), SEM of LiNi0.85Co0.25Mn0.17O2 shows that the average sidewall thicknesses are counted to be 0.08, 0.16 and 0.27 µm, and the average edge lengths are 0.17, 0.47 and 0.74 µm, respectively. The sample of 32 h reaction shows the best electrochemical performance. In addition, calcination temperature is also an important factor for reaction of LiOH and Ni0.76Mn0.14Co0.10(OH)2 [130]. By increasing calcination temperatures ranging from 725 °C to 900 °C for 20 h in air, it was found that calcination temperature (≥800 °C) resulted in a significant growth of primary particle size, as well as extended lithium-ion diffusion pathways and inferior rate performance. The preparation process of single-crystal Ni0.83Co0.10Mn0.17(OH)2 and Ni0.8Co0.2Mn0.1(OH)2 precursors is similar with that of traditional secondary particles [131, 132]. The formation process of a single-crystal LiNi0.8Mn0.15Co0.1O2 cathode material was measured by Qian et al. and the ex-situ SEM images showed evolution of particle morphology and size [133]. Single crystal LiNi0.85Co0.15Mn0.10Al0.05O2 displays less aggregation, better homogeneity and a smaller size (~4 µm) compared with that of the secondary particles (~10 µm) [134]. Furthermore, cracks, nanopores and other defects are great suppressed in these single-crystal nickel rich cathode materials.

Moreover, it is found that a core–shell structure is an effective method to improve electrochemical performance of nickel-rich cathodes, and the most studied core–shell materials are LiNi0.85Co0.10Mn0.05O2 (~6 µm) [135], LiNi0.8Co0.10Mn0.10O2 (~5–10 µm) [136], LiNi0.65Co0.08Mn0.17O2 (~10 µm) [137], LiNi0.48Co0.26Mn0.26O2 and LiNi0.5Co0.18Mn0.23O2 (~10 µm) [138], and their synthesis process involves two-time co-precipitation. Thermal-driven degeneration frequently occurs during the sintering process [139], thus, an additional pre-oxidization process was employed to regulate the Li+/Ni2+ cation ordering, various pre-oxidization reagents have been studied such as polyvinylpyrrolidone (PVP) [140] and Na2S2O8 [141]. Tang et al. prepared surface-oxidized LiNi0.81Co0.15Al0.03O2 via dissolving NCA precursors in mixed aqueous solution containing Na2S2O8 and NaOH [142]. TEM analysis indicated that there is an well-organized β-NiOOH layer (4–11 nm), whereas a higher peak intensity ratio of (001)/(101) was found on the precursors surface. After 100 cycles at 90 mA g⁻¹ within 2.75–4.5 V, pre-oxidated NCA delivered 80.3% of its initial capacity in contrast to 67.4% for the raw NCA.

To investigate effect of Mn and Co contents on the nickel rich cathode materials performance, LiNi0.85Co0.15Mn0.15O2 (Ni0.85Co0.15Mn0.15(OH)2 (x = 0–0.15) have been synthesized via traditional co-precipitation method [143], as a result of which, LiNi0.85Co0.05Mn0.1O2 showed the best property. Similar study has been explored for effect of Ni and Mn contents on the nickel-rich cathodes performance.
Figure 1. (A), (C), (E) Schematic illustration of the co-precipitation process of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811), (B), (D), (F) SEM images of NCM811, (A) and (C)–(F) Reprinted with permission from [55]. Copyright (2019) American Chemical Society. (B) Reprinted with permission from [124]. Copyright (2015) American Chemical Society. (G) Schematic illustration of the hydrothermal process of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$\@x{Li–Mn–O}. Reprinted with permission from [153]. Copyright (2018) American Chemical Society. (H) SEM images of LiNi$_{0.8}Co_{0.1}Mn_{0.1}O_2$. Reprinted from [60], Copyright (2020), with permission from Elsevier. (I) SEM images of LiNi$_{0.9}Co_{0.1}Mn_{0.1}O_2$. Reprinted from [159], John Wiley & Sons. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (J) SEM images of LiNi$_{0.9}Co_{0.1}Mn_{0.1}O_2$. Reprinted from [160], Copyright (2019), with permission from Elsevier. (K) SEM images of Li[Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$]O$_2$–Li$_2$MnO$_3$. Reprinted from [161], Copyright (2013), with permission from Elsevier. Solid-state method: (N) and (O) SEM images of NCM811. Reprinted from [162], Copyright (2020), with permission from Elsevier.

Ni$_{0.8-x}$Co$_{0.1}$Mn$_{0.1+x}$(OH)$_2$ ($x = 0, 0.04, 0.08$) were synthesized via traditional co-precipitation [144], all precursors have a spherical morphology ($\sim 10 \mu$m). Cyclability is clearly improved as the Mn content increase and Ni content decrease due to less irreversible side reactions. He et al prepared Ni$_{0.85-x}$Co$_{0.15}$Al$_x$(OH)$_2$ ($x = 0.02, 0.05$ and $0.10$) precursors via traditional co-precipitation method utilizing NaAlO$_2$ as Al solution [145]. The LiNi$_{0.85-x}$Co$_{0.15}$Al$_x$O$_2$ ($5 \mu$m) showed 93.4% of its initial capacity after 100 cycles at $0.5 \degree$C between 2.5 and 4.3 V.
As shown in figure 1(C), rapid co-precipitation was observed when aqueous solution of ammonia and NaOH were pre-added into the reactor, afterwards, aqueous solutions of metal sulfates, NaOH and NH$_4$OH were continuously infused into reactuator, and this process lasted for 1 h. After filtering and washing, the precursor was dried under vacuum at 110 °C for 12 h. Huang et al prepared the Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$OH$_2$ precursors by this rapid co-precipitation, and spherical secondary particles (NCM811) have a diameter ranging from 2 to 50 µm (figure 1(D)). For comparison, some precipitates were ball milled for 3 h, and the obtained powders were spray dried for 5 h (spray dried NCM811 (SD-NCM), figure 1(E)), with an average particle diameter of NCM811 was ∼ 12 µm as shown in figure 1(F) [55]. The SD-NCM displays superior cycling stability under an upper cut-off voltage of 4.5 V. Extensive studies about the facile co-precipitation approach remain interesting, for example, precursor was prepared through dissolving chloride in absolute ethanol [146]. Then, the mixture was mixed with ammonia aqueous solutions following vigorous stirring by peristaltic pump for 2 h. The precipitations were orderly separated, washed, dried and annealed to obtain spheroidal precursors. Well-ordered NCM811 layered oxides have been obtained by calcination with the precursors mixed with Li$_2$CO$_3$ at 800 °C, and the NCM811 powders exhibited suppressed capacity fading. Carbonate co-precipitation has been investigated to improve the electrochemical property of secondary particles, such as core–shell structured Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$CO$_3$ precursors [147]. C$_6$H$_5$NiO$_2$ ethanol solution was added into aqueous solutions containing nickel sulfate, cobalt sulfate, and manganese sulfate to obtain a Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$CO$_3$ core, then Na$_2$CO$_3$ was added to mixture solution and stirred violently for 12 h to obtain carbonate precursors. After calcination at high temperature, core–shell structured 3% C$_6$H$_5$NiO$_2$–NCM811 powders were obtained. To prepare porous microspheres LiNi$_{0.2}$Co$_{0.2}$Mn$_{0.6}$O$_2$, spherical MnCo(0.4) precursors were synthesized by carbonate co-precipitation using Na$_2$CO$_3$ and NH$_3$·H$_2$O as a chelating agent. Then, porous microspheres were obtained by an impregnation method and dispersing MnCo(0.4), LiNO$_3$ and Ni(NO$_3$)$_2$·6H$_2$O in absolute ethanol [78]. To form an homogeneous disperis, the solution was stirred vigorously at 80 °C for 12 h, and then the mixture was dried and calcined in flowing oxygen. The verage diameter of the porous microspheres was ∼ 3 µm. Ma et al synthesized MnCo(0.4) precursors by a similar carbonate co-precipitation using NH$_4$HCO$_3$ as a chelating agent, and the obtained secondary spherical particles had an average diameter of 1.5–4 µm [148]. Similarly, (Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$)CO$_3$(OH)$_{2·2x}$ precursors were synthesized via a carbonate co-precipitation route using NaOH and (NH$_4$)$_2$CO$_3$ as a chelating agent [149]. This process has a faster particle growth rate than hydroxide process using NH$_4$OH as a chelating agent, and the fabricated spherical precursors have an average diameter of 10 µm. Liu et al prepared Ni$_{0.8}$Co$_{0.2}$Al$_{0.1}$OH$_2$ precursors by green and low-cost co-precipitation using C$_6$H$_5$O$_2$KNa·4H$_2$O as a chelating agent. Spherical precursors comprised of primary needle-like primary particles and exhibited a diameter of 5–8 µm [150]. The combination of Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$(OH)$_2$ precursors and MnCO$_3$ is an effective method to prepare xLi$_x$MnO$_2$ · (1 − x)Li[Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$]O$_2$ [151]. Firstly, spherical Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$(OH)$_2$ particles were obtained via a co-precipitation method. Then, the core–shell structured composition was obtained via a solid state ration method using Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$(OH)$_2$ precursors, and MnCO$_3$ and LiOH·H$_2$O as raw materials. All samples exhibited a spherical or elliptical shape and a uniform size distributed with a diameter of around 9 µm. Moreover, Zhou et al synthesized the Ni$_{0.75}$Co$_{0.15}$Al$_{0.1}$(OH)$_2$ precursors via an improved co-precipitation using nano Al$_2$O$_3$ particles as the precipitate nucleus [152]. Perfect spherical LiNi$_{0.75}$Co$_{0.15}$Al$_{0.1}$O$_2$ powders with in diameter of about 10 µm were obtained, and they were composed of primary particles with a diameter of about 1 µm.

3.1.2. Hydrothermal method. Hydrothermal methods have been used to synthesize nickel rich cathode materials. As shown in figure 1(G), core–shell structured Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$O$_2$ was prepared via a combination of co-precipitation and hydrothermal methods [153]. The oxide precursors Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$C$_2$O$_4$·xH$_2$O was prepared by the co-precipitation method using H$_2$C$_2$O$_4$ as a chelating agent. Then, Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$C$_2$O$_4$·xH$_2$O was treated with solution of melamine and manganese acetate based on a hydrothermal method to obtain Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$C$_2$O$_4$·xH$_2$O@Mn$^{2+}$. To alleviate the formation microcracks, Zhang et al prepared primary particle Ni$_{0.8}$Co$_{0.2}$Mn$_{0.1}$O$_2$ by hydrothermal method using urea hydrolyzed into carbonate to precipitate transition metal ions (figure 1(H)) [60]. Otherwise, LiNi$_{0.75}$Co$_{0.15}$Mn$_{0.1}$O$_2$ was synthesized using flower-like Ni(OH)$_2$ precursors (5 µm) [154]. Precursors were prepared hydrothermally using urea and hexadecyl trimethyl ammonium Bromide (CTAB) as surfactants, (Ni:urea = 1:3) showing lower Li$^+$/Ni$^{2+}$ mixing. Similarly, to decrease Li$^+$/Ni$^{2+}$ mixing of LiNi$_{0.75}$Co$_{0.15}$Mn$_{0.15}$O$_2$ materials, Ni$_{0.75}$Co$_{0.15}$Mn$_{0.15}$(OH)$_2$ precursors were prepared through a solvothermal method [155]. Precursors were composed of flowerlike microspheres with a dimension around 2–6 µm. Tian et al prepared Ni$_{0.7}$Co$_{0.15}$Mn$_{0.15}$(OH)$_2$ precursors via a hydrothermal treatment after co-precipitation reaction [156]. As shown in figure 1(I), the LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$ particles were nanoplate-like, which have an average diameter around 300 nm. To investigate the effect of concentration, temperature, and reaction time, Ni$_{0.3}$Co$_{0.2}$Mn$_{0.5}$O$_2$ precursors were prepared by controlling reaction conditions in the hydrothermal method [157]. TEM images showed that spherical particles were composed of primary grains (200–500 nm). When reaction time was 24 h, LiNi$_{0.3}$Co$_{0.2}$Mn$_{0.5}$O$_2$ showed the best cyclability and rate capability. Moreover, Zuo et al prepared Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ precursors by a hydrothermal method [158]. As shown in figure 1(J), the rugby ball-like morphology was the most regular when the molar ratio of urea to the total transition metal cations was set as 5:1.

3.1.3. Sol–gel method. To distinguish surface state and/or bulk structure roles in the cathode materials electrochemical performance, Zhang et al prepared LiNi$_{0.9}$Mn$_{0.1}$O$_2$ via sol–gel
method [159], and then calcined in oxygen and air, respectively. Samples in oxygen were constituted by irregular polyhedral primary particles (200–500 nm) (figure 1(K)) and showed better electrochemical performance. In order to tailor the Li$_2$CO$_3$ surface phase, oxidation extent of Ni$^{2+}$/Ni$^{3+}$ was controlled and oxygen vacancies on LiNi$_{0.8}$Mn$_{0.2}$O$_2$ surface were modulated. Synthesis was accomplished via a sol–gel method and then gel was calcined in air [160]. LiNi$_{0.8}$Mn$_{0.2}$O$_2$ secondary spheres (10 µm) were constituted by primary particles with diameters ranging from 200 to 500 nm (figure 1(L)). However, because of the coating effect, the Li$_2$CO$_3$ surface phase can not only suppress the H$_2$/H$_3$ phase transition but also alleviate the side ration of LiNi$_{0.9}$Mn$_{0.1}$O$_2$ with electrolyte, and eventually lead to a good cycling stability of LiNi$_{0.9}$Mn$_{0.1}$O$_2$. Cyclicity of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ improved by designing a Li$_2$MnO$_3$ shell (0.2–0.3 µm) prepared via a sol–gel deposition method (figure 1(M)) [161].

3.1.4. Solid-state method. To clarify the importance of the size effect, Zhang et al prepared the pristine NCM-811 cathode materials by solid-state method using Li$_2$CO$_3$, NiO, Co$_3$O$_4$, and MnO$_2$ as the initial reactants [162]. Particle size increased with raised calcination temperature (750 °C–950 °C). As shown in figures 1(N) and (O), NCM811–900 °C with D50 for 7.7 µm displays the best discharge specific capacity and cyclability.

3.1.5. Other methods. A simple combustion has also been used to synthesize LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ with a nitrate/urea mixture as fuel [77]. The fabricated samples exhibit a spherical morphology. While, Li et al prepared Ni$_{1−x}$Co$_x$Mn$_{0.5}$O$_2$ ($x = 0.075, 0.05, 0.025$) precursors by ultrasonic spray pyrolysis of metal chlorides solution [163]. The spherical precursors were composed of numerous closely packed primary particles and the particle sizes increase with the increase of Ni content. A hydrometallurgical method has also been proposed to treat high-grade nickel matte and produce LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode materials. This strategy includes oxidation roasting, two-stage leaching, solvent extraction, spray pyrolysis and solid sintering [164], abundant micro pores are observed in the products. Moreover, Zhu et al prepared single-crystal LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ by a spray pyrolysis method, field emission scanning electron microscope (FESEM) images show that their precursors are composed of regular microspheres with diameter of 1–5 µm [165].

In summary, numerous efforts have been devoted on these synthetic methods and great improvements have been obtained for these nickel rich cathode materials for LIBs. Their electrochemistry performance has been summarized in table 1.

3.2. Characterizations

Many characterization techniques are used to confirm the structure and morphology of nickel-rich cathode materials and investigate their structural evolution during charge–discharge process [166, 167]. Firstly, ex-situ and in-situ characterization techniques are used to show phase transition of nickel-rich cathodes during charge/discharge process. Typical ex-situ measurements include XRD [168], focused ion beam (FIB) cutting-SEM and transmission electron microscopy (TEM)–fast Fourier transformed (FFT) [169], time-of-flight secondary ion mass spectrometry (ToF-SIMS), inductive coupled plasma emission spectrometer–atomic emission spectroscopy (ICP-AES), energy-dispersive x-ray (EDX) analysis, x-ray photoelectron spectroscopy (XPS), and Fourier transform (FT) infrared spectroscopy. To confirm the crystal structure of the nickel-rich cathode materials, ex-situ XRD analysis was used to investigate the peak phase [170]. Bulk compositions and surface morphologies of nickel-rich cathode materials can be initially analyzed by SEM and energy dispersive spectrometer (EDS) elemental mapping/ICP-AES/ToF-SIMS [171, 172]. To further explore the surface compositions and oxidation states of the nickel-rich cathode materials, XPS examination is an ideal method to analyze the pristine elements and generated byproducts [90, 170]. In addition, formation of intergranular cracks and void spaces within surface/interface structure can be evident through cross-sectional SEM images of nickel-rich cathode materials before and after cycling [51]. To analyze the surface phase transformation and oxygen reversibility of the cathode materials, high-resolution TEM with FFT, scanning TEM (STEM) and electron energy-loss spectroscopy (EELS) were used to analyze the structural evolution mechanisms of the cycled cathode materials by showing the atomic surface structure and EELS line scans of the O K edge [173, 174]. The phase transition of a cycled LiNi$_{0.9}$Co$_{0.05}$Ta$_{0.05}$O$_2$ (NCTa90) cathode was analyzed via high-resolution TEM image with FT [175]. The results indicate that Li$^+$–deintercalation NCTa90 cathodes exhibit an exceptional cycling stability, since cation ordering is preserved even after 2000 cycles. However, disassembling the batteries to obtain the cycled nickel rich cathode materials at different states may cause some errors due to the phase transition of the samples during the disassembling process [176]. Recently, in-situ XRD has been considered as a powerful technic in studying the real-time microstructural evolution of nickel-rich cathode materials in LIBs. It is beneficial to observe the tiny phase changes that are usually invisible from ex-situ XRD. Liu et al investigated the microstructural evolution including lattice parameters, Li/Ni disorder and $R_{wp}$ of LiNi$_{0.6}$Co$_{0.6}$O$_2$, LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ and LiNi$_{0.6}$Mn$_{0.4}$O$_2$ using in situ high-energy synchrotron-based synchrotron XRD [177].

4. Surface modification of nickel-rich cathode materials

4.1. The group IA and IIA, metal oxides (MO$_x$, $M = Na, K, Mg, Ca$)

Because the discharge processes (Li$^+$–intercalation) of cathode materials are concomitant with reduction processes of TM ions involving Li$^+$ re-intercalation into the nickel-rich cathode materials lattice, these dopants from group I and II A (Na, K, Mg, Ca) may impede to Li$^+$ reinsertion, due to their possible incorporation in the Li sites and formation
Table 1. Synthesis and electrochemical performance of various nickel-rich materials used in LIBs.

| Material | Synthesis method | Cycle performance | Rate performance | Reference |
|----------|------------------|-------------------|-----------------|-----------|
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 77.3/100/40/4.6/25 | 153.4/2000 | [124] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 87.9/200/190/4.3/25 | 148/1900 | [126] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 88/200/40/4.3/30 | 167/2600 | [125] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 84.8/400/100/4.35/25 | — | [132] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 82.7/100/0.5C/4.3/55 | 163.5C | [143] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 82.3/150/100/4.3/60 | 90/1000 | [135] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 76.6/200/204/4.4/30 | — | [136] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 96.5/50/102.8/4.3/55 | ~130/1000 | [137] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 93.2/100/100/4.5/55 | ~82/1000 | [138] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 91.1/100/100/4.5/55 | ~83/1000 | [138] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 90.7/100/0.2C/4.3/25 | — | [140] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 99/100/100/4.3/25 | 130/3/1000 | [141] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 84.1/50/100/4.3/25 | — | [139] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 83.2/100/6C/4.3/25 | — | [127] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 80/4/300/5C/4.3/45 | 151/10C | [128] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 94.7/50/40/4.4/30 | — | [131] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 78/50/100/0.4/3/25 | 103/10 000 | [129] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 70.2/100/100/4.5/55 | 155/1000 | [144] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 86.2/100/100/4.5/60 | 164/2000 | [130] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 80/3/100/90/4.5/25 | 168/360 | [142] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 88.5/200/5C/4.3/25 | ~150/5C | [145] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 94.9/100/210/4.3/45 | ~195/420 | [134] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 81.9/200/180/4.3/60 | 140.9/1800 | [55] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation and spray drying techniques | 72.8/500/500/80/4.5/25 | ~100/1600 | [147] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 89.7/100/200/4.3/30 | 79/10 000 | [78] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 81.5/100/200/4.3/25 | 100/1000 | [148] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 97.7/50/10/4.5/55 | — | [151] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 91/100/1C/4.3/25 | 138/5C | [149] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 91.5/100/0.5C/4.3/25 | 171/4/C | [150] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 73/300/200/4.5/60 | 140.6/2000 | [152] |
| LiNi0.8Co0.1Mn0.1O2 | Carbonate co-precipitation | 65.1/100/160/4.3/55 | 116/1600 | [153] |
| LiNi0.8Co0.1Mn0.1O2 | Hydrothermal, solvothermal | 94.1/100/900/4.3/25 | 155.6/1800 | [60] |
| LiNi0.8Co0.1Mn0.1O2 | Hydrothermal | 83.2/120/200/4.6/25 | 170.9/1000 | [154] |
| LiNi0.8Co0.1Mn0.1O2 | Solvothermal | 86/100/100/4.3/25 | ~145/400 | [155] |
| LiNi0.8Co0.1Mn0.1O2 | Co-precipitation | 84.4/100/200/4.5/25 | 143.0/2000 | [156] |
| LiNi0.8Co0.1Mn0.1O2 | Hydrothermal | 79.4/50/20/4.6/25 | ~115/800 | [157] |
| LiNi0.8Co0.1Mn0.1O2 | Hydrothermal | 82.9/100/36/4.3/25 | 112.4/1800 | [158] |
| LiNi0.8Co0.1Mn0.1O2 | Sol-gel | 57/100/276/4.5/25 | 109.7/2760 | [159] |
| LiNi0.8Co0.1Mn0.1O2 | Sol-gel | 71.3/100/276/4.5/25 | ~80/2760 | [160] |
| LiNi0.8Co0.1Mn0.1O2 | Sol-gel deposition | 97.7/100/100/4.5/55 | 135.4/1000 | [161] |

* Capacity retention (%)/cycle number/current density (mA g\(^{-1}\))/cut-off voltage (V)/cycle temperature (°C), room temperature at 25 °C.

of surface layers. However, cycling stability of the modified materials can be improved due to stability of bulk and surface structures of the surface modified nickel rich cathode materials. For example, Na-doped LiNi0.8Co0.2Mn0.1O2 (NCM523) was synthesized by a hydroxide co-precipitation route [178]. The substitution of Na for Li resulted in a more ordered α-NaFeO2 structure, accompanied by the slight enlargement of the layered distance and lower cation mixing, which was attributed to the pillaring effect of Na ions with large radius. As a result, Li0.97Na0.03Ni0.8Co0.2Mn0.5O2 delivered
specific capacities of 228.43, 163.12, 121.43, 95.56 and 60.09 mAh g$^{-1}$ at a current density of 40, 200, 2000, 6000 and 10 000 mA g$^{-1}$, which were superior to those of the bare NCM523 due to the rapid diffusion of Li-ion in the bulk lattice. Improved reversibility and electrochemical activity, low potential polarization after the substitution of Na for Li were further verified by stability of both potential and capacity as well as the integrated spherical morphology upon long-term cycling. In order to stabilize both capacity and potential, gradient Na-doped LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) was prepared by Wang et al [179]. Na-doped and un-doped NCA delivered specific capacities of 150 and 89 mAh g$^{-1}$ after 300 cycles at a current density of 200 mA g$^{-1}$, corresponding to capacity retention of 81.6% and 48.1%, respectively. Even at a high current rate of 1000 mA g$^{-1}$, Na-doped NCA achieved a capacity of 135.5 mAh g$^{-1}$.

It is worth noting that the inherent structural and thermal instability can be suppressed by using an optimized LiNi$_{0.90}$Co$_{0.07}$Mg$_{0.03}$O$_2$ with greater conductivity [45]. In the voltage range of 2.8–4.5 V, LiNi$_{0.90}$Co$_{0.07}$Mg$_{0.03}$O$_2$ demonstrated a capacity of 148.7 mAh g$^{-1}$ at 360 mA g$^{-1}$ after 300 cycles (84.3% capacity retention). Meanwhile, the LiNi$_{0.90}$Co$_{0.07}$Mg$_{0.03}$O$_2$ could deliver a considerably high capacity of 142.8 mAh h g$^{-1}$ at a high current rate of 1800 mA g$^{-1}$. When tested at −5 °C and 60 °C, capacity retention of 81.2% and 76.0% was achieved after 200 cycles at 180 mA g$^{-1}$, respectively. As shown in in-situ XRD data, LiNi$_{0.90}$Co$_{0.07}$Mg$_{0.03}$O$_2$ experienced a H1–H2–H3 phase transition at high voltage range, because Mg doping stabilized...
the layered structure by suppressing cation mixing. It should also be stated that Mg-doped NCA was synthesized through a solid state reaction [181]. Mg–NCA displayed a typical layered hexagonal structure without impurity phase, with an increased percentage of Ni^{2+} on the surface. After 100 cycles at 92.5 mA g⁻¹, Mg–NCA delivered 84.9% of its initial capacity in contrast to 63.2% for the pristine NCA (PNCA). Electrical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique tests confirmed that Mg-doped NCA showed a lower total resistance value after 100 cycles, and a higher Li⁺-ion diffusion coefficient compared to PNCA during charge/discharge process. Decoupling ultrathin MgO, Al₂O₃ and ZrO₂ coating layer atomic layer deposition (ALD) have been reported by Laskar et al. [182]. After 180 cycles at 1.0 °C, MgO-coated NCM cathode demonstrated a high capacity of 130 mAh g⁻¹ with capacity retention of 82%, while the capacity retention of pristine NMC was 70%. Even at a high current rate of 10.0 °C, MgO-coated NCM cathode exhibited a capacity of 115 mAh g⁻¹, in contrast the Al₂O₃-coated and uncoated NMC exhibited a capacity of 45 and 30 mAh g⁻¹, respectively. As shown in figures 2(C)–(E), MgO-coated NCM cathode had a higher Li⁺-diffusion coefficient, which resulted in lower overpotential on the surface and improved rate performance.

Ga doping, e.g. LiNi₀.8(1−x)Co₀.1Mn₀.1CaₓO₂ (x = 6%), has also been investigated by Chen et al, because Ga has a lower valence state and larger radius compared to Ni²⁺ [183]. In the voltage range of 2.5–4.5 V, LiNi₀.8(1−x)Co₀.1Mn₀.1CaₓO₂ exhibited a discharge capacity of 131 mAh g⁻¹ after 100 cycles at 32 mA g⁻¹, while bare LiNi₀.8Co₀.1Mn₀.1O₂ only delivered a capacity of 103 mAh g⁻¹. While, 6% Ca doped LiNi₀.8Mn₀.1Co₀.1O₂ possessed a lower degree of Li⁺/Ni²⁺ disorder and a faster diffusion coefficient of Li⁺ (figure 2(F)), and the voltage fading was also alleviated.

4.2. The group IIIA, metal oxides (MOₓ, M = B, Al)

B, as a typical element in IIIA group, can reduce the surface energy of the (003) planes of layered oxide cathode materials to produce a highly textured microstructure, because its ionic radius (B³⁺, 0.27 Å) is smaller than that of Li⁺ (0.76 Å), Ni²⁺ (0.69 Å), Co³⁺ (0.545 Å) and Mn²⁺ (0.53 Å). Some work has been done by Park et al to study the effects surface modification by using B₂O₃ with an in-situ high-temperature calcination method [57]. XRD and TEM results indicated that prepared samples had a rhombohedral crystal structure with a R-3m space group and average lengths of 0.55–1.1 µm. B₁₀–NCM90 with a highly textured microstructure delivered a capacity retention of 91% after 100 cycles at 90 mA g⁻¹ and 55 °C, which was 15% higher than that of pristine NCM90. Based on density functional theory calculation results, the higher capacity retention was attributed to the alleviation of intrinsic internal strain and the reduction of a small amount of Ni²⁺ to Ni³⁺. In contrast, obvious microcracks were observed in bare NCM (figure 3(A)). Ryu et al prepared Li[Ni₀.87Co₀.09Al₀.03B₁₀O₂ (B–NC88) by adding B₂O₃ during the lithiation of the hydroxide precursors and Al(OH)₃ [184]. TEM results indicated that elongated primary particles were ~500 nm long and ~100 nm wide. After 100 cycles at 90 mA g⁻¹ and 45 °C, B–NC88 exhibited a high-capacity retention of 88.7%, and that of pristine P–NCA89 is 74.4%. Even at a pouch-type full-cell with a graphite anode was cycled between 3.0 and 4.2 V at 180 mA g⁻¹, B–NC88 retained a capacity retention of 83% after 1000 cycles, while the capacity retention of P–NCA89 was only 49.0%. As shown in figures 3(B) and (C), the cycled B–NC88 cathode maintained its initial (003) contour plot well, even after repeated lattice contraction and expansion; particles were also free of micro-cracks. While, Li et al raised an interesting question regarding the state of B₂O₃ coating in polycrystalline cathode materials [185]. B₂O₃-coated LiNi₀.8Co₀.12Mn₀.05O₂ was synthesized through a mecano-chemical bonding technique, and SEM results indicated that B₂O₃ with a molten state filled in the boundaries among the primary particles. The 0.5% B₂O₃-coated LiNi₀.83Co₀.12Mn₀.05O₂ delivered a discharge capacity of 154.2 mAh g⁻¹ after 200 cycles at 200 mA g⁻¹ with a capacity retention of 87.7%, whereas the pristine sample delivered a capacity retention of 69.4%. The improved cycling stability was associated with a B₂O₃ coating layer, which could greatly inhibit the irreversible phase transitions and the extension of microcracks. However, the B₂O₃ coating layer acted as a resistance layer because of its electrically and electrochemically inactive properties. Therefore, lithium-ion conductors have been developed as alternative coating materials. Hashigami et al prepared lithium boron oxide (LBO)-coated LiNi₀.8Co₀.15Mn₀.05O₂ by an antisolvent precipitation method [186]. XRD results indicated that the diffraction peak intensity ratio of the (003) to the (104) decreased by the coating of LBO. After 50 cycles at 200 mA g⁻¹ within 2.5–4.5 V, the 5 wt. % LBO–NCM maintained 85.6% of its initial capacity, in contrast to 53.8% for the pristine NCM. Cross-sectional SEM images of cycled samples showed that crack formation was excluded from spray pyrolyzed particles (<1 µm), which was likely to be the reason why the LBO coating could improve the cycle ability and rate capability. Interestingly, in a more rigorous study on anion substitution, Li[Li₀.2Co₀.1MnₓO₂]–(BO₃)ₓ(BO₄)ₒ₋ₓO₁₋ₓ (x = y = 0, 0.01 and 0.03) were prepared by adding boric acid (H₃BO₃) before the lithiation of the hydroxide precursors [187]. In the voltage range of 2.8–4.5 V, Bₓ–NCM delivered 76.07% of the initial discharge capacity after 100 cycles at 180 mA g⁻¹, whereas the corresponding capacity retention of the pristine counterpart was only 59.15%. The improved performance was attributed to boracic polyanion doping, which could greatly enhance Li⁺ diffusion coefficient in NCM.

Al³⁺ doped nickel-rich compounds have attracted tremendous attention due to their high cycling stability derived from enhanced Li⁺ kinetics and structural stability, although their initial discharge specific capacities were descended due to incorporation of inactive Al³⁺. As expected, studies on heterogeneous Al³⁺ doped LiNi₀.7Co₁₅Mn₀.15O₂ show that it delivered a capacity retention of 90.6% after 100 cycles at 20 mA g⁻¹ and 50 °C, while pristine NCM delivered a capacity retention of only 68.5% [188]. XRD results indicated that the lattice parameter a value decreased...
Figure 3. (A) Mosaic dark-field STEM images of FIB-prepared NCM90 and B$_{1.0}$–NCM90 after 100 cycles at 55 °C [57]. John Wiley & Sons. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Contour plots of (003) reflection of P–NCA89 and B–NCA88 measured at 1st and 1000th cycles; (C) cross-sectional SEM images after 1000 cycles for P–NCA89 and B–NCA88 cathodes. Reprinted from [184], Copyright (2020), with permission from Elsevier. (D) Differential capacitance vs voltage curves of LiNi$_{0.88}$Co$_{0.095}$Mn$_{0.025}$O$_2$ (LNCMO) and LNCMO–Al$_{2}$% cathodes. Reprinted with permission from [189]. Copyright (2019) American Chemical Society. (E) Mosaic scanning and high-resolution TEM image of NCA90 and NCA–NCMA90 cathodes after 1000 cycles. Reprinted from [56], Copyright (2019), with permission from Elsevier. (F) TEM image of the cross-section of a single particle and linear scanning results on this cross-section of Al$_{3}^{3+}$-enriched LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$O$_2$. Reprinted from [191], Copyright (2019), with permission from Elsevier. (G) Cross-section SEM and high-angle annular dark-field (HAADF)-STEM pictures of NMC76 and 1% Al–NMC76 samples. Reprinted with permission from [192]. Copyright (2020) American Chemical Society. (H) Mosaic scanning-TEM image of cycled FCG76 and Al–2 FCG76 after 1000 cycles in a full cell; (I) full range (10° ≤ 2θ ≤ 80°) of TR-XRD patterns of partially deintercalated FCG76 and Al–2 FCG76 cathodes during heating from 30 °C to 600 °C. Reprinted with permission from [193]. Copyright (2017) American Chemical Society.

and the lattice parameter $c$ value increased after Al$_{3}^{3+}$ doping. The doped inactive-Al$_{3}^{3+}$ cations formed a solid solution with Ni$_{3}^{3+}$ and Co$_{3}^{3+}$ in the transition-metal 3$a$ sites, which was beneficial to Li$^+$ transportation during cycling. Therefore, Al$_{3}^{3+}$ doped NCM exhibited high capacities of 145 and 115 mAh g$^{-1}$ at high current rate of 2000 and 4000 mA g$^{-1}$, respectively, which was much better than that of the pristine NCM electrode. Yang et al fabricated the Al$_{3}^{3+}$ doped LiNi$_{0.88}$Co$_{0.095}$Mn$_{0.025}$O$_2$, in which Al$_{3}^{3+}$ preferred to substitute the Ni$_{3}^{3+}$/Ni$_{2}^{2+}$ sites in the sintering process [189]. The $c/a$ values increased with the increment introduction of Al$_{3}^{3+}$, suggesting that Al$_{3}^{3+}$-doping was conducive to the formation of the layered structure. Benefiting from the radial arrangement of primary grains, the
1.0%, 2.0%, 3.0% of Al$^{3+}$-doped LiNi$_{0.88}$Co$_{0.059}$Mn$_{0.025}$O$_2$ cathode exhibited discharge capacities of 160.4, 174.0, and 163.0 mAh g$^{-1}$ at 200 mA g$^{-1}$ after 150 cycles, corresponding capacity retention up to 83.45%, 91.58%, and 86.56%, respectively, while pristine LiNi$_{0.88}$Co$_{0.059}$Mn$_{0.025}$O$_2$ showed a capacity retention of only 52.2%. Particularly, the 2.0% Al$^{3+}$-doped LiNi$_{0.88}$Co$_{0.059}$Mn$_{0.025}$O$_2$ exhibited a discharge capacity of 165.7 mAh g$^{-1}$ even at 2000 mA g$^{-1}$. Moreover, voltage deterioration was significantly suppressed by homogeneous Al$^{3+}$ doping (figure 3(D)). Similar improvements with minimal cracking were observed in core–shell structured Li[Ni$_{0.886}$Co$_{0.049}$Mn$_{0.050}$Al$_{0.015}$]O$_2$ (NCA–NCMA90) after charging/discharging [56]. Magnified STEM images indicated that 9–10 µm spherical particles were composed of the rod-shaped primary particles (~300 nm) with a strong crystallographic texture, which expedited Li intercalation and nano-sized core primary particles suppressed the propagation of interparticle microcracks (figure 3(E)). As a result, NCA–NCMA90 maintained a capacity retention of exceeded 93% after 100 cycles at 100 mA g$^{-1}$ and 45 °C within 2.7–4.3 V, which was higher than Li[Ni$_{0.888}$Co$_{0.059}$Al$_{0.015}$]O$_2$ (NCA–NCMA90) (capacity retention of 83.3%). In the voltage range of 2.7–4.5 V, the NCA–NCMA90 cathode maintained 88.3% of the initial capacity after 200 cycles at 100 mA g$^{-1}$, whereas that of PNCMA90 cathode was limited to 71.7%. When cycled between 3.0 and 4.2 V at 200 mA g$^{-1}$ in a pouch-type full cell, NCA–NCMA90 cathode delivered 90.5% of its initial capacity after 1000 cycles. Kim et al investigated the electrochemical properties of Li[Ni$_{0.89}$Co$_{0.05}$Mn$_{0.05}$Al$_{0.01}$]O$_2$ (NCMA89), Li[Ni$_{0.90}$Co$_{0.05}$Mn$_{0.05}$]O$_2$ (NCM90) and Li[Ni$_{0.885}$Co$_{0.10}$Al$_{0.015}$]O$_2$ (NCA90) before and after long-term cycling [190]. In the voltage range of 2.7–4.5 V, NCMA90 maintained 87.1% of its initial capacities after 100 cycles at 90 mA g$^{-1}$, whereas the corresponding capacity retention of the NCA90 and NCM90 were 73.3% and 82.3%, respectively. After 500 cycles at 90 mA g$^{-1}$ and 45 °C, NCMA90 retained 82.6% of the initial capacity, while that of NCM90 and NCA90 were only 53.8% and 50.1%, respectively. There are no visible cracks in the cycled NCMA90 cathode, confirming its superior mechanical stability compared with cycled NCA90 and cycled NCM90 with microcracks. The respective average O vacancy formation energies for the NCMA90, NCA90 and NCM90 cathodes were 0.80, 0.87 and 0.72 eV, indicating that the oxygen atoms were most likely released from the NCMA90 cathode and improved structural stability in the NCMA90. A comprehensive study of surface-Al$^{3+}$-enriched LiNi$_{0.70}$Co$_{0.15}$Mn$_{0.15}$O$_2$ utilized an innovative coating-diffusion strategy [191]. TEM results confirmed that the Al$^{3+}$ content decreased while Ni, Co and Mn concentrations increased on the outer ~0.8 µm thick surface (figure 3(F)). Benefiting from decreased Li$^{+}$/Ni$^{2+}$ disorder, surface-Al$^{3+}$-enriched LiNi$_{0.70}$Co$_{0.15}$Mn$_{0.15}$O$_2$ maintained a capacity retention of 94.3% after 200 cycles at 100 mA g$^{-1}$ and 50 °C. Even at a high current rate of 2000 and 4000 mA g$^{-1}$, capacities of 162 and 145 mA h g$^{-1}$ were also achieved. SEM and STEM were used to get insights into bulk integrity, structure, and interfacial stability of Al-doped LiNi$_{0.70}$Co$_{0.15}$Mn$_{0.10}$O$_2$ (NMC76) [192]. The results indicated that the surface of doped NMC76 particles became rougher as Al doping increased, and Al species displayed a concentration gradient from the surface to the subsurface in the layered structure. In the voltage range of 2.7–4.5 V, 1% Al-doped NMC76 delivered a capacity retention of 79.2% after 500 cycles, whereas pristine NMC76 only retained a capacity retention of 3.4%. This bulk structural stability (figure 3(G)) was ascribed to Al doping into the NMC76 lattice, which suppressed chemical reactions with the acidic electrolyte. Kim et al prepared Al-doped LiNi$_{0.76}$Co$_{0.09}$Mn$_{0.15}$O$_2$ with concentration gradients to suppress the microcracking (figure 3(H)) and preserve the mechanical integrity of the cathode particles [193]. Benefiting from a slight decrease in cation mixing, the 2 mol% Al doped LiNi$_{0.76}$Co$_{0.09}$Mn$_{0.15}$O$_2$ retained 95% of its original capacity after 1000 cycles at 1.0 °C in pouch-type full cells with graphite anodes, whereas pristine and gradient NCM (FCG76) retained 80% and 88% of the initial capacity. As shown in in-situ time-resolved (TR)-XRD experiment (30 °C–600 °C) results, partially deintercalated of 2 mol% Al doped NCM transformed to a disordered spinel structure (Fd-3m) at higher temperatures (figure 3(I)).

The protective layer formed on the surface of nickel-rich cathode materials can effectively inhibit the dissolution of Ni, Co, and Mn ions and improved thermal stability by suppressing direct contact between electrolyte and Li$^{+}$-deintercalation nickel-rich cathode materials. Liao et al substantiated this by prepared Al$_2$O$_3$ coated gradient LiNi$_{0.62}$Co$_{0.14}$Mn$_{0.24}$O$_2$, and it can deliver 89% of its initial discharge capacity after 50 cycles at 36 mA g$^{-1}$ and 55 °C in the voltage range of 2.7–4.5 V, while the corresponding capacity retention of the pristine and gradient NCM were only 51% and 81%, respectively [194]. Li[Co$_{0.70}$Ni$_{0.12}$O$_{2.15}$]O$_2$ coated by Al$_2$O$_3$ have positive effects for suppressing the microcracking and preserving its mechanical integrity [195]. This modification ultimately results in lower cation mixing and leads to a capacity retention of 95.0% after 1000 cycles at 1.0 °C in pouch-type full cells with a graphite anode, whereas pristine Li[Ni$_{0.75}$Co$_{0.12}$Mn$_{0.15}$]O$_2$ only demonstrated a capacity retention of 87.9%. Nickel-rich cathode materials also undergo the H$_2$O effect during sintering process. Al$_2$O$_3$-coated LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ was prepared via liquid-phase trimethylaluminum treatment powders, which leads to formation of Al$_2$O$_3$ coating layer and the removal of H$_2$O [196]. As a result, Al$_2$O$_3$-coated LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ delivered a discharge capacity of 169 mA h g$^{-1}$ after 500 cycles at 1.0 °C and 45 °C in single-layer pouch cells with a graphite anode. While pristine LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ only demonstrated a discharge capacity of 150 mA h g$^{-1}$. To avoid the effect of carbon dioxide, ultra-thin Al$_2$O$_3$-encapsulated LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ was prepared by creating a uniform hydroxide layer on the LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ surface that employed carbon dioxide, ultra-thin Al$_2$O$_3$ coating layer and the removal of H$_2$O [196]. As a result, Al$_2$O$_3$-coated LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ delivered a discharge capacity of 169 mA h g$^{-1}$ after 500 cycles at 1.0 °C and 45 °C in single-layer pouch cells with a graphite anode. While pristine LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ only demonstrated a discharge capacity of 150 mA h g$^{-1}$. To avoid the effect of carbon dioxide, ultra-thin Al$_2$O$_3$-encapsulated LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ was prepared by creating a uniform hydroxide layer on the LiNi$_{0.6}$Co$_{0.1}$Mn$_{0.3}$O$_2$ surface that employed carbon dioxide, ultra-thin Al$_2$O$_3$ coating layer and the removal of H$_2$O [196].
function of nanoscale Al$_2$O$_3$ layer, pristine and the 2% Al$_2$O$_3$-encapsulated LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.8}$O$_2$ (A-O-2) delivered capacity retentions of 54% and 83% after 100 cycles at 1.0 °C and 55 °C within 3.0–4.6 V, respectively. In the voltage range of 3.0–4.35 V, the A-O-2 delivered a capacity retention of 80% after 800 cycles at 1.0 °C of pouch-type full-cells. Fourier filtered transforms and cross-sectional SEM images showed that no phase evolutions and cracks were found in the cycled A-O-2 sample, while the Al$_2$O$_3$ still existed in the edge of particles, which was highly consistent with the long-term life test results. Nevertheless, the strategy of using Al$_2$O$_3$ as a physical barrier coating is an effective way to overcome these instabilities in layered nickel-rich oxides [198]. As shown in Ni K-edge x-ray absorption near-edge spectroscopy data, the oxidation state of Ni in Al$_2$O$_3$ coated Ni-600 °C electrode is much lower than that of a pristine sample at 4.3 V. Also, the Al$_2$O$_3$ coated Ni-900 °C cathode can be continually oxidized more than at 4.3 V.

Ionic conductor LiAlO$_2$ deposited on the surface of nickel-rich cathode materials can effectively improve the diffusion coefficient of Li$^+$ ions and suppress the undesirable side reactions. Besides that, the partial migration of Al$^{3+}$ to the host of nickel-rich materials also improved the structure stability. As reported by Huang et al., LiAlO$_2$ coated LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$ delivered a discharge capacity of 191.8 mA h g$^{-1}$ after 50 cycles at 200 mA g$^{-1}$ in the voltage range of 2.8–4.5 V (capacity retention of 98.7%), while pristine LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$ delivered a discharge capacity of only 158.4 mA h g$^{-1}$ (capacity retention of 84.8%) [199]. EDS mapping indicated that most of the Al$^{3+}$ existed in the coating layer on the surface of LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$ rather than incorporating into bulk LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$. High resolution transmission electron microscope (HRTEM) images showed that the thickness of the coating layer was 5–7 nm for 1 wt.% LiAlO$_2$ coated LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$. The structural stability of LiNi$_{0.8}$Mn$_{0.2}$Co$_{1.0}$O$_2$ was enhanced by using LiAlO$_2$ coating, and it led to a capacity retention of 89.1% after 50 cycles at 280 mA g$^{-1}$ within 2.5–4.5 V, which was higher than pristine NCM (82.5% capacity retention) [200]. XRD results indicated that the intensity ratio of I$_{200}$/I$_{001}$ increased after LiAlO$_2$ surface modification. Electrical conductivities of pristine NCM and 5% LiAlO$_2$ coated NCM were 1.12 and 8.21 S m$^{-1}$, respectively. AlCl$_3$ solution has also been used as surface coating solvent, since the oriented deposition of Al(OH)$_3$ layer was formed on surface of hydroxide precursors [201]. HRTEM images showed that the thickness of the coating layer was about 5 nm for 2.2 wt.% LiAlO$_2$ coated NCM. Benefiting from lower Li$^+$/Ni$^{3+}$ disorder, the 2.2 wt.% LiAlO$_2$-coated NCM obtained a discharge capacity of 159.9 mA h g$^{-1}$ with a capacity retention of 85.8% after 800 cycles at 0.5 °C, while pristine NCM delivered a discharge capacity of only 112.8 mA h g$^{-1}$. Even at a high current rate of 10.0 °C, a capacity of 135.2 mA h g$^{-1}$ was also achieved for the 2.2 wt.% LiAlO$_2$-coated NCM. The cycling capability of the materials was also demonstrated by a LiAlO$_2$ coated LiNi$_{0.6}$Co$_{0.2}$Al$_{0.2}$O$_2$ cathode, which exhibited a capacity retention of 93.4% at 1.0 °C after 100 cycles, while that of pristine LiNi$_{0.9}$Co$_{0.07}$Al$_{0.03}$O$_2$ 80.8% [202].

XRD and HRTEM results indicated that a γ-NaFeO$_2$ type structured LiAlO$_2$ on the surface could be observed, with a thickness of about 10 nm.

4.3. The group IVA, metal oxides (MO$_x$, M = Si, Sn)

Carbon is low-cost with high electrical conductivity, and carbon coating on nickel rich cathode materials can resist acute side reactions between Ni$^{3+}$ and carbonate electrolyte. LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA) as the core and carbon composite as shell cathode material were synthesized by a solvent-free mecano-fusion method [203]. Discharge capacity of PNCA was 110 mA h g$^{-1}$ at 100 mA g$^{-1}$ after 250 cycles and the capacity retention was 71%, while discharge capacity of modified NCA was 150 mA h g$^{-1}$ (capacity retention of 84%). In particular, surface modified NCA exhibited a discharge capacity of 139 mA h g$^{-1}$ even at 800 mA g$^{-1}$, while discharge capacity of bare NCA was only 106 mA h g$^{-1}$. The core–shell structured materials experienced a much lower Li$^+$ diffusion barrier as compared to PNCA materials owing to slight expansion of the inter-slab distance along the c-axis (figure 4(A)). Volumetric change along the grain boundaries is also inevitable in cathode materials. Accommodated 3D graphene aerogel network aerogel was first introduced in 2019 for LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ by a modified Hummers’ method [204]. When tested at 200 mA g$^{-1}$, a capacity retention of 92.69% was obtained after 250 cycles. Particularly, the composites exhibited an outstanding rate performance of 130.9 and 106.8 mA h g$^{-1}$ at 1000 and 2000 mA g$^{-1}$, respectively. It was beneficial from the rapid Li$^+$ and electrons transportation mobility during the Li$^+$-intercalation/deintercalation process. Son et al. discovered a facile chemical vapor deposition process with CO$_2$ and CH$_4$ for LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$, and yielded a conductive and protective artificial SEI layer consisting of alkyl lithium carbonate (LiCO$_2$R) and Li$_2$CO$_3$ [205]. With cut-off voltage of 4.4, 4.5, and 4.6 V, CO$_2$ + CH$_4$ – LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ maintained capacity retentions of 98.5%, 96.5%, and 95.1% at 90–100 mA g$^{-1}$ after 100 cycles, respectively. With the same voltage ranges, lower retentions of 93.8%, 92.7%, and 91.1% were showed for pristine LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$. The high electrochemical performance of CO$_2$ + CH$_4$ – LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ was attributed to the surface coating effect toward mitigated side reactions, following suppression of oxygen evolution and consequent structural instability (figure 4(B)). Similar to CO$_2$ + CH$_4$, N$_2$ + CH$_4$ is also helpful for the modification of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$, which yielded a conductive and protective artificial SEI layer consisting of amorphous carbon, alkyl lithium carbonate, and lithium carbonate (Li$_2$CO$_3$) [206]. As shown in cross-sectional TEM and EDS analysis results (figure 4(C)), both the surface and internal voids were throughout coated during the coating process when using CH$_4$. In the voltage range of 2.5–4.5 V, the capacity retention values were 91.83% and 95.97% at 100/20 mA g$^{-1}$ after 100 cycles for pristine and CH$_4$-NCA, respectively. These reports effectively solve the issues resulting from unsatisfactory electrical conductivity and interfacial instability at high cut-off voltage. The LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$
structure was also modified by reduced graphene oxide (rGO) with electrostatic interactions and forming a ∼2 nm thickness coating layer [207]. Because of its interfacial stability, the obtained rGO–LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} maintained a reversibility of 179.9 mAh g^{-1} at 1.0 °C over 100 cycles in a potential range of 3.0–4.5 V without inner phase transformation and structural degradation (figures 4(D) and (E)). Following this concept of rGO wrapping, high-quality rGO-encapsulated LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2} was prepared to improve its Li-storage performances and thermal stability [208]. As a result, the fabricated rGO–LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2} exhibited a capacity retention of 86% at 180 mA g^{-1} at 0.5 °C, while the counterpart of LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2} was 73%. Even at a high current rate of 1800 mA g^{-1}, rGO–LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2} delivered an average discharge capacity of 135 mAh g^{-1} in contrast to 117 mAh g^{-1} for the LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2}. The remarkable cycle stability and rate property of the rGO–LiNi_{0.815}Co_{0.15}Al_{0.035}O_{2} were mainly attributed to the lower degree of Li^{+}/Ni^{2+} mixing, and the well-resigned rGO coating layers with excellent ionic and electronic conductivity.

In addition, forming a Si-based coating layer, on nickel rich cathode materials surface has also been considered as a promising strategy to improve its electrochemical performance, e.g. SiO_{2} [209], ultrathin Si–O film [210], Li–Si–O [211]. The effects on the crystal structure stability and electrochemical property vary for silicon compositions. For example, SiO{2} has been used to suppress the growth of interfacial impedance due to a scavenging effect for the HF. A SiO{2} coating layer (thickness <10 nm) was designed on LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} [209]; the 3.0 wt.% SiO{2}-coated LiNi_{0.6}Co_{0.2}Mn_{0.2}O_{2} exhibited a discharge capacity of 164.7 mAh g^{-1} at 0.5 °C and 60 °C after 50 cycles, while that of pristine NCM was 144.7 mAh g^{-1}. Meanwhile, a molecular coating strategy easily forms a ultrathin Si–O film on LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} [210]. The lithium silicate acted as a sintering agent on calcination, and resulting in a high-density grain boundary.
XRD results indicated that Si was usually coordinated to oxygen in a tetrahedral configuration, and TEM images indicated that the Si–O film could exist in a monolayer or a very few layers. After 300 cycles at 200 mA g⁻¹, the electrode with Si–O film surface-modified LiNi₀.₅Co₀.₂Mn₀.₃O₂ delivered 87.5% of its initial capacity, while that of pristine LiNi₀.₅Co₀.₂Mn₀.₃O₂ was 62.57%. A reversible capacity of 155.₈ mAh g⁻¹ was also achieved even at a high current rate of 400 mA g⁻¹. The characteristic peaks of electrodes obtained after 300 cycles at 1.₀ °C remained a typical layered α-NaFeO₂ structure. The Li⁺ diffusion coefficients increased from 1.₂₂ × 10⁻¹₁ cm² s⁻¹ to 2.₈₂ × 10⁻¹¹ cm² s⁻¹. It was reported that the formation of lithium silicate coating layer is effective for preventing crack formation and decomposition of electrolyte [212]. Cross-sectional TEM analysis indicated that Si-rich regions were concentrated not only on the particles surface, but also at the grain boundaries even at a depth of 4₀₀ nm. In the voltage range of 2.₅–4.₆ V, capacity retentions of 7₁.₄% and 8₁.₆% were obtained after 100 cycles for pristine and lithium silicate-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂, respectively. It revealed that in-situ Li–Si–O coating can enhance structural reversibility of LiNi₀.₅Co₀.₂Mn₀.₃O₂, where density of secondary particles was increased and pores between primary particles was greatly reduced [211]. TEM-EDX elemental maps showed that Si was localized at the grain boundaries and near the center of the particle. In the voltage range of 3.₀–4.₅ V, the 1 wt.% Li–Si–O–NCM811 delivered a discharge capacity of 1₈₃ mAh g⁻¹ after 100 cycles at 20 mA g⁻¹ (capacity retention ratio of 8₅.₉%), whereas the corresponding capacity retention of the pristine NCM811 was only 7₉.₀%. Cross-sectional SEM images showed that visible micro-intergranular cracks were observed for pristine NCM811, while the 1 wt.% Li–Si–O–NCM811 particle were almost free from visible microcracks after 100 cycles (figure 4(F)).

Recently, it was found that Sn-modification can obviously enhance the cycle behavior of nickel-rich cathode materials. For example, the cyclic stability of LiNi₀.₅Co₀.₂Mn₀.₃O₂ was greatly improved at high voltage with SnO₂ surface-modification [21₃]. XRD results indicated that the intensity of the (1₀₄) diffraction peak reduced, and the value of I₁₀₀₃/I₁₀₄₀ ratio was significantly enhanced. In the voltage range of 2.₈–4.₄ V, the 3 wt.% SnO₂ modified LiNi₀.₅Co₀.₂Mn₀.₃O₂ exhibited a capacity retention of 9₂.₃% after 1₅₀ cycles at 0.₅ °C, whereas the corresponding capacity retention of the other milled control materials and a commercial LiNi₀.₅Co₀.₂Mn₀.₃O₂ electrode were only 7₇.₄% and 8₇.₁%, respectively. The improved performance was attributed to the synergistic effect of high energy plasma and milling-induced oxygen vacancies in the SnO₂–x surface protection layers, which enabled greatly increased conductivity of the active materials and stable interfaces. Furthermore, the complex relationship between the Li-excess Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅ and SnO₂ coating layer is still ambiguous, thus SnO₂-coated Li-excess Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅SnO₂ coated LiNi₀.₅Co₀.₂Al₀.₅O₂, pristine LiNi₀.₅Co₀.₂Al₀.₅O₂ and Li-excess Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅O₂ were prepared [2₁₄]. XRD results suggested that presence of Sn could increase the crystal parameters. SEM and HRTEM images showed that both Li-excess-Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅SnO₂ and LiNi₀.₅Co₀.₂Al₀.₅O₂ coated LiNi₀.₅Co₀.₂Al₀.₅O₂ were all composed of uniform monodisperse nano/submicron sphere-like primary particles, with a thin SnO₂ coating layer on the surface. After 1₀₀ cycles at 2₀₀ mA g⁻¹, Li-excess-Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅SnO₂ coated LiNi₀.₅Co₀.₂Al₀.₅O₂ delivered 9₀.₅% of its initial capacity in contrast to 8₈.₁% for the LiNi₀.₅Co₀.₂Al₀.₅O₂ coated SnO₂, whereas the corresponding capacity retention of the LiNi₀.₅Co₀.₂Al₀.₅O₂ coated LiNi₀.₅Co₀.₂Al₀.₅O₂ and Li-excess-Li₁₋ₓNi₀.₅Co₀.₂Al₀.₅O₂ were only 7₂.₇% and 7₉.₈%, respectively. Benefiting from the cationic order of Li⁺/Ni²⁺, LiNi₀.₅Co₀.₂Al₀.₅O₂ coated SnO₂ and LiNi₀.₅Co₀.₂Al₀.₅O₂ coated LiNi₀.₅Co₀.₂Al₀.₅O₂ delivered capacities of 6₁.₇ and 8₆.₇ mAh g⁻¹ after 4₀₀ cycles at 2₀₀ mA g⁻¹, corresponding to a capacity retention ratio of ₆₅.₁% and ₇₀.₁%, respectively. To effectively optimize the ratio of Ni²⁺ and Li⁺ as well as improve the conductivity of the cathode, spherical-like LiNi₀.₅Co₀.₂Mn₀.₃O₂ samples were modified by synergetic effect of Sn-doping and in-situ formed LiSnO₂ nano-coating layer [2₁₅]. In the voltage range of 2.₇–₄.₆ V, the 3 mol% Sn-modified LiNi₀.₅Co₀.₂Mn₀.₃O₂ exhibited a discharge capacity of ₁₅₇.₃ mAh g⁻¹ with capacity retention of ₈₈.₄% after ₁₀₀ charge at ₁.₀ °C, while the discharge capacity of bare LiNi₀.₅Co₀.₂Mn₀.₃O₂ was ₁₂₄.₉ mAh g⁻¹ with a capacity retention of ₇₃.₂%.

4.4. The group VA, Li₃PO₄

The amounts of residual lithium compounds (e.g. Li₂O, LiOH, Li₂CO₃) increase with increasing Ni content in nickel-rich cathode materials, those residual lithium compounds hinder Li⁺ transport, which in turn causes resistance increased. Li₃PO₄ coating can partly inhibit the reaction of active material with the air because it is stable up to ₆.₀ V versus Li/Li⁺, and has excellent ionic conductivity. Also, PO₄⁻ ions react with those residual lithium compounds. Thus, strong covalent bonding of the PO₄⁻ contributes to improved high-voltage performance and thermal stability of nickel-rich cathode materials. Jo et al prepared Li₃PO₄-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ by dissolving LiNi₀.₅Co₀.₂Mn₀.₃O₂ powders into H₃PO₄ ethanol solution [2₁₆]. TEM images showed that the thickness of the coating layer was below ₁₀ nm and ToF-SIMS analysis indicated that H₃PO₄ reacted with residual lithium compounds during refluxing in anhydrous ethanol at ₈₀ °C. When cycled at ₂₈₀ mA g⁻¹ between ₃.₀ and ₄.₂ V at ₂₅ °C, Li₃PO₄-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ retained a capacity retention of ₉₄.₁% in contrast to pristine NCM for ₇₆.₁% after ₁₅₀ cycles. Similarly, Li₃PO₄-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ was prepared by dissolving LiNi₀.₅Co₀.₂Mn₀.₃O₂ powders into a gel containing Li⁺ ions captured by citric ions and PO₄⁻ [2₁₇]. TEM and SEM images and EDS mapping of phosphorous indicated that Li₃PO₄ particles were formed only on the surface of LiNi₀.₅Co₀.₂Mn₀.₃O₂ particles, and the thickness of Li₃PO₄ layer was about ₃.₀ nm. From TR-XRD patterns of charged pristine and Li₃PO₄-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ in the ₂₉ range of ₅₀°–₈₀°, the phase transition was completed at ₂₃.₂ °C and ₃₆.₀ °C, respectively. As a result, the surface-modified cathode materials could deliver ₇₉.₇% of the
initial discharge capacity after 100 cycles at 1.0 °C within 2.8–4.7 V, whereas the corresponding capacity retention of the pristine counterpart was only 63.9%. This can be attributed to Li$_3$PO$_4$ acting as a protection layer to improve the structural stability of the cathode materials, which therefore suppressed the interfacial reaction during cycling. A facile solid phase reaction method was developed to prepare Li$_3$PO$_4$-coated LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.2}$O$_2$ within primary particles [218]. XRD results indicated that a new phase of Li$_3$PO$_4$ may be formed in the coated sample. HRTEM and FFT of a primary particle showed that the coating layer was about 5–10 nm thick. After 200 cycles at 320 mA g$^{-1}$ within 2.7–4.5 V, its discharge capacity was 153.2 mAh g$^{-1}$, which was notably higher than that of pristine LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (107.8 mAh g$^{-1}$). Accordingly, the capacity retention of Li$_3$PO$_4$-coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ after 200 cycles was 82.8%, which was a significant improvement over LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (59.4%). Otherwise, Li$_3$PO$_4$-coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ retained 82.8% of its initial capacity in contrast to 59.4% for raw LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ at a current density of 800 mA g$^{-1}$ after 200 stable cycles within 2.7–4.5 V. As shown in the HRTEM image of cycled samples, the Li$_3$PO$_4$-coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ was stabilized by a spine phase hindering the transformation of layered structure towards rock-salt phase on the surface with cycling (figure 5(A)). Otherwise, Li$_3$PO$_4$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was prepared by an in-situ wet-chemical method by dissolving (NH$_4$)$_2$HPO$_4$ solution into a suspension containing precursor and LiOH · H$_2$O [219]. XRD results indicated that the 1.0 wt.% Li$_3$PO$_4$-coated sample showed the highest $c$ and $ca$ values, implying that it had the best ordered layered hexagonal structure and the largest channels for Li$^+$ ions intercalation and deintercalation transportation. After 50 cycles at 150 mA g$^{-1}$ in the voltage range of 2.8–4.5 V, capacity retention was 81.3%, 88.7% and 93.2% for the 0.5, 1.0 and 3.0 wt.% Li$_3$PO$_4$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$, respectively, while that of the pristine LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was only 78.4%. The improved performance was ascribed to the suppression of the side reactions between the cathode and the electrolyte, and the surface and charge transfer resistance was reduced during cycling owing to the Li$_3$PO$_4$ ionic conductor. Li$_3$PO$_4$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was prepared by a hydrothermal treatment method, and compared with bare LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ and LPO and NMC (prepared without the hydrothermal treatment process) [220]. XRD results and TEM images indicated that $c$ and $ca$ values increased after coating and thickness of coating layer was about 6 nm and
3 nm on the surface of the LPO and NMC and H-LPO and NMC, respectively. XPS results indicated that the intensity of the O 1s peaks of these residual lithium compounds was decreased, indicating that a coating layer can suppress the reaction of active material with the air and the electrolyte. Benefiting from the enhanced lithium ions diffusion, H-LPO and NMC obtained a capacity retention of 92.6% after 50 cycles at 180 mA g$^{-1}$ between 2.8 and 4.5 V at room temperature, which was higher than NCM811 and LPO and NMC with capacity retention of 84.0% and 90.5%, respectively. Yan et al. performed the deposition of Li$_2$PO$_4$ on LiNi$_{0.76}$Co$_{0.14}$Mn$_{0.10}$O$_2$ powders by introducing lithium tert-butoxide and trimethyl phosphate into reaction chamber including NCM powders [61]. After 150 ALD cycles, a lithium phosphate layer of ~10 nm in thickness was coated on the NMC powders. STEM-EDS mapping of the P distribution indicates that the grain boundaries and pockets of the triple grain junction were enriched with P. In the voltage range of 2.7–4.5 V, Li$_2$PO$_4$-infused NCM obtained 91.6% of its initial capacity in contrast to 79.0% for raw NCM after 200 cycles at 200/3 mA g$^{-1}$. After 200 cycles, these cracking features in pristine NCM did not occur in the Li$_2$PO$_4$-infused samples, fluoride and carbon in the liquid electrolyte only appeared at the outer surface of the secondary particles, not within them. Li$_2$PO$_4$-coated LiNi$_{0.4}$Co$_{0.15}$Al$_{0.05}$O$_2$ was studied by a simple precipitation reaction [221], and it was determined that the use of the coated NCA in aqueous electrode processing reduced the alkalinity of the slurry and thus the lithium leaching in water could be at least partially suppressed. As a result, capacity retentions of 94.5%, 94.8%, and 96.2% were obtained after 50 cycles at 200 mA g$^{-1}$ for N-methyl-2-pyrrolidone (NMP)/polyvinylidene fluoride (PVDF)-based NCA, H$_2$O/carboxymethyl cellulose (CMC)-based and NMP/PVDF-based c02-NCA, respectively.

4.5. The group VI A, metal sulfides/selenides/tellurides

Due to the sublimated gas-phase, S can react with detrimental residual Li compounds on the surface of the particles. Sulfur-coated LiNi$_{0.4}$Co$_{0.1}$Mn$_{0.5}$O$_2$ (SNCM) was prepared by a simple and novel sublimation-induced gas-reacting process [222]. As a result, the reacted layer of Li$_2$S$_2$O$_3$ phases forms on the outside surface of the secondary particles and boundaries within primary particles inside the secondary particles. TEM images indicated that a thin reacted layer containing S uniformly formed on the entire surface of the secondary particles (figure 5(B)). The 200 nm length boundary within the primary particles inside a secondary particle were completely filled with the S-containing phase, and the thickness of the reacted layer was about 15–20 nm. Because of its anisotropic volume stability, the obtained SNCM maintained a capacity retention of 83.8% at 200/3 mA g$^{-1}$ over 200 cycles in a potential range of 3.0–4.5 V, whereas the pristine LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ sample showed a capacity retention of only 70.1% after 200 cycles. Similarly, Se-coated LiNi$_{0.4}$Co$_{0.1}$Mn$_{0.5}$O$_2$ (Se@LNCM811) was prepared via mixing LiNi$_{0.4}$Co$_{0.1}$Mn$_{0.5}$O$_2$ and selenium powders and then heating under N$_2$ atmosphere [223]. The Se@LNCM811 delivered a reversible capacity of 132 and 105 mAh g$^{-1}$ at current density of 2.0 °C and 5 °C after 200 cycles, respectively, much higher than those of bare LNCM811. Such an improved cycling performance of Se@LNCM811 could be ascribed to reduced Li$^+$/Ni$^{2+}$ cation disorder. A metal–Se bond in bulk materials can maintain the structure stability during charge–discharge cycles (figure 5(C)), suppressing the contact of LNCM811 with the electrolytes and their subsequent side reactions. Te-doped LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ was prepared by using H$_2$TeO$_6$ treatment of hydroxide-precursors before the lithiation [224]. Bader atomic charge analysis indicated that there were more negative O atoms in the TeO$_6$ octahedron within LiNi$_{1−y}$Te$_y$O$_2$ than the one in the NiO$_6$ octahedron within bare LiNiO$_2$ (figure 5(D)). After 100 cycles at 900 mA g$^{-1}$, 1% Te–LiNi$_{0.88}$Co$_{0.09}$Al$_{0.03}$O$_2$ maintained 71.6% of its initial capacity, but that for bare LiNi$_{0.88}$Co$_{0.09}$Al$_{0.03}$O$_2$ was only 60.4%. In particular, 1% Te–LiNi$_{0.88}$Co$_{0.09}$Al$_{0.03}$O$_2$ obtained enhanced capacity retention (81.4% in 2.7–4.5 V, 76.5% in 2.7–4.7 V) after 100 cycles at 180 mA g$^{-1}$, while the capacity retention of pristine LiNi$_{0.88}$Co$_{0.09}$Al$_{0.03}$O$_2$ are only 64.9% and 56.7%, respectively. As shown in figure 5(E), the bulk regions I and II for cycled 1% Te–LiNi$_{0.88}$Co$_{0.09}$Al$_{0.03}$O$_2$ still retained the well-organized layered phase with R3m symmetry.

4.6. The group VII A, metal fluorides

The author’s approach to improve the electrochemical performance of nickel-rich cathode materials is to modify carbonates on their surface [226]. For example, LiNi$_{0.3}$Co$_{0.2}$Mn$_{0.5}$O$_2$ and LiPF$_6$ was mixed in distilled water before dehydrated and annealed in atmosphere, then, F-doped and LiF-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ was formed [225]. SEM and HRTEM images indicated that carbonates reacted with LiPF$_6$ to form LiF, many LiF grains preferentially nucleated at the crevice of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ surface. The LiF-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (LNCM-2) delivered a discharge capacity of 179.4 mAh g$^{-1}$ at 0.5 °C after 100 cycles within 3.0–4.5 V and retained 93.7% of its initial capacity, whereas the corresponding capacity retention of the pristine counterpart is only 65.8%. Even though the charging voltage increased up to 4.7 V, LNCM-2 showed a slow degradation compared with bare LNCM, because the parasitic reactions between cathode electrodes and electrolytes were suppressed (figure 5(F)). Subramaniyan et al. prepared fluorine-doped LiNi$_{0.5}$Co$_{0.15}$Mn$_{0.15}$O$_2$ via mixing their precursors, Li$_3$CO$_3$ and LiF, before annealing in an oxygen atmosphere [227]. Benefiting from a decreased c/a ratio, the LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.15}$F$_{0.05}$F$_{0.05}$ delivered a capacity of 170 mAh g$^{-1}$ with capacity retention of 86.0% after 100 cycles at 200 mA g$^{-1}$ within 2.8–4.4 V, and the reversible capacity of the pristine sample was only 131.8 mAh g$^{-1}$. The improved cycling stability was attributed to the M–F bond which directly modified the anionic oxidation processes at high voltage state. Concentration gradient LiNi$_{0.73}$Co$_{0.12}$Mn$_{0.15}$O$_2$ was modified with fluorine via mixing LiNi$_{0.73}$Co$_{0.12}$Mn$_{0.15}$O$_2$ powders and NH$_4$HF$_2$ before annealed in Ar flow [228]. HRTEM images displayed...
that a lattice fringe spacing of 0.215 nm was observed, implying that a partial phase transformation from a layered structure to a rock-salt structure on their surface. XPS spectra indicated that Li$_2$CO$_3$ had reacted with NH$_3$HF$_2$ during the fluorination modification procedure. After 200 cycles at 1 °C, Li[0.45Ni$_{0.8}$Co$_{0.12}$Mn$_{0.15}$]O$_{1.98}$F$_{0.02}$ material delivered 97.5% of its initial capacity in contrast to 87.4% for the raw LiNi$_{0.73}$Co$_{0.12}$Mn$_{0.15}$O$_2$. The improved electrochemical performance was ascribed to the stable fluoride layers that could protect the active materials from directly contacting the electrolyte. To form the stable local octahedron of halide, F$^-$-doped LiNi$_{0.6}$Co$_{0.075}$Mn$_{0.125}$O$_2$ was prepared with the favorable anti-site mechanism [229]. HRTEM images indicated that c parameter increased after F$^-$ doping, resulting from more negative Mulliken charges for O in local layered structure compared with the pristine sample. As a result, the 1% F–LNCM delivered a discharge capacity of 153.4 mAh g$^{-1}$ with a capacity retention of 83.3% after 120 cycles at 200 mA g$^{-1}$ and 55 °C, whereas pristine LNCM declined abruptly on the 85th cycle. As shown in figure 5(H), the 1% F–LNCM retained a morphology in contrast to pristine LNCM with structural deterioration. Huang et al prepared LiF-coated LiNi$_{0.95}$Co$_{0.05}$Al$_{0.02}$O$_2$ via in-situ hydrolysis of BdmmBF$_4$, because it could react with residual Li compound on the surface of LiNi$_{0.90}$Co$_{0.08}$Al$_{0.02}$O$_2$ forming a uniform LiF coating layer [230]. SEM and TEM images indicated that secondary particles with a blurred and rough surface and thickness of coating layer was about 10 nm. Li$^+$-conducting LiF coating layer could effectively inhibit side reactions and protected the electrode from HF corrosion, thus LiNi$_{0.90}$Co$_{0.08}$Al$_{0.02}$O$_2$@LiF sample delivered a capacity retention of 79.9% after 200 cycles at 180 mA g$^{-1}$, while pristine LiNi$_{0.90}$Co$_{0.08}$Al$_{0.02}$O$_2$ obtained a capacity retention of 61.2%. To improve thermal stability and rate performance of LiNi$_{0.85}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA), a dry and low-temperature fluorination (350 °C) method was used to form surface-fluorinated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (FNCA-2) [231]. SEM, TEM and XPS results indicated that the free lithium residues reacted with NH$_3$HF$_2$ forming about 2–5 nm LiF coating layer on the surface of NCA particles. FNCA-2 delivered a maximum discharge capacity of 186.78 mAh g$^{-1}$ after 50 cycles at 180 mA g$^{-1}$ and 55 °C with a capacity retention of 92.3%, whereas PNCA exhibited 86.1% of its maximum initial capacity.

4.7. The group III B metal oxides (MO$_x$, M = Y, Ce, Dy)

Because a Y$_2$O$_3$ coating layer could well inhibit the structural degradation, hamper the interface reaction and promote the conduction of Li$^+$ ions, Dai et al prepared Y$_2$O$_3$-coated LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (YO@LNCM-2) by a wet-chemical method [232]. HRTEM of YO@LNCM-2 sample indicated that the thickness of coating layers was about 5–12 nm. YO@LNCM-2 sample obtained a capacity retention of 91.45% after 100 cycles at 1.0 °C within 3.0–4.3 V at 25 °C, while that of the pristine sample was only 85.03%. CeO$_2$ coated and Ce$^{3+}$ doped LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) was prepared via dispersing nickel-rich cathode materials into a Ce(NO$_3$)$_3$ · 6H$_2$O ethanol solution [233]. SEM, TEM and FFT images indicated that the surface of 600 °C-CeO$_2$-modified NCM811 became rougher with a thickness of about 2–3 nm coating layers. XPS results imply that the Ce$^{3+}$ ions have been doped into the bulk structure, along with the oxidation of Ni$^{2+}$ to Ni$^{3+}$, thus reducing Li$^+$/Ni$^{2+}$ mixing. When cycled at 40 mA g$^{-1}$ between 2.75 and 4.5 V at 25 °C, capacity retentions of 92.5%, 97.84%, 99.23%, and 94.92% were obtained after 50 cycles for pristine, 500 °C, 600 °C and 750 °C-CeO$_2$-modified NCM811, respectively. The improved performance is associated with the inert Ce$^{3+}$ ions in transition metal slabs with strong Ce–O bonds that could maintain the layered structure at high Li$^+$-deintercalation state. To improve structural stability and suppress side reaction on the electrode materials, Ce-modified Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ was prepared via a solid state method mixing precursor, LiCoO$_2$ and Ce(NO$_3$)$_3$ · 6H$_2$O [234]. TEM images and XPS results indicated that the remainder of the Ce formed an 8 nm thick coating layer on the surface of Ce-modified Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$, and the O1s shifted to a higher value after Ce-modification, indicating a strong electron-donating capacity. It exhibits a discharge capacity of 135.4 mAh g$^{-1}$ after 200 cycles at 1.0 °C, which was notably greater than that of raw Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (46.9 mAh g$^{-1}$). Accordingly, the capacity retention of Ce-modified Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ after 200 cycles was 84.6%, which was a significantly higher than that of the raw materials (31.2%). When the batteries were discharged at 10.0 °C, Ce-modified Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ retained a capacity of 99.5 mAh g$^{-1}$ in contrast to raw Li1.02Ni$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ with a capacity of 67.7 mAh g$^{-1}$. Yan et al prepared Dy-doped LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ by an aerosol synthesis method through controlling the precursors concentrations and heating parameters [235]. SEM and XRD results indicated that the crystal size of the primary structure gradually increased with increasing Dy concentration, and impurity phase-LiDyO$_2$ was formed at 1.5% Dy doping and became obvious at 3% Dy doping, which caused easier Li$^+$-intercalation/deintercalation. CV and impedance measurements demonstrated that Dy doped sample had a smaller charge transfer resistance and lower charge–discharge polarization than the pristine sample. The results showed that Dy doped cathode materials shifted the O$_2$ onset temperature to a higher temperature and reduced O$_2$ release by 80%, thus showing a dramatically increased thermal-chemical stability and improving the fire safety of cathode materials. As a result, the 1.5% and 3% Dy-modified NCM811 obtained capacity retention of 91.6% and 91.2% after 50 cycles at 200 mA g$^{-1}$ between 2.8 and 4.3 V at 25 °C, respectively, whereas pristine NCM811 delivered a capacity retention of 77%.

4.8. The group IV B metal oxides (MO$_x$, M = Ti, Zr)

To improve the reversibility of H2-H3 phase transition for LiNi$_{0.8}$Co$_{0.1}$O$_2$, Ti$^{4+}$ doping was designed using fluidized bed chemical vapor deposition [236]. XPS and TEM images indicated that more Ni$^{2+}$ ions were observed at the surface after Ti$^{4+}$ doping, forming a Li/Ni mixed region with a thickness
of \( \sim 5 \) nm in the 5% Ti doped sample. As a result, 5% Ti doped sample obtained a capacity retention ratio of 97.94% after 100 cycles at 38 mA g\(^{-1}\), which was higher than the pristine sample with a capacity retention ratio of 89.08%. Even at a high current rate of 950 mA g\(^{-1}\) and 1900 mA g\(^{-1}\), the 5% Ti doped sample delivered capacity of 159.5 mAh g\(^{-1}\) and 143.4 mAh g\(^{-1}\), respectively. After 30 cycles, the H3 diffraction peaks of 5% Ti doped sample showed unobservable changes (figure 6(A)), implying the contraction in crystallographic c-direction was reversible, thus the generation of microcracks could be suppressed (figure 6(B)). The interfacial chemistry of LiNi\(_{0.8}\)Mn\(_{0.1}\)Co\(_{0.1}\)O\(_2\) was improved by...
Ti$^{4+}$ doping using a modified co-precipitation method [237]. The EELS scanning showed that Ti$^{4+}$ was present throughout the primary particles and enriched at the top 1–2 nm surface. When Ti$^{4+}$ was doped into NCM, capacity retention at 1.0 °C within 2.5–4.5 V was increased from 69% to 80% over 300 cycles and from 58% to 70% over 500 cycles compared to the pristine sample. STEM-EDS mapping illustrated that Ti$^{4+}$ chemical environment was highly reversible due to intact Ti$^{4+}$ distribution after 300 cycles (figure 6(C)). To inhibit formation of NiO inactive phase for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ during cycling, Ti-doping was used [238]. SEM images indicated that prepared samples were spherical particles with a size of 3–5 μm and 10–13 μm in diameter. TEM-EDX elemental mapping indicated that Ti was found to be mostly concentrated at the boundaries and surface edges of the grains. In the voltage range of 2.5–4.5 V, Ti-doped NCA obtained 74% of its initial capacity in contrast to 67% for PNCA after 50 cycles at 1.0 °C. For perfectly balancing the coating quality and scale-up production, fluidized bed chemical vapor deposition was used to prepare TiO$_2$-coated LiNi$_{0.8}$Mn$_{0.2}$Co$_{0.8}$O$_2$ [239]. There was a good linear relationship between TiO$_2$ coating content and coating time, and a smooth particle surface caused by increasing flow rates of carrier gas Ar (TiCl$_4$). TiO$_2$-coated NCM811 delivered a capacity retention of 95.89% after 50 cycles at 1 °C between 2.75 and 4.2 V, which was much better than pristine NCM811 (89.08%). Chen et al designed TiO$_2$-coated LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ via a hydrolyzation method to improve its electrochemical performance at high cut-off voltage of 4.5 V [240]. TEM and SEM images indicated that the surface of the particles became rough, and coating layer thickness was about 25–35 nm. About 1.0 wt.% TiO$_2$-coated NCM exhibited 88.7% of its initial capacity compared to 78.1% for pristine NCM622 after 50 cycles at 140 mAh g$^{-1}$ between 3.0 and 4.5 V. Such improved electrochemical properties could be ascribed to the improvement of the structural stability of the materials and the suppression of the interface reaction between the cathode and the electrolyte. Performance degradation of NCM622 at high cut-off voltage was mitigated by designing a functional interfacial layer that consists of a Ti$^{4+}$ surface doping and a TiO$_2$ surface coating [241]. TEM and SEM images indicated that the surface of the primary particles became rougher, the thickness of the layer/particle agglomerations ranged from 5 to 20 nm. As a result, TiO$_2$-coated NCM622 obtained nearly 70% of its original capacity under a 1025 mA g$^{-1}$ between 2.8 and 4.4 V at 30 °C. As shown in figure 6(D), the coated sample showed a slightly lower leakage current and smaller static leakage current values compared to the bare materials. It could be ascribed to the TiO$_2$ acting as a protection layer to suppress the irreversible phase transformation, whilst also reducing the rate of the electron-transfer reaction between the Li$^+$-deintercalation cathode and solvent. NCM622 was prepared with a high-quality ultrathin TiO$_2$-coating layer by a commercial ALD system [242]. TEM images and SEM mapping indicated that Ti elements were evenly distributed across the micrograph and coating layer thickness was about 5 nm. Benefiting from the high-quality ultrathin oxide TiO$_2$ layer coated on the surface of NCM622, HF attack and the dissolution of metal ions were suppressed and Li$^+$ diffusion was improved, thus, TiO$_2$-coated NCM622 achieved a capacity retention of 85.9% at 1.0 °C after 100 cycles. For pristine NCM622, a capacity retention of 67.5% was obtained under the same test condition. Even at a high current rate of 5.0 °C, TiO$_2$-coated NCM622 delivered a capacity of 130.2 mAh g$^{-1}$. To demonstrate the criticalness of the interfacial parasitic reactions, ALD system was used to prepare TiO$_2$-coated NCM622 [243]. After 100 cycles at 4.4 and 4.5 V vs Li/Li$^+$ under 0.1 °C, capacity retention ratio of 95.6% and 93.0% were obtained, respectively. This enhancement of capacity retention was also obtained for NMC622/graphite full cells. Both results illustrated those interfacial parasitic reactions were suppressed including the oxidation of the electrolyte at high potentials, dissolution of transition metals, cation mixing and particle fragmentation (figure 6(E)). Li et al prepared pouch cells with graphite anodes and bare and TiO$_2$-coated NCM523 cathodes were used to test their thermostability and cycle life [244]. TiO$_2$-coated NCM523 had a smaller volume contraction (1.1%) than pristine NCM523 (1.53%). When cycled at 200 mAh g$^{-1}$ at room temperature between 2.7 and 4.5 V, a capacity retention of 30% was obtained after 120 cycles for pristine NCM523 and 80% was obtained after 200 cycles for TiO$_2$-coated NCM523. This improved cycling stability was ascribed to the signal of the TM species being weak, as shown in ToF-SIMS chemical mapping (figure 6(F)). TiO$_2$ coating was helpful for enhancing NCM523 thermostability because of the higher phase transformation temperatures (figure 6(G)). TiO$_2$ nanofibers (TNFs)-coated NCA were prepared via an electrosprinning method [245]. XRD results indicated that the characteristics of TNF on the secondary particle surface included higher amounts of anatase phase TiO$_2$ than the rutile phase TiO$_2$, and FESEM images showed that TNF was acted like a connecting bridge between particles. The 1 wt.% TiO$_2$-coated NCA could deliver 81.4% of the initial discharge capacity after 50 cycles at 0.1 °C and 60 °C, whereas the corresponding capacity retention of the pristine counterpart was only 64.7%. NCA was prepared with the high quality, dense, ultrathin and amorphous TiO$_2$ coating layer via ALD system [246]. XRD results and TEM images indicated that lattice parameters a, c and c/a slightly increased, and the thickness of dense thin coating layer was 5 and 8 nm for 5% and 8% TiO$_2$-coated NCM, respectively. Because of its structure stability imparted by the TiO$_2$ coating layer, which protected the cathode particles from hydrofluoric acid attack, the obtained 5% and 8% TiO$_2$-coated NCA obtained capacity retention of 90.21% and 85.54% after 100 cycles at 1.0 °C in a potential range of 2.5–4.5 V, respectively, whereas the corresponding capacity retention of the PNCA was only 50.13%. In particular, the 8% TiO$_2$-coated NCA exhibited a capacity retention of 64.72% even at 1.0 °C rate and 55 °C after 100 cycles, while the PNCA was only 43.97%. To restore structural stability and electrochemical performance, a targeted solvothermal followed by re-oxidation approach was used to prepare Li$_3$TiO$_2$-coated NCA [247]. XPS results indicated that intensity of Ni$^{2+}$ decreased to the lower level compared with the PNCA, SEM images indicated that the thickness of coating layer was 20 nm. Benefiting from the minimal polarization and
side-reaction, TiO$_2$-coated NCA maintained a capacity retention of $\sim$82% at 180 mA g$^{-1}$ after 200 cycles, whereas the bare sample obtained a capacity retention of 68% under the same testing conditions. Even at 180 mA g$^{-1}$ and 55 °C, TiO$_2$-coated NCA delivered capacity of 189 and 104 mAh g$^{-1}$ at the 100th and 500th cycles, respectively.

4.9. The group VB metal oxides (MO$_x$, M = V, Nb, Ta)

Theoretical analysis showed that V would be a promising doping source among transition metals configured with an oxidation state of 3$^+$. The two electrons occupied in the $t_{2g}$ band of V$^{3+}$ would be donated for Ni redox reactions, resulting in V$^{5+}$ because of its lower electronegativity in comparison with Ni’s electronegativity [248]. Sim et al stabilized the crystal structure and improved the Li$^+$-ion transportation kinetics of LiNi$_{0.84}$Co$_{0.10}$Mn$_{0.06}$O$_2$ by doping with V$^{5+}$ [249]. XRD, EDX mapping and XPS results indicated that the cation mixing was decreased after 0.005 mol% V$^{5+}$ uniformly distributed in the sample. After 80 cycles at 0.5 °C, 0.005 mol% V$^{5+}$-doped LiNi$_{0.84}$Co$_{0.10}$Mn$_{0.06}$O$_2$ delivered 88.1% of its initial capacity in contrast to 81.7% for the raw LiNi$_{0.84}$Co$_{0.10}$Mn$_{0.06}$O$_2$. Electrochemical impedance spectroscopy (EIS) indicated that V$^{5+}$-doped LiNi$_{0.84}$Co$_{0.10}$Mn$_{0.06}$O$_2$ exhibited lower solid electrolyte interface ($R_{SEI}$) and charge transfer resistance ($R_{ct}$) than those of pristine LiNi$_{0.84}$Co$_{0.10}$Mn$_{0.06}$O$_2$. The Nb with a slightly larger ion radius can enlarge the lattice distance as a ‘supporting point’ to elevate the Li-ion diffusion coefficient. Sun et al prepared Nb-doped single-crystal LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ via a solid phase method aimed at improving the cycle stability and inhibiting the voltage decay [250]. XRD results indicated that the spilt of (006)/(102) and (108)/(110) was more noticeable, and Li$^+$/Ni$^{2+}$ mixing decreased after Nb doping, with XPS results showing the presence of Nb$^{5+}$ in the layered structure. The 1% Nb-doped NCM maintained a capacity retention of 99.3% at 180 mA g$^{-1}$ after 100 cycles, which was much better than pristine NCM (capacity retention of 80.3%). After being cycled, Nb-doped NCM811 had a higher Li-ion diffusion coefficient and larger electronic conductivity than pristine NCM811. The structural instability and high surface reactivity of NCM811 was suppressed by constructing a Li–Nb–O coating layer, since Li–Nb–O treatment not only enhanced the diffusion of Li$^+$ ions but also introduced a strong distortion field by Nb$^{5+}$ incorporation into the bulk structure [251]. XRD and STEM images indicated that the unit cell volumes became slightly larger and the boundary of the primary particles became blurred after coating (figure 7(A)). TEM and EDS images of 1% Li–Nb–O-modified NCM811 showed that the Nb concentration maintained around 0.2 at. % for a few hundred nanometers depth until dropping to zero. The 3% Li–Nb–O-modified NCM811 retained 89.6% of its initial capacity and delivered 189.1 mAh g$^{-1}$ at a current density of 200/3 mA g$^{-1}$ after 60 cycles within 2.8–4.6 V, while the pristine electrode showed a gradual decrease in capacity, leading to a capacity retention of only 81.6%.
during the same cycling period. Although Ta\(^{5+}\) was easy to move to lithium sites, its pillar effect significantly reduced the migration of Ni\(^{2+}\) to the lithium site, and Ta\(^{5+}\) doping in the TM layer intensified the TM-O layer due to electrostatic repulsion and stronger Ta–O bonding. Oxygen retention of LiNi\(_{0.88}\)Co\(_{0.09}\)Al\(_{0.03}\)O\(_2\) was enhanced by intensifying the TM-O layer based on Ta\(^{5+}\)-doping [252]. XRD results indicated that Li\(^+\)/Ni\(^{2+}\) mixing decreased after Ta\(^{5+}\) doping, and SEM images showed that particle size decreased with increasing the doping content of Ta\(^{5+}\). As shown in partial density of states (DOS) calculations (figures 7(B) and (C)), with Ta doping into the structure of LiNiO\(_2\), a large proportion of oxygen ions were observed near the Fermi level. This characteristic could be attributed to TM redox because the probable positioning of TM-d states and O-p states was more obvious. In the voltage range of 2.7–4.5 V, the 1 wt.% Ta-doped NCM delivered 75% of its initial capacity in contrast to 61% for the raw NCM after 100 cycles at 1 °C. Even at a high current rate of 10.0 °C, a discharge capacity of 175.8 mAh g\(^{-1}\) also was achieved. The effect of doping LiNi\(_{0.9}\)Co\(_{0.1}\)O\(_2\) (NC90) with Mn, Al, B, W and Ta on the cathode microstructure was summarized [175] and the LiNi\(_{0.9}\)Co\(_{0.09}\)Ta\(_{0.01}\)O\(_2\) exhibited the highest cycling stability. When cycled at 200 mA g\(^{-1}\) in a full cell, NCTa90-730 °C delivered a capacity retention of 90% after 2000 cycles at full DOD, corresponding to a cathode energy density >850 Wh kg\(^{-1}\). This exceptionally stable cycling was ascribed to the cation ordering preserved even after 2000 cycles, which stabilized the Li\(^+\)–deintercalation structure of the cathode and improved the reversibility of the electrode reaction. Otherwise, consolidation of the primary particles was inhibited during lithiation and growth of primary particles was limited in the lateral direction since these twins with boundaries aligned along the longitudinal axis of the primary particles.

4.10. The group VIB metal oxides (MO\(_x\), M = Cr, Mo, W)

Among the group VIB elements, Cr, Mn and W have been investigated as modified elements for nickel-rich cathode materials. Cr\(^{3+}\) doped NCM622 was prepared using a solid grinding approach combined with high-temperature calcination [253]. The 1 mol% Cr-modified NCM622 exhibited good cycle and thermal stability in a potential range of 2.7–4.5 V (166.8 mAh g\(^{-1}\) at 510 mA g\(^{-1}\) and 50 °C after 200 cycles) and a remarkable rate performance (100.6 mAh g\(^{-1}\) at 1700 mA g\(^{-1}\) in 2.7–4.3 V after 200 cycles). Electrochemical testing results showed that a moderate amount of Cr\(^{3+}\) doping can not only expand pathways for Li\(^+\) insertion and extraction, but also suppress cation mixing. Xue et al prepared Li(Ni\(_{0.6}\)Co\(_{0.2}\)Mn\(_{0.2}\)–1.007:Mn\(_{0.07}\)O\(_2\) with enlarged lithium slab spacing and obtained a high capacity of 180 mA h g\(^{-1}\) after 50 cycles at 165 mA g\(^{-1}\) and 55 °C under a high cut-off voltage of 4.6 V [254]. Even at a high current rate of 1320 mA g\(^{-1}\), a capacity of 159.9 mAh g\(^{-1}\) was also achieved. Electrochemical testing results show that Mo\(^{6+}\) doping can not only suppress the pulverization of particles, but also reduce the charge transfer resistance. Li(Ni\(_{0.5}\)Mn\(_{0.5}\)Co\(_{0.5}\)–1:y:1:Mn\(_{0.07}\)O\(_2\) was prepared via spray pyrolysis to yield submicron-sized aggregates in the shape of hollow spherical sites [255]. The NCM111–Mo and NCM622–Mo showed capacity retentions of 80% and 81% at 170 mAh g\(^{-1}\) over 20 cycles, respectively. The porous structure with the expanded Li gap and reduced cation mixing should be responsible for the improved performance, which can shorten Li\(^+\) ions diffusion distance in the electrode and enhance the structural stability. MoO\(_3\) coated NCA was prepared via an ALD system injecting the gas-phase Mo(CO)\(_6\) source into the grain boundaries of primary particles and obtained a high capacity of 156.3 mAh g\(^{-1}\) after 100 cycles at 180 mA g\(^{-1}\) [256]. Even at a high current rate of 1800 mA g\(^{-1}\), a capacity of 113.4 mAh g\(^{-1}\) was also achieved. After cycling, the modified NCA particles suggested a substantially thinner CEI layer than bare NCA, and a well-maintained layered structure of the modified NCA particles (figure 8(A)). Thus, MoO\(_3\) coating layer can not only suppress the interfacial side reactions, but also provide additional Li\(^+\) insertion sites. Li,Ni,W,O-like heterostructures were designed on surface of LiNi\(_{0.91}\)Co\(_{0.05}\)Mn\(_{0.04}\)O\(_2\) by a solid-state reaction method [172]. Benefiting from the formation of radially aligned grains, doping W to the primary particle surface and the effect of armor-type tungsten-rich heterostructure, LiNi\(_{0.91}\)Co\(_{0.05}\)Mn\(_{0.04}\)O\(_2\)@2 W retained a capacity of 179.6 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) after 500 cycles with a capacity retention ratio of 85%. After modification, the inner cracks and outer Fm-3m rock salt phase were reduced greatly during cycles (figure 8(B)). Becker et al constructed WO\(_3\) coated LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\) via a sol–gel method, followed by a heat treatment process [257]. The (NH\(_4\))\(_2\)H\(_2\)(W\(_2\)O\(_7\)) \(_6\) acted as a reactant, which could react with residual lithium species during the annealing process. The Li\(_2\)WO\(_3\) possessed good ionic conductivity and WO\(_3\) enhanced the thermal stability of the composite. Therefore, when utilized as coating layer of NCM, the WO\(_3\) coated NCM/graphite full cells delivered state-of-health of 80% after 865 cycles at 180 mA g\(^{-1}\), exhibiting superior high-rate cycling stability. As shown in figure 8(C), the coating layer was able to suppress particle cracking caused by the reaction between the active material surface and the electrolyte during cycling. WO\(_3\) modified NCM811 was synthesized by mixing Ni\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)(OH)\(_2\) precursors, LiOH·H\(_2\)O and WO\(_3\), followed by heat treatment process [258]. In the voltage range of 2.8–4.5 V, WO\(_3\) modified NCM811 (WNCM-0.5) delivered a capacity retention ratio of 92.1% after 100 cycles at 200 mA g\(^{-1}\). Even at a high current rate of 2000 mA g\(^{-1}\), a capacity of more than 160 mAh g\(^{-1}\) was also achieved. As shown in figure 8(D), the WO\(_3\) coating layer contributed to the restraint of the diffusion of the rock salt phase from the surface to the interior, and enlarge the interplanar distances, thus enhancing its better cycling performance and retarding the degradation rate of capacity. WO\(_3\) coated NCM622 was prepared via a liquid phase method using H\(_2\)WO\(_4\) as a raw material [259]. The XRD and TEM results indicated that the 1.0 wt.% WO\(_3\) bonded into clumps as a result of reunion and discontinuous distribution on the surface, with a thickness of 3.15 nm. Capacities of 140.82 mAh g\(^{-1}\) could be obtained at current densities of 165 mA g\(^{-1}\) after 200 cycles. Li\(_2\)WO\(_3\)-decorated NCM622 was formed via high-temperature solid reaction using 2 wt.%
(NH₄)₂H₂W₁₂O₄₀ as W source [90]. The compositions displayed the capacity retentions of 93% and 86.3% with cut-off voltages of 4.3 V and 4.6 V after 100 cycles at 180 mA g⁻¹, respectively. High-resolution TEM images indicated that the Li₂WO₄ layer had a thickness of ~10 nm, with only a small amount of rock-salt formed on the NCM622 surface with an increasing cut-off voltage. Thus, Li₂WO₄ acted as an effective coating layer to prevent side reactions, reduce formation of the LiF and Li₂CO₃, and improve conductivity by facilitating charge transport (figure 8(E)).

4.11. The group VIIIB and VIII metal oxides (MOₓ, M = Mn, Fe, Co, Ni)

Mn is a low-cost metal with good prospect as a partial substitution of nickel-rich cathode materials. Gradient Mn⁴⁺-doped Li(Ni₀.₈₈Co₀.₀₉Al₀.₀₃)₁₋ₓMnₓO₂ (NCAM) was fabricated by Xu et al., and NCAM exhibited a capacity retention of 80.0% at 900 mA g⁻¹ over 500 cycles, which is an extremely stable capacity as compared to bare NCA (only 40.1%) [260]. The NCAM/graphite full cell exhibited a great capacity retention of 89.5% after 100 cycles at 340 mA g⁻¹. The NCAM were assembled by appropriate amounts of pillar ions (Ni²⁺ ions) and stability ions (Mn⁴⁺ ions), which could maintain stable surface/interfacial structure, and thus retain high reaction and kinetic activities. In view of this, Li et al. fabricated Li(Ni₀.₈₈Co₀.₀₉Al₀.₀₃)₁₋ₓMnₓO₂ composite by a facile high-shear dry mixing and high-temperature calcination process [261]. In the voltage range of 2.7–4.5 V, M₀.₀₁–NCA delivered a capacity retention ratio of 86% at 200 mA g⁻¹ after 100 cycles. When used as a pouch-type cell for LiIBs, M₀.₀₁–NCA achieved a high capacity retention of 80% at 200 mA g⁻¹ after 600 cycles. Mn-doped LiNi₀.₈₈Co₀.₀₉Al₀.₀₃O₂ was prepared via sol–gel method using Mn(CH₃COO)₂ · 4H₂O as precursors [262]. The obtained Mn-NCA exhibited excellent capacity retentions of 91% at 360 mA g⁻¹ over 500 cycles in a potential range of 2.8–4.3 V. The Mn-NCA/Li₄Ti₅O₁₂ full cell exhibited a great capacity retention of 86% after 1000 cycles at
180 mA g$^{-1}$. Except for the Mn-doped NCA can improve the cycling performance owing to enlarged $c$-axes of the crystal lattice, the authors attributed the phase and structural stabilities to intrinsic properties (figure 9(A)), including small primary grains as well as strong Mn–O bond at the interface. In this respect, this finding can provide an effective way to improve the cycling stability via engineering size and geometry of the primary grains in the integrated structure. Cho et al improved the thermal and structural stabilities of LiNi$_{0.82}$Co$_{0.12}$Mn$_{0.06}$O$_2$ by proposing a facile LiNi$_{0.82-x}$Co$_{0.12-x}$Mn$_{0.06}$+$2x$O$_2$ surface [263]. As shown in figures 9(B) and (C), Mn concentration was increased at the surface of the 1 wt. % Mn–NCM811 particle, and its bulk structure was not affected by the formation of a reliable Mn-rich surface layer. FESEM images revealed that the Mn-rich surface could enhance interconnection between the primary particles in NCM811 due to relatively strong Mn–O bonds, thus Mn–NCM811 achieved a capacity retention of 87.3% in contrast to 57.0% for the raw NCM811 after 50 cycles at 190 mA g$^{-1}$ and 60 °C. Following Mn$^{4+}$ sites existed in the TM layer, a certain amount of Ni$^{3+}$ has to be reduced to Ni$_2$$^{2+}$ to maintain the electric neutrality. In order to investigate this effect, MnO$_2$-modified NCM811 was prepared via wet chemical method using KMnO$_4$ as precursors [264]. The obtained MnO$_2$-modified NCM811 showed superior electrochemical performance, including long-term cycling stability (96.3% capacity retention after 50 cycles at 200 mA g$^{-1}$), thermal stability (92.5% capacity retention after 50 cycles at 200 mA g$^{-1}$, 50 °C), and high rate-capability (204.7 and 200 mA g$^{-1}$ at 600 and 1000 mA g$^{-1}$, respectively). Some portion of the Ni$_2$$^{2+}$ ions that migrate from the transition metal layer to the lithium layer should be positive for preventing inter-slab collapse and improving structural stability as well as rate capability. XRD and HRTEM analysis indicated that some Mn$^{4+}$ ions were incorporated into the bulk showing increased lattice parameters. Thus, partial Ni$_3$$^{3+}$ would be reduced to Ni$_2$$^{2+}$, and there was a coating layer with thickness of 6–12 nm for MnO$_2$-modified NCM811. Electrolyte decomposition was suppressed by forming a thin SEI film. In addition, MnO$_2$-coated NCM811 (LNMC and M) was prepared via treating the precursor with strong oxidant KMnO$_4$ [265]. The increase of $c/a$ value indicated the priority of lattice grew along the $c$ axis and provides large channels for Li$^+$ transportation process. LNMC and M delivered a capacity of 200.6 mA h g$^{-1}$ after 50 cycles at 200 mA g$^{-1}$ and 50 °C with the capacity retention of 99.8%, and exhibited superior rate performance (190.3 and 185.2 mA h g$^{-1}$ at 400 and 1000 mA g$^{-1}$, respectively).
improved performance was ascribed to the ~12 nm coating layer that suppressed electrolyte decomposition and side reactions, thus a thin SEI film was formed on the surface of the LNMC and M. The electrochemical performance of NCM811 was improved by coating a thin MnO_{2} layer and combined with the formation of single crystal primary particles (S and T) [266]. A 4–7 nm MnO_{2} coating layer on the single crystal morphology was formed by a reaction between MnO_{2} and Ni^{2+} under calcined process. When applied as a cathode for LIBs, a high capacity of 193.5 mAh g⁻¹ could be obtained at 200 mA g⁻¹ after 50 cycles, which was better than the performance of pristine NCM (S and U). As shown in figures 9(D) and (E), S and T showed a smaller shift of (003) peak and cracks than S and U.

The decreased migration barrier of Ni ion due to the oxygen vacancy and the lowering of the system energy by the Li⁺ compensation causes extra cation mixing and lattice distortion [267]. Hence, Ni ion migration introduces strain perpendicular to the Ni layers with oxygen defects and Li vacancies, which leads to dislocations and defects with lattice distortion. Yang et al proposed to adjust the valence state of Ni and avoid the oxygen defects by designing a manganese oxide coating method and using 2 wt. % (CH₂COO)₂Mn as precursors [268]. EDS mapping results indicated that the lattice of the interstitial coating layer matched with the internal Ni-rich layered structure and released stress concentration to avoid the damage by lithium migration. Rietveld refinement results indicated that the unit cell volume was extended at a degree of 0.4%. As shown in figures 9(F)–(H), the effect of Mn coating was that the ratio of Ni^{3+} to Ni^{2+} decreased from 9.49 to 2.46, and oxygen content increased after cycles. In the voltage range of 2.8–4.25 V, the M–NCM88 cathode delivered 80.6% of its initial capacity in contrast to 47.2% for the B–NCM88 at 190 mA g⁻¹ after 200 cycles. This report effectively solves the issues resulting from extra cation mixing and lattice distortion. Additionally, Wu et al prepared LiNi_{0.71}Co_{0.09}Mn_{0.2}O_{2} with a uniform layered R-3m phase following a self-assembled concentration-gradient shell via a wet chemical method [269]. EDX scanning analysis showed that the thickness of the concentration-gradient shell was over 1 μm on the obtained LiNi_{0.71}Co_{0.09}Mn_{0.2}O_{2} materials (RM). In the voltage range of 2.8–4.5 V, LiNi_{0.71}Co_{0.09}Mn_{0.2}O_{2} (RM) delivered a discharge capacity of 164.4 mAh g⁻¹ with a capacity retention of 92.2% after 100 cycles at 20 mA g⁻¹, while modified material LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} (PM) showed a capacity retention of 74.7%. HRTEM analysis indicated that the whole RM region was composed of a uniform R-3m phase in contrast to bare NCM after 1st cycle (figure 9(I)). Meng et al synthesized NCM811 with lower surface oxygen defects (LOD@NCM) by covering Ni_{0.3}Co_{0.1}Mn_{0.1}O{2} (OH)₂ with Mn(CH₂COO)₂ · 4H₂O and sintering with LiOH · H₂O at high temperature [270]. The LOD@NCM showed a stable capacity of 166 mAh g⁻¹ with a capacity retention of 90.4%, while pristine NCM exhibited a discharge capacity of 136 mAh g⁻¹ with only 77.2% of capacity retention after 200 cycles at 200 mA g⁻¹. The improved performance could be ascribed to the improved surface oxygen-keeping capacity, which was benefited for decreasing particle crack and Li⁺/Ni⁺ disorder.

Among the group VIII metals, Fe and Co have been investigated as modified elements for nickel-rich materials. The lithium-deficient Li[Li_{0.74}Co_{0.11}Mn_{0.11}]Fe_{0.023}O_{2} (NCMF) was prepared by co-precipitation method [271]. The related characterization indicated that secondary particles exhibited a bimodal size distribution with a size of ~10 μm. The parts of Fe³⁺ and Ni²⁺ ions that resided in the 3a sites could reduce the ratio of Ni²⁺ and cation mixing, and thus restrain the local collapse of the Li₂O inter-slab space. Moreover, the Fe³⁺ doping could reduce the residual lithium compounds on the surface of NCMF. Therefore, NCMF delivered a capacity retention of 70.9% after 100 cycles at 360 mAh g⁻¹ in the voltage range of 3.0–4.5 V. High-angle annular dark-field (HAADF)-STEM analysis displayed that the cation-disordered region of cycled NCMF was increased from ~1 nm to ~5 nm, whereas, the raw sample was significantly increased from ~2 to ~35 nm (figure 10(A)). Du et al constructed partial substitution of Co with Fe in LiNi_{1−x}Co_{x}O_{1−y}Al_{y}O_{2} via ball-milling followed by a two-step solid reaction [272]. The significantly improved cyclability was mainly attributed to the effect of the FeO₆ octahedron on the edge-shared NiO₆ octahedra via enhanced electron localization. The partial substitution of Co with Fe could suppress the formation of the single monoclinic phase and SEI film. Therefore, when cycled at 200 mA g⁻¹ at room temperature in the voltage range 2.8–4.3 V, LiNi_{0.8}Co_{0.1}Fe_{0.2}Al_{0.05}O_{2} (NCF1) and LiNi_{0.8}Co_{0.05}Fe_{0.025}Al_{0.05}O_{2} (NCF3) delivered capacities of 114.2 and 122.8 mAh g⁻¹ after 350 cycles, respectively. Even at 200 mA g⁻¹, 55 °C, NCF3 delivered a capacity of 127.6 mAh g⁻¹ after 350 cycles, corresponding to a capacity retention ratio of 77.5%. As shown in XPS spectra of NCA and NCF3 after cycles (figure 10(B)), the relative intensities of C–C, C–O, ROLi, ROCO₂Li, LiCoO₂ and LiF bands for NCF3 are weaker than those for NCA, indicating thinner SEI film formed and side reactions greatly suppressed on NCF3.

In addition, Co₃O₄, LiCoO₂ and Li₄/₃Co₂O₄ have been investigated as coating materials for nickel-rich cathode materials and exhibited superior electrochemical performance. To suppress the release of divalent nickel ions from the LiNi_{0.4}Co_{0.1}Mn_{0.1}O₂, a nanostructured stabilizer (Co₃O₄, Li₄CoO₂, LiCoO₂) with an epitaxial structure was created on the NS–NCM surface [273]. In the crystal structure, nanostructured stabilizer on the NS–NCM could prevent the nickel ion crossover from the cathode to the anode side by mitigating the nickel defect formation at the cathode surface during battery cycling. The HAADF-STEM images with the line EDX results showed that the TM concentration gradient throughout the NS–NCM particles in combination with the physically blocked surface led to the gradual oxidation of the Ni²⁺ towards the Ni³⁺, thus decreasing the thickness of the cation mixing layer. In particular, the suppression of the TM defect formation could restrain the catalytic reaction of the solvent, maintaining a uniform and stable anode SEI layer. As a result, NS–NCM delivered a ~33% higher discharge capacity retention and lower overpotential than raw NCM811 after 150 cycles at 60 °C with charge and discharge rates of 0.5 °C and 1.0 °C. The designed NS–NCM/graphite full-cell delivered
Figure 10. (A) HAADF-STEM analysis of the structural degradation after 100 cycles. Reprinted from [271], Copyright (2020), with permission from Elsevier. (B) XPS spectra of PNCA and NCF3 electrodes after cycles. Reprinted from [272], Copyright (2019), with permission from Elsevier. (C) and (D) Band structures and partial DOS of Li_{0.73}CoO_2 and Li_{0.73}Co_{1-x}Al_xO_2. Reprinted with permission from [278]. Copyright (2020) American Chemical Society.

a ~51% higher discharge areal capacity retention and lower overpotential than the NCM/graphite full-cell after 500 cycles at 45 °C within a voltage window of 2.8–4.2 V. Tao et al prepared Co_3O_4 coated NCM622 by a PVP-assisted method [274]. The 1 wt.% Co_3O_4 modified NCM622 delivered a discharge capacity of 114.1 mAh g^{-1} with a capacity retention of 60.3% after 100 cycles at 180 mA g^{-1} within a voltage window of 2.8–4.6 V. The improved capacity and cyclability were mainly attributed to inactive lithium residues consumed and the interface reactions being suppressed by a coating layer Co_3O_4 with a thickness of ~7 nm. Otherwise, LiCoO_2-coated NCA was synthesized by a molten salt method [275]. Benefiting from the decrease in NiO-type surface layer on the coated sample, the 3.0 wt.% LiCoO_2-coated NCA delivered 95.8% of its initial capacity in contrast to 87.9% for the raw NCA after 50 cycles at 2.0 °C. LiCoO_2-coated NCA was synthesized by a molten salt method, the thickness of coating layer was 40–100 nm [276]. Among the four composites, 3.0 wt.% LiCoO_2-coated NCA sintered at 800 °C for 4 h at weight ratio of KCl/NCM = 2 displayed the highest specific capacity of 193.6 mAh g^{-1} with capacity retention of 98.7% at 36 mA g^{-1} after 50 cycles. Even at a high current rates such as 90, 180, 360 and 540 mA g^{-1}, as well as at a high temperature of 55 °C, the discharge capacities of coated NCA were obviously more than that of the raw NCA. Liu et al synthesized 3 wt.% LiCoO_2-coated NCA by a co-oxidation-controlled crystallization method [277]. This fresh LiCoO_2-coated NCA delivered a discharge capacity of 193.6 mAh g^{-1} with a capacity retention of 98.7% after 50 cycles at 0.2 °C. LiCoO_2-coated NCA also maintained a fiftieth discharge capacity of 183.4, 175.1 and 167.9 mAh g^{-1} after storage at a relative humidity of 40%, 60% and 80% for 3 months, respectively. After FTIR spectra and XPS analysis, the improved stability was ascribed to the LiCoO_2 coating layer that suppressed effectively the reactions between NCA and atmosphere and was resistant to H_2O and CO_2 in air. Lu et al prepared a composite that the Li_{0.73}Co_{1-x}Al_xO_2 coated on NCA by the reaction of the surface residual lithium with cobalt oxalate nanomaterials (Al-doped CoC_2O_4 precursors), and achieved a capacity of 107 mAh g^{-1} at 1000 mA g^{-1} after 200 cycles [278]. To exploit the effect of the heteroatom Al in the coating compound, they performed an electrochemical test of the Li_{0.73}CoO_2-coated NCA, and after 200 cycles discharging at 1000 mA g^{-1}, a 102.3 mAh g^{-1} capacity could be achieved, corresponding to 61.3% capacity retention. The advances of Li_{0.73}Co_{1-x}Al_xO_2 coating was mainly attributed...
to the synergistic effects of the Co–O bond and the coexistence of Co^{3+} and Al^{3+}, which could help to form a stable cathode–electrolyte interface in the Li^{+} intercalation/deintercalation process, as well as boost the ion diffusion and electrical conductivity of the coated NCA cathode (figures 10(C) and (D)). This surface chemical state modulation strategy provides a new possibility of surface engineering with nickel-rich cathodes for high-performance LIBs.

4.12. Multi-element coating and doping

To date, many studies have reported multi-element modification for nickel-rich cathode materials with high-rate capability and cycle stability. Constructing multi-element ion surface modification is an effective approach to improve electrochemical performance compared to their single-element ion modification, originating from the synergetic effect of multiple metal species [279, 280]. Sun et al prepared Li_{1-x}Na_{x}[Ni_{0.8}Co_{0.1}Mn_{0.1}]_{1-x}Mg_{x}O_{2} through simultaneously mixing precursors LiOH · H_{2}O, C_{2}H_{3}NaO_{2} and C_{4}H_{6}MgO_{2} · 4H_{2}O followed by calcination to combine their synergistic effect on increased lithium layer spacing and the presence of a strong Mg–O bond [281]. As a result, the sample for x = 0.01 exhibited a capacity retention rate of 85% in contrast to 67% for bare NCM at 1.0 °C after 300 cycles. Similarly, Mg and Zr doped LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} were prepared by co-precipitation method, respectively [282]. SEM showed that surface area increased with the addition of dopants, which was partly due to the reduced secondary particle size. The 1% Zr-dopants at 900 °C had a capacity of 8 mAh g\(^{-1}\) lower than the pristine material at 90 mA g\(^{-1}\). After 25 cycles, the 0.5% Mg-dopants at 900 °C have a capacity that is only 2 mAh g\(^{-1}\) lower than the pristine materials, which is likely an effect of the improved crystallinity at higher calcination temperature. XRD plots showed that Mg-doped NCM showed evidence of the NCM breaking down into two phases (figure 11(A)). The Mg-doped NCM appeared to be stable and underwent phase transformation from 200 °C to 400 °C, followed by the pristine, and then the Zr-doped materials (figure 11(B)). Choi et al synthesized Na_{2}SO_{4} coated LiNi_{0.88}Co_{0.10}Mn_{0.02}O_{2} by a heated mixing of NCM and Na_{2}SO_{4} in deionized water and followed by calcination [283]. Na_{2}SO_{4}-coated NCM showed a more stable capacity retention of 85.2% compared to 65.2% and 80.3% of washed-NCM and bare-NCM after 100 cycles, respectively. The Na_{2}SO_{4}-coated NCM and graphite full cell delivered a capacity retention of 96.1% at 190 mA g\(^{-1}\) over 300 cycles. The improved performance was attributed to the ionic conductor coating layer that improved their conductivity significantly, as well as reducing their resistance and nickel dissolution. To improve the thermal stability of NCM811, a 100 nm sulfated zirconium coating layer was designed [284]. S–ZrO_{2}-coated NCM delivered a capacity retention of 88.9% after 100 cycles at 200 mA g\(^{-1}\) and 60 °C, whereas pristine and ZrO_{2}-coated NCM obtained capacity retentions of 64.9% and 79.2%, respectively. These results were directly attributed to the sulfated zirconia coating layer that was effective in reducing side reactions and forming a more stable SEI layer on the active material surface. The thermal stability of NCA was improved by Al and Ti doping, respectively [285]. Al-doped and Ti-doped cathodes delivered capacity retentions of nearly 99% and 78% after 100 cycles at 100% DOD, 1.0 °C and 45 °C, respectively, while un-doped material obtained a capacity retention of less than 74%. In particular, Al doped and Ti doped samples exhibited discharge capacities of 159 and

![Figure 11](image-url)
163 mAh g\(^{-1}\) even at 5.0 °C, respectively, while the counterpart of NCM was 157 mAh g\(^{-1}\). Doping with Al and Ti, could reduce the formation of cracks in the particles, facilitate the Li intercalation processes and reduce voltage hysteresis upon cycling. The mechanical stress of LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_{2}\) (Ni0.90) was remitted by adjusting electrons distribution with appropriate cations substitution [286]. Density functional theory (DFT) calculated results indicated that the change of O–(Li)–O interlayer spacing was obviously alleviated due to the Ti\(^{4+}\) and Al\(^{3+}\) doping by drawing the oxygen’s charge to the TM layer. The ∆c was aggrandized by Zn-substitution indicating that the pushing effect played a dominant role. As a result, the pristine and Zn-substituted Ni 0.90 samples only attained capacity retention of 67.9% and 68.2% after 200 cycles at 100 mA g\(^{-1}\), whereas Ti- and Al-substituted Ni 0.90 cathodes delivered capacity retentions of 93.4% and 82.1%, respectively. Li, Xu et al proposed a hybrid coating strategy of incorporating a lithium ion conductor LiAlO\(_2\) with a superconductor Li\(_x\)Ti\(_2\)O\(_4\) (LTAO) through capturing the lithium residue on the surface of NCM811 as an Li source [287]. SEM and HRTEM images showed that the hybrid nanomembrane homogeneously encapsulated on every single primary particle with a thickness of 20 nm, and XRD results indicated that the increased lattice volume was caused by the substitution of smaller Mn\(^{4+}\) (0.53 Å) ions by larger Ti\(^{4+}\) (0.605 Å) ions. The Li\(_x\)Ti\(_2\)O\(_4\) coated NCM811 (NCM–LTAO) sample retained a discharge capacity of 187 mAh g\(^{-1}\) at 1.0 °C after 100 cycles, corresponding to excellent capacity retentions of 96%, while NCM–LTO and NCM–LTC cathodes obtained the capacity retention of 90% and 85%, respectively, XRD patterns showed that the layered phase remained basically unchanged for the NCM–LTAO sample, leading to good stability of the cathode material by the acidic species during cycling. Zr-doped and LiAlO\(_2\)–Al\(_2\)O\(_3\) coated NCM811 (Zr–NCM811@LTO–AO) was prepared to combine their synergistic effect on improving structural stability, enlarging the Li\(^{+}\) ion diffusion channel, suppressing the side reaction and reducing the TMs dissolution [288]. Zr–NCM811@LTO–AO delivered a capacity retention of 96.8% at 200 mA g\(^{-1}\) and 50 °C after 60 cycles, while pristine NCM811, Zr-doped NCM811 (Zr–NCM811) and LiAlO\(_2\)–Al\(_2\)O\(_3\) coated NCM811 (NCM811@LTO–AO) showed capacity retentions of 73.3%, 92.2% and 90.2%, respectively. Even at a high current rate of 800 mA g\(^{-1}\), NCM811@LTO–AO exhibited a capacity of 141 mAh g\(^{-1}\) in contrast to 108 mAh g\(^{-1}\) for the raw NCM811. Lee et al improved thermal stability of NCM622 by fabricating Al\(_2\)O\(_3\) nanoparticles and a highly conductive poly(3,4-ethylenedioxythiophene)-co-poly(ethylene glycol) polymer double coating layer with a thickness of 37.4 nm (figure 12(C)) [289]. Benefitting from the lowest amount of metal dissolved in the liquid electrolyte and lower interfacial resistances, double coated-NCM622 retained 94.3% of its initial discharge capacity after 100 cycles at 55 °C and 0.5 °C. The Al\(_2\)O\(_3\)–NCM622 and conductive poly (3,4-ethylenedioxythiophene)-co-poly(ethylene glycol)–NCM622 delivered capacity retentions of 92.8% and 93.5% in contrast to 91.0% for pristine NCM622 under the same testing condition. Ti\(_3\)C\(_2\)(OH)\(_2\) was formed on LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\) by chemical reaction between Ti\(_3\)AlC\(_2\) and HF and showed excellent hexagonal ordering and the low ratio of I(006+103)/I(101) [290]. Among three compositions, the 3.0 wt.% Ti\(_3\)C\(_2\)(OH)\(_2\) coated NCM622 delivered the highest capacity of 124.5 mAh g\(^{-1}\) over 200 cycles at 100 mA g\(^{-1}\) with a retention rate of 86.4%, while the pristine sample delivered a capacity of 104.1 mAh g\(^{-1}\) with capacity retention of 71.2%. Weigel et al prepared Mg\(^{2+}\), Al\(^{3+}\), Si\(^{4+}\), Ti\(^{4+}\), Zr\(^{4+}\), and Ta\(^{5+}\) doped NCM811 via a ‘top-down’ approach [291]. There are segregation phenomena near the particles’ surfaces that may increase the electrodes’ impedance. All of the dopants improved the electrodes’ cycling stability during prolonged cycling at 360 mA g\(^{-1}\) and 720 mA g\(^{-1}\) (45 °C), compared to the un-doped NCM811 electrodes, which was due to lower volumetric changes in the active mass upon lithiation/de-lithiation processes. Mg\(^{2+}\) doping worsened the initial capability of the material because of its possible incorporation in the lithium sites and the formation of surface layers. Recently, single-crystal LiNi\(_{0.87}\)Co\(_{0.06}\)Mn\(_{0.07}\)O\(_{2}\) (AZO.3–SNCM) was prepared by a combination of co-precipitation and calcination processes [292]. It can achieve a reversible capacity of 163.0 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) after 150 cycles within a voltage range of 2.75–4.6 V. It is confirmed that Al/Zr co-doping in a SNCM lattice is stable against internal strain and Li/Ni cation mixing upon cycling at a high cut-off voltage. A pouch cell of single-crystal AZ0.3–SNCM reveals an alternative path towards developing ideal cathode materials beyond the spherical secondary particles.

Nanthagopal et al prepared a nitrogen-doped carbon (NC)-coated NCM811 cathode via a dry–solid state reaction method followed by calcination in Ar [293]. Benefiting from a coating thickness of 4 nm NC, preventing surface degradation and HF acid attacks, the 0.2 wt.% NC@NCM811 composite exhibited an initial discharge capacity of 183 mAh g\(^{-1}\) and maintained a capacity retention of 65.74% after 50 cycles at 1.0 °C, which was higher than bare NCM811 with a capacity retention of 63.15%. Chen et al utilized NC as a coating material, and synthesized NCM622/NC composites by simple mechanical activation and pyrolysis methods [294]. The incorporation of N makes carbon more electron-rich; thus, the electron clouds will be biased to NCM622 from NC, generating a stronger electronic coupling between NC and NCM622. Benefiting from the enhanced electron-conductivity, cation ordering, and decreased surface impurities, the NCM622/NC-0.1 delivered a capacity retention of 92.0% after 100 cycles at 195 mA g\(^{-1}\) within 3.0–4.5 V, better than that of bare NCM622 with capacity retention of only 76.4%. Even at 975 mA g\(^{-1}\), NCM622/NC delivered a high discharge capacity of 156.6 mAh g\(^{-1}\). Nitrogen and sulfur dual-doped carbon (NSC) was prepared and subsequently coated over NCM811 by a simple and one-step process [295]. In the voltage range of 3.0–4.5 V, the 0.3 wt.% NSC@NCM811 delivered a capacity of 177.89 mAh g\(^{-1}\) with the corresponding capacity retention of 90.64% after 100 cycles at 0.1 °C, while raw NCM811 delivered 65.67% of its initial capacity. The 0.3 wt.% NSC@NCM811 delivered a discharge capacity of 111.39 mAh g\(^{-1}\) even at a high rate of 2.0 °C. These results were ascribed to a coating layer that
improved ionic and electronic transfer as well as prevented the degradation of the electrodes. NCM811 was wrapped with a pyrazine-linked 2D sheet by the condensation reaction of amine and ketone in the presence of NCM811 particles. The TEM image indicated that the coating layer was uniform with an approximate thickness of 1 nm (figure 11(D)) [296]. After 100 cycles at 600 mA g$^{-1}$ and 60 °C, this composite delivered 68.2% of its capacity retention in contrast to 17.9% for the raw NCM811. In addition, the Pyr-2D coating turned out to improve the air stability and rate performance of NCM811 as indicated by the robust cycling performance. This improved performance was ascribed to a protective layer mitigated by the growth of a resistive layer and did not inhibit the Li$^+$ diffusion much in the electrode. Cyclized-polyacrylonitrile (cPAN) coated NCM622 was prepared via a wet-coating method to combine the high ion conductivity of the conductive polymer and the good electronic conductivity of the delocalized sp$^2$ π bonds in graphite group with pyridinic-N [297]. The TEM image of the 2 wt.% cPAN-coated NCM622 revealed that the thickness of the amorphous film was about 25–30 nm. In the voltage range of 2.8–4.5 V, the 2 wt.% cPAN-coated NCM622 delivered a capacity of 161.5 mAh g$^{-1}$ with a capacity retention of 88.6% at 1.0 °C after 200 cycles, while bare NCM622 obtained a capacity retention of 73.3%. The polypyrrole coated NCA (PL-LNCA-2) was prepared by a liquid-phase chemical oxidation polymerization method [298]. Among the three composites, the PL-LNCA-2 displayed the highest capacity retention of 88.8% at 180 mA g$^{-1}$ after 100 cycles and an outstanding rate performance of 163.5 mAh g$^{-1}$ at 900 mA g$^{-1}$, while the pristine LNCA material exhibited a capacity retention of 71.6% at 180 mA g$^{-1}$ after 100 cycles. The PL-LNCA-2 cathode material still remained the spherical morphology and as the rhombohedral phase after cycles. This likely indicated that the PPy maintained the structural stability of cathode material during the cycles. Xu et al fabricated polymer poly(3,4-ethylenedioxythiophene) skin decorated on both secondary and primary particles of LiNi$_{0.85}$Co$_{0.1}$Mn$_{0.85}$O$_2$ by an oxidative chemical vapor deposition technique [299]. The ultra-conformal poly(3,4-ethylenedioxythiophene) skin significantly restrained the undesired phase transformation and the associated oxygen loss, retarded intergranular and intragranular mechanical cracking, boosted the transport of lithium ions and electrons, and effectively stabilized the cathode-electrolyte interface. As a result, this composite obtained 91% of its initial capacity in contrast to 54% for bare LiNi$_{0.85}$Co$_{0.1}$Mn$_{0.85}$O$_2$ upon 100 cycles at 200 mA g$^{-1}$. A ~3 µm sized NCM622 with a thin polyphenylene film was prepared via the spontaneous reaction between NCM622 and C$_6$H$_5$N$_2^+\cdot$BF$_4^-$ [300]. In this unique structure, the aromatic diazonium cations are reduced to phenyl radicals (C$_6$H$_5$N$_2^+ \rightarrow$ C$_6$H$_5$N$^-$) via electron transfer from bare NCM622, forming LNCM (figure 11(E)). Therefore, polyphenylene/LNCM-3 displayed a thin conductive polymer layer with a thickness of ~10 nm, which endowed this composite with a high discharge capacity of ~148 and ~105 mAh g$^{-1}$ at 0.1 °C and ~20 °C or at 1.0 °C and ~20 °C, respectively, and a superior low-temperature cycle stability (capacity retention was up to 90% at 0.5 °C over 1150 cycles). Similarly, NCM811 with a 5–8 nm cathode electrolyte interphase (CEI) layer was modified through chemical reactions between the lithium tetra(trimethylsilyl) borate (LTB) layer and the NCM811 electrode (figure 11(F)) [301], and 0.025 LTB–NCM811 delivered a capacity retention of 75.5% at 200 mA g$^{-1}$ and high temperature after 100 cycles. This cycling stability was ascribed to the CEI layer preventing boundary between the primary particles covered with decomposed adducts from electrolyte decomposition. Li et al designed a NCM811 surface with a layer of 4-vinylbenzeneboronic acid (4-VBBA) to make the surface less hydrophilic [302]. Benefiting from less F-containing species formed in the SEI film on the surface, NCM811@4-VBBA maintained a high capacity of 105.6 mAh g$^{-1}$ at 2 °C after 500 cycles, while pristine NCM811 only delivered a capacity of 85.9 mAh g$^{-1}$ under similar conditions. A thermal treatment was used to prepare dimethoxydimethylsilane (DODSi)-functionalized LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ with (Si–O) functional groups on surface [303]. Benefiting from the Li$_2$SiO$_4$-based CEI layer on the surface through chemical interaction with nucleophilic residual Li$^+$ species, the 1% DODSi-modified NCM811 displayed much improved cycle stability with 71.8% capacity retention after 100 cycles at 55 °C compared to its pristine (47.1% retention). A graphene-silica (SiO$_2$) coated on LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ was prepared by pumping CH$_4$ into a fixed-bed vertical tube reactor [304]. In the voltage range of 2.5–4.5 V, the graphene ball LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (GB-NCM) composite delivered a capacity retention of 91.0% at 190 mA g$^{-1}$ and 60 °C after 50 cycles, which was higher than that of bare LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (79.9%). Additionally, the practicability of the GB–NCM composite was further evaluated by fabricating full cells using graphene balls as anodes. At both 25 °C and 60 °C, it delivered a capacity retention of 84.1% and 78.6% at 700 mA g$^{-1}$ after 500 cycles, respectively, which showed a great promise for the practical application of the GB–NCM electrode. The high electrochemical performance of the GB–NCM composite was ascribed to the homogeneous integrated SiO$_2$ and graphene, which could effectively enhance the electric conductivity of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ powders, block electrolyte penetration and phase transition. To hinder the direct interface reaction, rGO and SiO$_2$ nanoparticles coated NCM523 were prepared [305]. The rGO with hierarchically organized 2D nanosheet subunits exhibited a large surface and a shortened Li$^+$ diffusion pathway, facilitating the kinetic properties and ultimately increased power density. As a result, rGO–SiO$_2$@NCM523 sample exhibited an excellent cyclic retention of 80% compared to 46.1% for the pristine cathode after 100 cycles at 180 mA g$^{-1}$ and 55 °C. Even at 360 and 900 mA g$^{-1}$, the rGO–SiO$_2$@NCM sample delivered high capacities of 146.9 and 126.7 mAh g$^{-1}$, respectively. A facile wet chemical method was used to prepare rGO (outer)SiO$_2$ (inner) double layer-coated NCM523 composite with a homogeneous graphene sheet surface [306]. Benefiting from the rGO–SiO$_2$ coating layer with an improved Li$^+$ and electron conductivity, this material could maintain a capacity retention of 88.5% with an intact morphology compared to 57.8% for
pristine NCM523 with damaged particles after 100 cycles at 18 mA g$^{-1}$. Even at a high current rate of 900 mA g$^{-1}$, a capacity of 103.2 mAh g$^{-1}$ was also achieved, which was higher than bare NCM523 (48.6 mAh g$^{-1}$) and 0.5 wt.% SiO$_2$ coated NCM 523 (42.2 mAh g$^{-1}$).

In recent studies, a simultaneous bulk doping and surface-coating approach of multi-transition metals was proposed to exploit their advantages while maintaining cathode stability, high capacity, safety, and good charge transport. Among them, LiNi$_{0.8}$Co$_{0.2}$O$_{2.05}$Cu$_{0.05}$O$_{2}$ (NCACF) was prepared to decrease the relative ratio of Ni$^{2+}$/Ni$^{3+}$ on the surface and increase the performance of the Li$^+$ diffusion coefficient, structure stability, and charge transfer [307]. When applied as a cathode for LIBs, NCACF displayed discharge capacity of 164.2 mAh g$^{-1}$ after 100 cycles at 180 mA g$^{-1}$, corresponding to a capacity retention of 92.50%, whereas the capacity retention of NCA, LiNi$_{0.8}$Co$_{0.2}$O$_{2.05}$Cu$_{0.05}$O$_{2}$ (NCAC), and LiNi$_{0.8}$Co$_{0.2}$O$_{2.05}$Cu$_{0.05}$O$_{2}$ (NCACF) was 86.62%, 91.12%, and 89.19%, respectively. In particular, NCACF delivered an impressive rate capability (143.12 mAh g$^{-1}$ at 1800 mA g$^{-1}$). Then, NCM811 was modified with an in-situ Li$_{Ni_{1-x}}$Fe$_{2}$O$_{4}$ and NiFe$_{2}$O$_{4}$ (LNFO and NFO) surface by a sample wet-chemical method [308]. Due to LNFO and NFO being used as the coating layer, bonding with the surface oxygen vacancies of the bulk material meant it was confirmed to be an effective approach to improve the electrical and ionic conductivity at the interface. As a result, the LNFO and NFO delivered 74.32% of its initial capacity in contrast to 51.59% for raw NCM811 after 100 cycles at 200 mA g$^{-1}$ and 55 °C within a voltage range of 2.75–4.4 V. Even at a high current of 2000 mA g$^{-1}$, LNFO and NFO also obtained a capacity of 140.56 mAh g$^{-1}$. The in-situ XRD results showed that the maximum position shifts of the (003), (101) and (104) peaks for the LNFO and NFO sample are less than those of NCM during the charge process. Chen et al. prepared single crystalline NCM811 coated on cobalt (0.6 wt.%) and manganese (0.08 wt.%) in comparison to NCM811 coated by cobalt (0.6 wt.%) and bare NCM811 [309]. Benefiting from the formation of the spinel Co$_3$O$_4$ and LiMn$_2$O$_4$ layer on the surface, Co$_3$O$_4$ and LiMn$_2$O$_4$ coated NCM811 (Co and Mn–NCM811), Co$_3$O$_4$ coated NCM811 (Co–NCM811) and NCM811 delivered capacity retentions of 91.4%, 89.9% and 86.5% at 185 mA g$^{-1}$ after 100 cycles, respectively. Even at a high current rate of 925 mA g$^{-1}$, Co and Mn–NCM also achieved a capacity of 161.7 mAh g$^{-1}$. To improve cycle stability and rate performance of NCA, Sb-doped tin oxide (ATO) and Li$_2$TiO$_3$ (LTO) were used as coating materials [310]. The composite delivered a capacity retention of 88.56% in contrast to 76.15% for bare NCA at 200 mA g$^{-1}$ and 60 °C after 200 cycles. Even cycled at 1000 mA g$^{-1}$, a discharge capacity of 153 mAh g$^{-1}$ also was obtained, which was 24 mAh g$^{-1}$ higher than that of the bare NCA. Such an enhanced performance could be ascribed to the ATO/LTO coating layer, which suppressed increase of lithium residues during storage and facilitated the Li$^+$ diffusion. To improve cycling stability and increase the lithium-ion diffusion coefficient of LiNi$_{0.92}$Co$_{0.06}$Al$_{0.02}$O$_2$ (NCA92), W$^{6+}$ and BO$_3^{3-}$ co-doping LiNi$_{0.92}$Co$_{0.06}$Al$_{0.02}$O$_2$ (NCA92–W–B) was formed [311]. NCA92–W–B achieved a high capacity of 189.3 mAh g$^{-1}$ with a capacity retention of 93.4% after 100 cycles at 200 mA g$^{-1}$, whereas the pristine cathodes and W$^{6+}$-doping LiNi$_{0.92}$Co$_{0.06}$Al$_{0.02}$O$_2$ (NCA92–W) exhibited capacity retentions of 53.0% and 85.6%. In particular, NCA92–W–B obtained a capacity of 155.3 mAh g$^{-1}$ at a high current of 2000 mA g$^{-1}$. The improved performance was ascribed to co-doping that could suppress the detrimental H2–H3 phase transition and enlarge the interlayer spacing of NCA92. The structural stability of LiNi$_{0.88}$Co$_{0.06}$Mn$_{0.03}$Al$_{0.03}$O$_2$ (NCMA–Z) was strengthened by a two-step modification of Zr-doping and LiBO$_2$-coating [312]. The Zr$^{4+}$ doped in the Ni slab and the Li slab can enhance the structure stability due to the strong binding energy of Zr–O. On the other hand, the LiBO$_2$ coating layer also prevented the transition metal ion loss, improved the surface Li ion conductivity, benefited to reduce the residual alkali and suppressed the electrolyte etch. For such a low-cobalt Zr-doped and LiBO$_2$-coated LiNi$_{0.88}$Co$_{0.06}$Mn$_{0.03}$Al$_{0.03}$O$_2$ (NCMA–ZB) cathode for LIBs, a high retention ratio of 97.8% was achieved at 200 mA g$^{-1}$ at 45 °C after 50 cycles, whereas Zr-doped LiNi$_{0.88}$Co$_{0.06}$Mn$_{0.03}$Al$_{0.03}$O$_2$ (NCMA–Z) and NCMA obtained capacity retentions of 93.0% and 86.7%, respectively. Moreover, when NCMA–ZB was used as the cathode in full cells, a capacity retention of 95.8% was obtained after 1000 cycles at 200 mA g$^{-1}$ within 2.75–4.2 V. Cross-section SEM images showed that there were no visible cracks in cycled NCMA–ZB samples, demonstrating the significant improvement of structural and thermal stability after modification (figure 12(A)). LiNi$_{0.7}$Mn$_{0.1}$Co$_{0.1}$Al$_{0.7}$O$_2$ was encapsulated in the glassy LiBO$_2$ network (NMCA–LBO) within the primary particles [313], and NMCA–LBO retained 92.2% of its initial capacities after 200 cycles at 100 mA g$^{-1}$, while that of pristine NMCA- was ~89.0%. Even at a high current rate of 2000 mA g$^{-1}$, NMCA–LBO achieved a capacity of 96.4 mAh g$^{-1}$. In a full cell with Si/C-400 as an anode, capacity retention of 85% was maintained after 1000 cycles at 100 mA g$^{-1}$ even under ~20 °C. The suppression of the microcrack evolution and phase transition (figure 12(B)) and enhanced ion conduction upon the LBO encapsulation accounted for the satisfactory rate capability of the modified cathode. The cycling stability of LiNi$_{0.9}$Co$_{0.06}$Al$_{0.02}$O$_2$ was improved via the synergistic effect of excellent fluidity of H$_2$BO$_3$ and the outstanding stability of Y$_2$O$_3$ (NCA–BY0.1) [314]. Benefiting from the interface reaction being mitigated, NCA–BY0.1 showed a capacity retention of 93.7% at 1 °C over 100 deep charge–discharge cycles, which was much better than bare NCA (91.6%). The soft-packing battery of NCA–BY0.1 also exhibited a capacity retention of 81.7% after 800 cycles at 1 °C. Chae et al prepared LiNi$_{0.2}$Co$_{0.2}$Mn$_{0.2}$O$_2$ electrode using metal–organic framework (MOF) as a multifunctional additive for selectively trapping transition-metal components [315]. The MOF can trap the volume of nickel ions through its porous structure to suppress surface degradation triggered by the nickel-ion dissolution. As a result, the obtained compositions retained more than 95.0% of their capacity at 1 °C, 25 °C and over 50 cycles, and 5 wt.% MOF–NCM622 exhibited 82.2% of its initial capacity in contrast to 65.5% for raw NCM622 after 100 cycles at 1 °C.
that the thickness of the modifying layer was approximately on a mechanical mixing method.\textsuperscript{200} \[\text{LiNi}_{107}\text{mAh g}^{-1}\] after 200 cycles corresponding to a capacity retention ratio of a discharge capacity of 148 mAh g\(^{-1}\) in the voltage range of 3.0–4.6 V, LFO@NCM523 delivered cathode material for use at a higher operating voltage.\textsuperscript{ling. Zhang} SEI formation and severe electrolyte decomposition upon cycling.\textsuperscript{NCA–NTO cathode can alleviate the problems of HF attack, capacity of 170 mAh g\(^{-1}\) at high current density of 500 mA g\(^{-1}\) was achieved. Even when subjected to a high current density of 5 °C, the composite also delivered a capacity of 170 mAh g\(^{-1}\). TEM images illustrated that the NCA–NTO cathode can alleviate the problems of HF attack, SEI formation and severe electrolyte decomposition upon cycling.\textsuperscript{Zhang et al} prepared LaFeO\(_3\) (LFO) coated NCM523 cathode material for use at a higher operating voltage.\textsuperscript{318} In the voltage range of 3.0–4.6 V, LFO@NCM523 delivered a discharge capacity of 148 mAh g\(^{-1}\) at 180 mA g\(^{-1}\) after 200 cycles corresponding to a capacity retention ratio of 80%, while raw NCM523 obtained a discharge capacity of 167 mAh g\(^{-1}\) with a capacity retention ratio of 63%. The LiNi\(_{0.88}\text{Co}_{0.09}\text{Al}_{0.03}\text{O}_2\) was modified by Y-doped ZrO\(_2\) based on a mechanical mixing method.\textsuperscript{319} TEM images indicated that the thickness of the modifying layer was approximately 50 nm, XPS results indicated that less adsorbed species (LiOH or Li\(_2\)CO\(_3\)) were formed on the surface of the modified particles. After 100 cycles at 200 mA g\(^{-1}\), capacity retention was enhanced from 67.5% to 85.5%. This improved rate capability was ascribed to the existence of oxygen vacancies in Y-doped ZrO\(_2\). To improve structure stability of NCM811, Ce\(_{0.2}\text{O}_{1.9}\) (CD) solid electrolyte was designed.\textsuperscript{320} The different redox voltages of Ce and Dy elements can achieve a synergetic effect between the two components, in which Dy doping may cause lattice defects and accelerate the redox reaction (Ce\(^{4+}\) + Ni\(^{2+}\) → Ce\(^{3+}\) + Ni\(^{3+}\)), which is associated with decreased Li\(^+/Ni^{2+}\) cation disorder. Otherwise, oxygen vacancies in the CD-modified layer can enhance structure stability (figure 12(C)). As a result, NCM811–CD delivered 91.15% of its initial capacity in contrast to 67.23% for the raw NCM811 after 100 cycles at 900 mA g\(^{-1}\). High-ionic-conductivity a-Li–La–Zr–O was implemented as an artificial SEI coating layer on NCM811 via a sol–gel method.\textsuperscript{321} After 75 cycles at 2 °C and 30 °C in voltage range of 2.8–4.4 V, the 0.75 wt.% a-Li–La–Zr–O coated NCM811 obtained a capacity retention of nearly 80%, while the bare NMC showed only 47.4% capacity retention. Thermal stability of NCM523 was improved by thermo-forming La\(_2\)NiLiO\(_8\) (NLNO) shields to simultaneously boost charge conduction characteristics and circumvent the electrolytic degradation of NCM523 (figure 12(D)).\textsuperscript{171} In the voltage range of 2.7–4.5 V, 5 wt.% NLNO-mixed-NCM523 delivered a discharge capacity of 164 mAh g\(^{-1}\) after 200 cycles at 1 °C, 60 °C (capacity retention ratio of 84.18%),
which was higher than NCM523 of 71 mAh g\(^{-1}\) (capacity retention of 45.51%). Similarly, NCM523 was modified by using La\(_2\)NiLiO\(_4\) (LNLO) as a void-filling agent within secondary particles [322]. Benefiting from low grain boundaries and bulk resistances, 6 wt.% LNLO-mixed-NCM523 delivered a discharge capacity of 155.3 mAh g\(^{-1}\) after 500 cycles at 1.0 °C in a 2.7–4.5 V voltage range, corresponding to a capacity retention ratio of 81.5%, while pristine NCM523 obtained a discharge capacity of 101 mAh g\(^{-1}\) (capacity retention ratio of 58.9%). To decrease the migration of oxygen near the Li\(_{0.05}\)Co\(_{0.05}\)Al\(_{0.65}\)O\(_2\) surface, a La\(_2\)NiLiO\(_4\) coating layer was fabricated [323]. Benefiting from the structural stability of the lattice and the side reactions alleviated on the surface, La-coated NCA nanotubes delivered 82.8% of its initial capacity in contrast to 61.9% for bare NCA after 200 cycles at 50 mA g\(^{-1}\). Even at a high current rate of 1000 mA g\(^{-1}\), the La-coated NCA sample also delivered a capacity of 114.4 mAh g\(^{-1}\). The Li\(_3\)PO\(_4\), Li\(_2\)ZrO\(_3\) and Li\(_4\)Ti\(_5\)O\(_12\) coated NCM811 were prepared via a hydrothermal reaction and a heat treatment process, respectively [324]. In the voltage range of 2.8–4.5 V, capacity retentions of 84.4% and 93.3% were obtained after 45 cycles at 150 mA g\(^{-1}\) for pristine and coated samples, respectively. The discharge capacities of Li\(_3\)PO\(_4\) coated NCM811, Li\(_2\)ZrO\(_3\) coated NCM811 and Li\(_4\)Ti\(_5\)O\(_12\) coated NCM811 were 191.1, 169.3 and 172.2 mAh g\(^{-1}\) at 5.0 °C, respectively, while that of bare NCM811 was only 163 mAh g\(^{-1}\). The improved performance was ascribed to the minimization of the side-reaction, and the undesirable SEI layer, surface and charge-transfer resistances were obviously suppressed after cycles. The PO\(_3\)^{1-} polyanion and Mn\(^{4+}\) cation co-doped NCA (NCA–PM) was prepared to enlarge the channel for Li\(^{+}\)-intercalation/deintercalation, lower the cationic mixing, and suppress the structural degradation during cycling [325]. As a result, 3 wt.% NCA–PM (NCA–PM3) could deliver 80.9% of the initial discharge capacity after 100 cycles at 180 mA g\(^{-1}\) and 55 °C, whereas the corresponding capacity retention of the 1 wt.% NCA–PM (NCA–PM1) and PNCA were only 60.4% and 33.6%, respectively. In particular, the NCA–PM3 and NCA–PM1 exhibited capacity retention of 85.4% and 85% even at a 900 mA g\(^{-1}\) rate, while the counterpart of NCA was 81.2%. In the voltage range of 2.7–4.5 V, NCA–PM3, NCA–PM1 and NCA retained capacity retentions of 78.8%, 71.0% and 61.3% after 100 cycles at 180 mA g\(^{-1}\), respectively. Song et al prepared Ca\(_3\)(PO\(_4\))\(_2\) (CP) modified NCM811 via a solid phase method [326]. Benefiting from cathode–electrolyte interphases layer with thickness of 1.0 nm, 0.1 CP-modified NCM811 showed less electrolyte decomposition, and exhibited 72.5% of its capacity retention in contrast to 39.9% for raw NCM811 at 45 °C after 150 cycles. Cross-sectional SEM images illustrated that the formation of microcracks were suppressed during electrochemical cycling. Benefiting from the development of an anionic PO\(_4\) functional group on the CEI layer and strong binding of calcium ions with oxygen elements, 0.1 CP–NCM811/graphite full-cell delivered a capacity retention of 86.7% after 150 cycles at 0.3 °C. To achieve a long-term cycling stability at elevated temperatures and voltages, Mn\(_3\)(PO\(_4\))\(_2\) (MP) coated NCM622 was fabricated [327]. When cycled at 10.0 °C and 60 °C within voltage range of 3.0–4.3 V, bare NCM and MP–NCM delivered capacity retentions of 68.8% and 83.1% after 100 cycles, respectively. MP–NCM also delivered 86.9% of its capacity retention in contrast to 67.4% for raw NCM within voltage range of 3.0–4.6 V after 50 cycles at 0.1 °C. Even at a high current rate of 10.0 °C, MP–NCM electrode obtained a discharge capacities of 114.5 mAh g\(^{-1}\). Such enhanced improvement was attributed to the MnPO\(_4\) layer, which could dramatically reduce transition metal dissolution and the occurring side reactions with the electrolyte, especially at higher temperatures and cut-off voltages. Because of the strong PO\(_4\) (P) covalent bonds, nano-sized crystalline MP coating layer was designed on NCM622 to improve its thermal properties [328]. After 50 cycles at 0.5 °C and 60 °C, discharge capacities of 142.2 and 160 mAh g\(^{-1}\) were obtained for P–NCM and MP–NCM, corresponding to a capacity retention ratio of 81.3% and 90.9%, respectively. This improved performance also was associated with decreased interfacial impedance investigated by AC impedance spectroscopy. In view of this, Lee et al manufactured Ni\(_3\)(PO\(_4\))\(_2\)–coated NCA by a ball milling [329], and its capacity retention after 100 cycles at 100 mA g\(^{-1}\), 55 °C was 75%, which was notably greater than that of PNCA (53%). For instance, the discharge capacity of Ni\(_3\)(PO\(_4\))\(_2\)-coated NCA at a 2000 mA g\(^{-1}\) rate was 149 mAh g\(^{-1}\), while the PNCA delivered only 127 mAh g\(^{-1}\). This result encouraged us to believe that the Ni\(_3\)(PO\(_4\))\(_2\) coating layer on NCA did protect the cathode from chemical attack by HF and thus suppress an increase in charge transfer resistance. A thin LaPO\(_4\) coating layer was designed on an NCM811 surface through a facile wet chemical route to improve its cycle stability and rate performance [330]. A LaPO\(_4\)-coated sample showed smaller charge transfer resistance and higher Li\(^{+}\) diffusion coefficient in compare with pristine sample, and therefore it delivered 91.2% of its capacity retention in contrast to 76.4% for raw NCM811 after 100 cycles at 1 °C. Even at a high current rate of 10.0 °C, a capacity of 124 mAh g\(^{-1}\) was also achieved, which was higher than those of the pristine sample (108.6 mAh g\(^{-1}\)). An in-situ ZrP\(_2\)O\(_5\) coating layer was introduced to improve cycle and rate performance of NCM811 [331]. After 100 cycles at 1.0 °C, pristine NCM811 and ZrP\(_2\)O\(_5\) coated NCM811 (1.0ZPO–NCM811) delivered capacity retention ratios of 66.35% and 86.92%, respectively. The discharge capacity of 1.0ZPO–NCM811 at a 10 °C rate was 148.0 mAh g\(^{-1}\), while the PNCA delivered only 108.2 mAh g\(^{-1}\). The high electrochemical performance of the 1.0ZPO–NCM811 cathode was ascribed to the dense inorganic pyrophosphate layer, which not only had strong Zr–O covalent bonds against the electrolyte but also eliminated surface residual lithium. Zhu et al prepared LiFePO\(_4\) (LFP)-coated LiNi\(_0.5\)Co\(_0.2\)Mn\(_0.3\)O\(_2\) by the high-speed dispersion and mechanical fusion method [332]. In the voltage range of 2.75–4.5 V, the capacity retentions of NCM/MesoCarbon MicroBead graphite anode (MCMB) and NCM-LFP/MCMB pouch cells were 81.4% and 90% after 100 cycles at 180 mA g\(^{-1}\), respectively. In-situ XRD patterns showed that the phase transition temperatures were increased.
from 405 °C to 445 °C after coating. Thus, postponed structure evolution led to the increased thermal decomposition temperature, which was quite significant toward a broad application prospect of NCM–LFP composites as cathode materials in LIBs. Thermal stability of NCA was improved by constructing a LiFePO₄ coating layer, which helps to reduce the formation of a cathode–electrolyte interface layer and the extent of cation mixing in NCA [333]. Even in a full pouch cell configuration versus graphite-based anodes, NCA–LFP obtained a capacity retention of 95% after 150 cycles at 90 mA h g⁻¹ and 55 °C, whereas the NCA cathodes faded 2.5 times faster. The SEM images showed that NCA–LFP surface seemed relative smooth and clean after 100 cycles, indicative of less electrolyte decomposition, whereas the NCA surfaces appeared to be covered by a thick layer of CEI. A sol–gel method was used to fabricate a fast ionic conductor Li₅₋ₓAlₓZrₓPO₃₋ₓ (LAZP) coated NCM811 [334], and the discharge capacity of NCM@LAZP-1 was 179.3 mA h g⁻¹ after 200 cycles at 200 mA g⁻¹ in the potential range of 2.8–4.5 V, which was notably greater than that of pristine NCM (112.1 mA h g⁻¹). Accordingly, the capacity retention of NCM@LAZP-1 after 50 cycles was 84.8%, which was a significant improvement over pristine NCM (52.3%).

The good cycle stability of cathode material at high cutoff voltage resulted from the decreased Li⁺/Ni²⁺ cation mixing, enhanced Li⁺ diffusion rate and structural stability. Because the LiTa₂PO₄ coating layer had an ordered channel with three-dimensional Li⁺ ion transport, the side reaction was inhibited and the surface structure stability of the NCM materials was enhanced. As such a 2–4 nm LiTa₂PO₄ coating layer was based on the surface of NCM811 to improve electrochemical performance of NCM811 at high voltage [335]. In the voltage range of 2.7–4.6 V, LiTa₂PO₄ coated NCM811 (NCMT3) delivered a high capacity of 175.9 mA h g⁻¹ at 180 mA g⁻¹ after cycling 100 times, corresponding to a capacity retention ratio of 84.85%, while the pristine NCM811 cathode delivered only 140.8 mA h g⁻¹, matching with a capacity retention rate of 71.58%. The discharge capacity of NCMT3 at 540 mA g⁻¹ rate was 164.1 mA h g⁻¹, while the pristine NCM811 delivered only 125.6 mA h g⁻¹. High-voltage performance of LiNi₀.₅Co₀.₅Al₀.₀₂O₂ was improved by Li₃O–BPO₄ (LBP) coating [170]. Benefiting from the decreased cation mixing and increased Li⁺ conductivity, NCA@LBP nanotubes delivered 76.2% of its initial capacity in contrast to 68.7% for raw NCA after 100 cycles at 200 mA g⁻¹ within 2.7–4.7 V. TEM-FFT images ensured that NCA@LBP cathode still maintained the R-3m space group from surface to bulk during electrochemical cycling (figure 12(E)).

An anion slab is forced closer to the TM slab when nitrogen is used as anionic dopants in nickel-rich cathode materials as nitrogen has higher charge relative to oxygen, resulting in an enlarged inter-slab distance for the migrating Li⁺. Binder et al prepared nitrogen doped Li₁₋ₓ(NiₓCo₀.₅Mn₀.₅)₀.₉₈O₂ via heating it in ammonia and oxygen, and prepared F-doped Li₁₋ₓ(Ni₀.₈Co₀.₁Mn₀.₁)₀.₉₈O₂ (Li₁₋ₓ(Ni₀.₈Co₀.₁Mn₀.₁)₀.₉₈O₂) by decomposing of PVDF at 500 °C [336]. ToF-SIMS results indicated that fluoride ions were concentrated near the outer surface of the secondary particles and not detected in the core of the particles. In contrast, nitrogen was primarily found within the core of the particles. Benefiting from the samples with higher interlab distances, the 100 and 200 N-doped samples delivered the capacity of 147 and 123 mA h g⁻¹ at 2 °C, respectively, as compared to 116 mA h g⁻¹ for the pristine sample. However, when tested at a rate of 2 °C, initial discharge capacities of 116, 107, 66, 50, and 41 mA h g⁻¹ were obtained for pristine and 1, 1.3, 2, and 4 wt.% F-doped sample, respectively. Except for a fluoride containing surface layer with a low ionic conductivity, it was also found that the transition metal (TM) reduction led to the contraction of the Li–O interslab distances, and an increase in cation site mixing with increasing fluoride concentration was observed, thereby hindering the performance at such high C-rates. To suppress the increase in charge transfer resistance and NCA material pulverization during cycling, NCA was prepared with a 50 nm thick AlF₃ layer [337]. When cycled at 100 mA g⁻¹ and 55 °C, AlF₃-coated NCA delivered a capacity retention of 84.7% compared to that of PNCA (79.1%) after 100 cycles. Subsequently, a full cell was constructed using graphite as the anode material and capacity retentions of 66.5% and 86.2% were obtained for bare and AlF₃-coated NCA after 1000 cycles. The stability of NCM811 at high-voltage was enhanced by ALD AlₓWₓFₓ/AlF₃ coating [338]. The impedance rise was mitigated by ~80% compared to the NMC811 baseline after ~300 h of high-voltage exposure during cycling. The NCM811 electrode was prepared with LiAlF₃ solid thin film interfacial layer to realize the wide electrochemical window [339]. This electrode showed excellent capacity retention within 100 cycles at 200 mA h g⁻¹, 50 °C with an electrochemical window of 2.75–4.5 V vs Li⁺/Li, which was ascribed to the LiAlF₃ interfacial layer not only improving cycle stability through reduced parasitic reactions, but also maintaining satisfactory ion conductivity. The structural degradation and intergranular cracks of NCM622 were mitigated by constructing a LiAlO₂/LiF and AlF₃ hybrid coating layer [340]. Benefiting from the synergistic effect of LiAlO₂ with high ionic conductor and LiF and AlF₃ in suppressing the attack by HF, the NCM622@LiAlO₂/LiF and AlF₃ displayed a discharge capacity of 124.3 mA h g⁻¹ with a capacity retention of 74.5% after 300 cycles at 5 °C in the voltage window of 2.7–4.5 V. However, NCM622 and NCM622@LiAlO₂ showed discharge capacities of close to 7.5 and 88.1 mA h g⁻¹ after 300 cycles at 5 °C, respectively. A solid vent-out crystallization process was used to form a 10–20 nm thick Fe₃O₄ layer on the surface of NCA, accordingly, the thermal stability of NCA was enhanced [341]. This composite delivered a capacity of 105.4 mA h g⁻¹ at 1 °C, 55 °C over 100 cycles with capacity retention of 57.8%, which was higher than that of bare NCA (capacity retention of 45.2%). This enhanced thermal stability was ascribed to the protection effect of the Fe₃O₄ coating layer, which suppressed the reactivity of Ni⁴⁺ ions and the release of oxygen through prohibiting the oxidized cathode from being directly contacted with electrolyte solution.
5. Conclusions and perspectives

As a promising alternative cathode for LIBs, Li[Ni_{x}Co_{1-x}Mn_{1-x}\cdot y]O_{2} (NCM) and Li[Ni_{x}Co_{y}Al_{1-x-y}]O_{2} (NCA) (x \geq 0.8) nickel-rich cathode materials have received noteworthy achievements in commercial applications, due to their low-cost and high theoretical capacities. However, large amount of cation disorders were formed in the cathode materials during the charge/discharge process, which would inevitably lead to phase transition from layered to disordered spinel/rock-salt structure and microcracks following severe capacity loss. In addition, other issues include oxygen loss, transition metal dissolution, side reactions between electrode and electrolytes, as well as thermal instability under high voltage and deep charging/discharging. In recent years, many efforts have been devoted to alleviate these problems and obtained considerable progresses by optimizing secondary particles, pre-oxidating of precursors, designing electrolyte additives, introducing extrinsic element with strong electrons, or designing 2–5 μm single crystals. In this review, we summarize these works in order to provide a clear understanding about the present achievements. According to the previous reports, the synthesis of core–shell/concentration gradient secondary particles is an effective method to mitigate Li^{+}/Ni^{2+} mixing and particle crack with side reactions during synthesizing and cycling process. The typical core–shell structures of concentration gradient composites are high nickel structure coated on the low nickel structure. For modifying the surface structure of precursors, one Na_{2}S_{2}O_{3} is commonly the oxidizing agent for the enhanced oxidation state of Ni. The poor cycle stability of nickel-rich system can be partly ascribed to the anisotropic shrinkage/expansion breaking layered structure. The results indicate that by simply synthesizing the core–shell secondary particles with a concentration gradient, the cycle stability of NCM/NCA towards high capacity can be significantly enhanced. In addition, designing various electrolyte additives, such as lithium bis(oxalato)borate (LiBOB) additive in the LiPF_{6} can stabilize the interface, is also an effective way to improve cycling stability. Most of the nickel-rich cathode materials exhibit a combination of phase transition and oxygen release when charging/discharging. Integrating extrinsic element into bulk and surface can control the degree of cation disorder and realize a higher reversible reaction. Rational improvements to the mechanical stability of nickel-rich cathode materials focused mostly on three aspects: increasing the layered distance to improve Li^{+} diffusion path; constructing strong metal-oxygen bonds to improve the structure stability or electric conductivity of materials, such as Zr–O, Ta–O, Ce–O, etc; designing an ionic conductor with suitable void space to use its inner void space improving the lithium ions diffusion, such as Li2ZrO2 and LBP coating structure. Moreover, optimization of the synthesis process, such as processing active material into micron-sized single crystals, also exhibits a good promising in applications. Single crystal-based cathode materials possess the performance of low specific surface area and outstanding mechanical stability, which is capable of maintaining particle integrity and eliminating intergranular cracks during charge/discharge processes. As the price of Co is high, combining the effective modified strategies and high voltage performance, low/zero Co materials show the most promising for practical application.

Although some effective measures have been taken to improve the capacity and cycle stability of nickel-rich cathode materials in LIBs, there are still several challenges to be addressed. Research on the degradation mechanism of materials can provide guidance for rational design improvement strategies, but there are still some degeneration mechanisms to be clarified, and there also exists some controversial perspectives. The in-situ and ex-situ characterizations combined with theoretical calculation is a promising method to further explore the degeneration mechanisms. Moreover, many modified nickel-rich cathode materials displayed excellent performance in half cells, but their application in full LIBs should be noticed in the future. There is no doubt that the performance of nickel-rich cathode materials in full LIB is crucial for practical applications.

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References

[1] Manthiram A 2020 A reflection on lithium-ion battery cathode chemistry Nat. Commun. 11 1550
[2] Liu Y, Yu Z X, Chen J, Li C X, Zhang Z J, Yan X Y, Liu X H and Yang S C 2022 Recent development and progress of structural energy devices Chin. Chem. Lett. 33 1817–30
[3] Li W D, Erickson E M and Manthiram A 2020 High-nickel layered oxide cathodes for lithium-based automotive batteries Nat. Energy 5 26–34
[4] Zhang J, Wang J, Shi Z Q and Xu Z W 2018 Mesoporous carbon material as cathode for high performance lithium-ion capacitor Chin. Chem. Lett. 29 620–3
[5] Pender J P et al 2020 Electrode degradation in lithium-ion batteries ACS Nano 14 1243–95
[6] Xu J, Lin F, Doeff M M and Tong W 2017 A review of Ni-based layered oxides for rechargeable Li-ion batteries J. Mater. Chem. A 5 874–901
[7] Bianchini M, Roca-ayats M, Hartmann P, Brezesinski T and Janek J 2019 There and back again—the journey of LiNiO2 as a cathode active material Angew. Chem., Int. Ed. 58 10434–58
[8] Mesnier A and Manthiram A 2020 Synthesis of LiNiO2 at moderate oxygen pressure and long-term cyclability in lithium-ion full cells ACS Appl. Mater. Interfaces 12 52826–35
[9] Kong P T, Liang C P, Wang L H, Zheng Y P, Peranathan S, Longo R C, Ferraris J F, Kim M and Cho K 2019 Kinetic stability of bulk LiNiO2 and surface degradation by oxygen evolution in LiNiO2-based cathode materials Adv. Energy Mater. 9 1802586
[10] Toma T, Maezono R and Hongo K 2020 Electrochemical properties and crystal structure of Li‘/H‘ cation-exchanged LiNiO2 ACS Appl. Energy Mater. 3 4078–87
[11] de Biasi L, Schiele A, Roca-ayats M, Garcia G, Brezesinski T, Hartmann P and Janek J 2019 Phase transformation behavior and stability of LiNiO2 cathode material for li-ion batteries obtained from in situ gas
analysis and operando x-ray diffraction ChemSusChem 12 2240–50
[12] Li M and Lu J 2020 Cobalt in lithium-ion batteries Science 367 979–80
[13] Saadoun I and Delmas C 1996 LiNi1−xcox2 positive electrode materials: relationships between the structure, physical properties and electrochemical behaviour J. Mater. Chem. 6 193–9
[14] Wilk P, Marzec J and Molen J 2003 Structural and electrical properties of LiNi1−xcox2 Solid State Ion. 157 109–14
[15] Song M Y, Bang E Y, Mumm D R and Park H R 2012 Electrochemical properties of LiNi1−xcox2 (y = 0.1, 0.3 and 0.5) synthesized from LiOH−H2O, NiO and CoO2 by solid state reaction method Ceram. Int. 38 4953–9
[16] Arai H, Okada S, Sakurai Y and Yamaki J I 1998 Thermal behavior of Li1−xNiO2 and the decomposition mechanism Solid State Ion. 109 295–302
[17] Venkatraman S and Manthiram A 2003 Structural and chemical characterization of layered Li1−xNi1+yMn2−yO2−δ (y = 0.25 and 0.5, and 0<(1−x)<1) oxides Chem. Mater. 15 5003–9
[18] Mohan P and Kalaigian G P 2013 Structure and electrochemical performance of LiFe2X1−xVOx−y−z cathode materials for rechargeable lithium-ion batteries J. Electroceramics 31 210–7
[19] Song M Y, Lee D S and Mumm D R 2006 Electrochemical properties of LiNi1−xTi2O2 synthesized by ball milling and solid-state reaction method Mater. Res. Bull. 41 1720–8
[20] Song M Y, Lee D S and Park H R 2012 Electrochemical properties of LiNi1−xTi2O2 and LiNi0.85Mn0.25O2 (M=Zn, Al, and Ti) synthesized by the solid-state reaction method Mater. Res. Bull. 47 1021–7
[21] Pouillerie C, Crogueucq L and Delmas C 2000 The Li1−xNi1+yMg2−yO2−δ (y=0.05, 0.10) system: structural modifications observed upon cycling Solid State Ion. 132 15–29
[22] Sathiyanamorthi R, Shakkhivel P, Ramalakshmi S and Shul Y-G 2007 Influence of Mg doping on the performance of LiNiO2 matrix ceramic nanoparticles in high-voltage lithium-ion cells J. Power Sources 171 922–7
[23] Kim J and Amine K 2002 A comparative study on the substitution of divalent, trivalent and tetravalent metal ions in LiNi1−xmMx2O2 (M=Ca2+, Al3+ and Ti4+) J. Power Sources 104 33–39
[24] Julies C, Nazri G A and Rougier A 2000 Electrochemical performances of layered LiM1−xM′xO2 (M=Ni, Co; M′=Mg, Al, Bi) oxides in lithium battery Solid State Ion. 135 121–30
[25] Mohan P, Kalaigian G P and Muralidharan V S 2012 Improved the electrochemical performance of LiCo1−xNi2O4 cathode material for rechargeable lithium ion battery J. Nanosci. Nanotechnol. 12 7052–9
[26] Nishida Y, Nakane K and Satoh T 1997 Synthesis and properties of gallium-doped LiNi2O4 as the cathode material for lithium secondary batteries J. Power Sources 68 561–4
[27] Kudo T and Mizutani N 1999 Effect of addition of a foreign to LiNiO2 by complex polymerized method on its electrochemical properties Key Eng. Mater. 169–70 217–20
[28] Yang Z H, Zhang Z J, Pan Y J, Zhao S, Huang Y Q, Wang X Y, Chen X Y and Wei S Y 2016 First-principles investigation of the effects of Sb doping on the LiNiO2 J. Solid State Chem. 244 52–60
[29] Cui P, Jia Z J, Li L Y and He T 2011 Preparation and characteristics of Sb-doped LiNiO2 cathode materials for Li-ion batteries J. Phys. Chem. Solids 72 899–903
[30] Kwon I H, Park H R and Song Y J 2013 Effects of Zn, Al and Ti substitution on the electrochemical properties of LiNiO2 synthesized by the combustion method Russ. J. Electrochem. 49 221–7
[31] Song M, Kwon S, Kwon I and Park H 2007 Variation of LiNiO2 cathode properties with substitution of Ga, In and Ti by the combustion method J. Appl. Electrochem. 37 421–7
[32] Naghash A R and Lee J Y 2001 Lithium nickel oxyfluoride (Li1−xNi1+yF2−y−z) and lithium magnesium nickel oxide (Li1−y(Mg,Ni1−y)x1−yO2) cathodes for lithium rechargeable batteries: part I: Synthesis and characterization of bulk phases Electrochim. Acta 46 941–51
[33] Park S H, Sun Y-K, Park K S, Nahm K S, Lee Y S and Yoshih M 2002 Synthesis and electrochemical properties of lithium nickel oxysulfide (LiInO2−x) material for lithium secondary batteries Electrochim. Acta 47 1721–6
[34] Zheng F H, Yang C H, Xiong X H, Xiong J W, Hu R Z, Chen Y and Liu M J 2015 Nanoscale surface modification of lithium-rich layered-oxide composite cathodes for suppressing voltage fade Angew. Chem., Int. Ed. 54 13058–62
[35] Cao F et al 2022 Inhibiting Mn migration by Sb-pinning transition metal layers in lithium-rich cathode material for stable high-capacity properties Small 18 2200713
[36] Chen J X, Huang Z, Zeng W H, Ma J J, Cao F, Wang T T, Tian W X and Mu S C 2022 Surface engineering and trace cobalt doping suppress overall Li/Na mixing of Li-rich Mn-based cathode materials ACS Appl. Mater. Interfaces 14 6649–57
[37] Julien C and Massot M 2002 Raman scattering of Li1−xAlxO2 cathode Solid State Ion. 148 53–59
[38] Stoyanova R, Zhecheva E, Kuzmanova E, Alcántara R, Lavela P and Tirado J L 2000 Aluminium coordination in Li1−xAlxO2 solid solutions Solid State Ion. 128 1–10
[39] Kim J and Amine K 2001 The effect of tetravalent titanium substitution in LiNi1−xTi2O2 (0.025≤x≤0.2) system Solid State Ion. 148 53–59
[40] Kim U-H et al 2018 Pushing the limit of layered transition metal oxide cathodes for high-energy density rechargeable Li ion batteries Energy Environ. Sci. 11 1271–9
[41] Yoon C S, Choi M-J, Jun D-W, Zhang Q, Kaghazchi P, Kim K-H and Sun Y-K 2018 Cation ordering of Zr-doped LiNiO2 cathode for lithium-ion batteries Chem. Mater. 30 1808–14
[42] Yoon C S, Kim U-H, Park G-T, Kim S J, Kim K-H, Kim J and Sun Y-K 2018 Self-passivation of a LiNiO2 cathode for a lithium-ion battery through Zr doping ACS Energy Lett. 3 1634–9
[43] Muralidharan N et al 2020 Lithium iron aluminum nickelate, LiNiFeAlO2—new sustainable cathodes for next-generation cobalt-free Li-ion batteries Adv. Mater. 32 2002960
[44] Muralidharan N, Esselhi R, Hermann R P, Parejija A, Amin R, Bai Y C, Du Z J and Belharouak I 2020 LiNiFe2AlO4, a new cobalt-free layered cathode material for advanced Li-ion batteries J. Power Sources 471 228389
[45] Li H, Zhou P F, Liu F M, Li H X, Cheng F Y and Chen J 2019 Stabilizing nickel-rich layered oxide cathodes by magnesium doping for rechargeable lithium-ion batteries Chem. Sci. 10 1374–9
[46] Ryu H-H, Park K-J, Yoon D R, Aishova A, Yoon C S and Sun Y-K 2019 LiIn2O3Cu0.09W0.91O2: a new type of layered oxide cathode with high cycling stability Adv. Energy Mater. 9 1902698
[47] Yang X, Tang Y W, Qu Y H, Shang G Z, Wu J, Zheng J F, Lai Y Q, Li J and Zhang Z A 2019 Bifunctional
nano-ZrO$_2$ modification of LiNi$_{0.5}$Co$_{0.2}$O$_2$ cathode enabling high-energy density lithium ion batteries *J. Power Sources* **438** 226978

[48] Wang J, Kim H, Hyun H, Jo S, Han J, Ko D, Seo S, Kim J, Kong H and Lim J 2020 Probing and resolving the heterogeneous degradation of nickel-rich layered oxide cathodes across multi-length scales *Small Methods* **4** 2000551

[49] Hou P Y, Yin J M, Ding M, Huang J Z and Xu X J 2017 Surface/interfacial structure and chemistry of high-energy nickel-rich layered oxide cathodes: advances and perspectives *Small* **13** 1701802

[50] Li W D, Liu X M, Celio H, Smith P, Dolocan A, Chi M F and Manthiram A 2018 Mn versus all in layered oxide cathodes in lithium-ion batteries: a comprehensive evaluation on long-term cyclability *Adv. Energy Mater.* **8** 1703154

[51] Liang L W, Zhang W H, Zhao F, Denis D K, Zaman F U, Hou L R and Yuan C Z 2020 Surface/interface structure degradation of Ni-rich layered oxide cathodes toward lithium-ion batteries: fundamental mechanisms and remedying strategies *Adv. Mater. Interfaces* **7** 1901749

[52] Liu W, Oh P, Liu X E, Lee M J, Cho W, Chae S, Kim Y and Cho J 2015 Nickel-rich layered lithium transition-metal oxide for high-energy lithium-ion batteries *Angew. Chem., Int. Ed.* **54** 4440–57

[53] Yan W W, Yang S Y, Huang Y Y, Yang Y and Yuan G H 2020 A review on doping/coating of nickel-rich cathode materials for lithium-ion batteries *J. Alloys Compd.* **819** 153048

[54] Manthiram A, Knight J C, Myung S-T, Oh S-M and Sun Y-K 2016 Nickel-rich and lithium-rich layered oxide cathodes: progress and perspectives *Adv. Energy Mater.* **6** 1501010

[55] Huang B H, Liu D Q, Zhang L H, Qian K, Zhou K, Cai X K, Xia Y, Zheng J M, Wang C M and Gu M 2018 Designing Ni-rich cathode materials with high energy density for practical applications *Nano Energy* **49** 434–52

[56] Seo M-J, Jung H-G, Kuo L-Y, Kaghazchi P, Yoon C S and Zeng W H, Xia F J, Tian W X, Cao F, Chen J X, Wu J S, Yan P F, Zheng J M, Liu J, Wang B Q, Cheng X P, W M Y, Yabuuchi N and Ohzuku T 2003 Novel lithium insertion material of LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ with the Ni(OH)$_2$ phase for Li-ion batteries *Solid State Ion.* **144** 87–97

[57] Yan H P et al 2019 Simultaneously dual modification of Ni-rich layered oxide cathode for high-energy lithium-ion batteries *Adv. Funct. Mater.* **29** 1808825

[58] Li J L et al 2022 B-doped and La$_x$Ni$_{1-x}$O$_2$-coated Ni-rich cathode with enhanced structural and interfacial stability for lithium-ion batteries *J. Energy Chem.* **71** 588–94

[59] Zhang Y J, Du K, Cao Y B, Lu Y, Peng Z D, Fan J, Li L Y, Xue Z C, Su H D and Hu G R 2020 Hydrothermal preparing agglomerate LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode material with submicron primary particle for alleviating microcracks *J. Power Sources* **477** 228701

[60] PAN P F, Zheng J M, Liu J, Wang B Q, Cheng X P, Zhang Y F, Sun X L, Wang C M and Zhang J-G 2018 Tailoring grain boundary structures and chemistry of Ni-rich layered cathodes for enhanced cycle stability of lithium-ion batteries *Nat. Energy* **3** 600–6

[61] Manthiram A, Song B H and Li W D 2017 A perspective on nickel-rich layered oxide cathodes for lithium-ion batteries *Energy Storage Mater.* **6** 125–39

[62] Myung S-T, Maglia F, Park K-J, Yoon C S, Lamp P, Kim S-J and Sun Y-K 2017 Nickel-rich layered cathode materials for automotive lithium-ion batteries: achievements and perspectives *ACS Energy Lett.* **2** 196–223

[63] Kim J, Lee H, Cha H, Yoon M, Park M and Cho J 2018 Prospect and reality of Ni-rich cathode for commercialization *Adv. Energy Mater.* **8** 1702028

[64] Sun H H, Ryu H-H, Kim U-H, Weeks J A, Heller A, Sun Y-K and Mullinis C B 2020 Beyond doping and coating: prospective strategies for stable high-capacity layered Ni-rich cathodes *ACS Energy Lett.* **5** 1136–46

[65] Xu G-L, Liu X, Daali A, Amine R, Chen Z H and Amine K 2020 Challenges and strategies to advance high-energy nickel-rich layered lithium transition metal oxide cathodes for harsh operation *Adv. Funct. Mater.* **30** 2004748

[66] Zeng X Q, Zhan C, Lu J and Amine K 2018 Stabilization of a high-capacity and high-power nickel-based cathode for Li-ion batteries *Chemistry* **4** 690–704

[67] Xia Y, Zheng J M, Wang C M and Gu M 2018 Designing Ni-rich cathode materials with high energy density for practical applications *Nano Energy* **49** 434–52

[68] Fuji H, Xia F J, Tian W X, Cao F, Chen J X, Wu J S, Song R G and Mu S C 2022 Single-crystal high-nickel layered cathodes for lithium-ion batteries: advantages, mechanism, challenges and approaches *Curr. Opin. Electrochem.* **31** 108831

[69] Lee N, Sallis S, Papp J K, Wei J, McCluskey B D, Yang W L and Tong W 2019 Unraveling the cationic and anionic redox reactions in a conventional layered oxide cathode *ACS Energy Lett.* **4** 2836–42

[70] Han J R, von Sacken U and Michel C A 1990 Structure and electrochemistry of Li$_{0.5}$Ni$_{0.5}$O$_2$ and a new Li$_2$Ni$_2$O$_4$ phase with the Ni(OH)$_2$ structure *Solid State Ion.* **4** 271–82

[71] Yabuuchi N and Ohzuku T 2003 Novel lithium insertion material of Li$_{0.8}$Ni$_{0.2}$Mn$_{0.2}$O$_2$ for advanced lithium-ion batteries *J. Power Sources* **119–121** 171–4

[72] Lee M-H, Kang Y-J, Myung S-T and Sun Y-K 2004 Synthetic optimization of Li$_{0.5}$Ni$_{0.5}$Co$_{0.2}$Mn$_{0.2}$O$_2$ via co-precipitation *Electrochem. Acta* **50** 939–48

[73] Huang Z-D, Liu X-M, Oh S-W, Zhang B, Ma P-C and Kim J-K 2011 Microscopically porous, interconnected single crystal LiNi$_{0.8}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode material for lithium-ion batteries *J. Mater. Chem.* **21** 10777–84

[74] Kim S M, Nam K M, Hwang E H, Kwon Y G, Kang D H, Kim S S and Song S W 2014 Interfacial origin of performance improvement and fade for 4.6 V LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ battery cathodes *Phys. Chem. C* **118** 10631–9

[75] W M Y et al 2019 High-voltage charging-induced strain, heterogeneity, and micro-cracks in secondary particles of a nickel-rich layered cathode material *Adv. Funct. Mater.* **29** 1900247

[76] Ahn W, Lim S N, Jung K N, Yeon S H, Kim K B, Song H S and Shin K H 2014 Combustion-synthesized LiNi$_{0.6}$Mn$_{0.2}$O$_2$ as cathode material for lithium ion batteries *J. Alloys Compd.* **609** 143–9

[77] Zheng Z, Guo X D, Chou S L, Hua W B, Liu H K, Dou S X and Yang X S 2016 Uniform Ni-rich LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ porous microspheres: facile designed synthesis and their improved electrochemical performance *Electrochim. Acta* **191** 401–410

[78] Sun H H and Manthiram A 2017 Impact of microcrack generation and surface degradation on a nickel-rich layered LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ cathode for lithium-ion batteries *Chem. Mater.* **29** 8486–93

[79] Kondrakov A O, Schmidt A, Xu J, Geplans N, Hönsig R, Hartmann P, Sommer H, Breslin S T and Janek J 2017 Anisotropic lattice strain and mechanical degradation of high- and low-nickel NCM cathode materials for Li-ion batteries *J. Phys. Chem. C* **121** 3286–94

[80] Ryu H H, Park K J, Yoon C S and Sun Y K 2018 Capacity fading of Ni-rich LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (0.6≤x≤0.95)
cathodes for high-energy-density lithium-ion batteries: bulk or surface degradation? Chem. Mater. 30 1155–63

[82] Kim J H, Ryu H H, Kim S J, Yoon C S and Sun Y K 2019 Degradation mechanism of highly Ni-rich LiNi_0.8Co_0.2Mn_0.8O_2 cathodes with c>0.9 ACS Appl. Mater. Interfaces 11 30096–42

[83] Nam G W, Park N Y, Park K J, Yang J H, Liu J, Yoon C S and Sun Y K 2019 Capacity fading of Ni-rich NCA cathodes: effect of microcracking extent ACS Energy Lett. 4 2995–3001

[84] Zou L F, Zhao W G, Liu Z Y, Jia H P, Zheng J M, Wang G F, Yang Y, Zhang J G and Wang C M 2018 Revealing cycling rate-dependent structure evolution in Ni-rich layered cathode materials ACS Energy Lett. 3 2433–40

[85] Venkatraman S, Choi J and Manthiram A 2004 Factors influencing the chemical lithium extraction rate from layered LiNi_1-x-Co_x-Mn_2O_4 cathodes Electrochem. Commun. 6 832–7

[86] Yamamoto Y, Ohtsuka M, Azuma Y, Takahashi T and Muto S 2018 Cation mixing in LiNi_0.8Co_0.15Al_0.05O_2 positive electrode material studied using high angular resolution electron channeling x-ray spectroscopy J. Power Sources 401 263–70

[87] Ghanty C et al 2015Li^+ ion-extraction/insertion of Ni-rich Li_{1+y}(Ni,Co,Mo)O_2 (0.005<y<0.03; y_z=1, w≈1) electrodes: in situ XRD and Raman spectroscopy study ChemElectroChem 2 1479–86

[88] Kim U H, Lee E J, Yoon C S, Myung S T and Sun Y K 2016 Compositionally graded cathode material with long-term cycling stability for electric vehicle application Adv. Energy Mater. 6 1601417

[89] Wang Q, Shen C H, Shen S Y, Xu Y F, Shi C G, Huang L, Li J T and Sun S G 2017 Origin of structural evolution in capacity degradation for overcharged NMC622 via operando coupled investigation ACS Appl. Mater. Interfaces 9 24731–42

[90] Zhao Z K, Wen Z Y, Li C L, Ding Y, Jiang Y, Wu F, Wu B R, Chen S and Mu D B 2020 Effects of different charge cut-off voltages on the surface structure and electrochemical properties of LiNi_0.8Co_0.2Mn_0.8O_2 Electrochim. Acta 353 136518

[91] Park K J, Hwang J Y, Ryu H H, Maglia F, Kim S J, Lamp P, Yoon C S and Sun Y K 2019 Degradation mechanism of Ni-enriched NCA cathode for lithium batteries: are microcracks really critical? ACS Energy Lett. 4 1394–400

[92] Kim J H, Kim S J, Yuk T, Kim J, Yoon C S and Sun Y K 2018 Variation of electrochemical conductivity within secondary particles revealing a capacity-fading mechanism of layered Ni-rich cathode ACS Energy Lett. 3 3002–7

[93] Schweidler S, de Biasi L, Garcia G, Mazilikin A, Hartmann P, Brezesinski T and Janek J 2019 Investigation into mechanical degradation and fatigue of high-Ni NCM cathode material: a long-term cycling study of full cells ACS Appl. Energy Mater. 2 7375–84

[94] Zhu B H, Ni C Z, Wang N N, Zhao X Y, Guo W Q, Zhang P M, Zhang J J, Chen S Q, Lv W D and Zhu Y 2016 Determination of anions in lithium-ion batteries electrolyte by ion chromatography Chin. Chem. Lett. 27 864–6

[95] Faenza N V et al 2018 Phase evolution and degradation modes of R3M-LiNi_1/3-xCo_1/3-Al_2O_3 electrodes cycled near complete delithiation Chem. Mater. 30 7545–74

[96] Lai J, Zhang J, Li Z W, Xiao Y, Hua W B, Wu Z G, Chen Y X, Zhong J Y, Xiang W and Guo X D 2020 Structural elucidation of the degradation mechanism of nickel-rich layered cathodes during high-voltage cycling Chem. Commun. 56 4886–9

[97] Morin H R et al 2020 Transition-metal dissolution from NMC-family oxides: a case study ACS Appl. Energy Mater. 3 2565–75

[98] Intan N, Klyukin K and Alexandrov V 2019 Ab initio modeling of transition metal dissolution from the LiNi_{0.8}Mn_{0.2}O_2 cathode ACS Appl. Mater. Interfaces 11 20110–6

[99] Yang X R, Chen J W, Zheng Q F, Tu W Q, Xing L D, Liao Y H, Xu M Q, Huang Q M, Cao G Z and Li W S 2018 Mechanism of cycling degradation and strategy to stabilize a nickel-rich cathode J. Mater. Chem. A 6 16149–63

[100] Tian C X, Nordlund D, Xin H L, Liu Y J, Sokaras D, Lin F and Doeff M M 2018 Depth-dependent redox behavior of LiNi_{0.8}Mn_{0.2}CoO_2 Li. Electrochem. Soc. 165 A696–704

[101] Wang L, Zhang B, Fang J, Liu Y, Wang X, Chang Z H and Lu S G 2018 Aging process analysis of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2/pouch SiO_2 electrode Electrochem. Acta 286 219–30

[102] Zheng S Q, Ge X T and Chen C H 2017 Synthesis of carbon-coated LiTiO_12 and its electrochemical performance as anode material for lithium-ion battery Chin. Chem. Lett. 28 2274–7

[103] Wendt J, Freiberg A, Thomas R, Gorlin Y, Siebel A, Jung R, Gasteiger H A and Tromp M 2016 Transition metal dissolution and deposition in Li-ion batteries investigated by operando x-ray absorption spectroscopy J. Mater. Chem. A 4 18300–5

[104] Jung R, Linsenmann F, Thomas R, Wendt J, Solchenbach S, Maglia F, Stinner C, Tromp M and Gasteiger H A 2019 Nickel, manganese, and cobalt dissolution from Ni-rich NMC and their effects on NMC222-graphite cells J. Electrochem. Soc. 166 A378–89

[105] Lehn-Higgins Z W et al 2019 Surface chemistry dependence on aluminum doping in Ni-rich LiNi_{0.8}Co_{0.2}Al_2O_3 cathodes Sci. Rep. 9 17720

[106] Na Y, Sun X H, Fan A R, Cai S and Zheng C M 2021 Methods for enhancing the capacity of electrode materials in low-temperature lithium-ion batteries Chin. Chem. Lett. 32 973–82

[107] Li F, Huang W H and Gong X Q 2018 Unique adsorption behaviors of NO and O_2 at hydrogenated anatase TiO_2(101) Chin. Chem. Lett. 29 765–8

[108] Zheng N C, He X, Guo W Q and Hu Z F 2021 Enhancement of mass transfer efficiency and photoelectrochemical activity for TiO_2 nanorod arrays by decorating Ni^{2+}-states functional NiO water oxidation cocatalyst Chin. Chem. Lett. 32 1993–7

[109] Cui C Q, Li G D and Tang Z Y 2021 Metal-organic framework nanosheets and their composites for heterogeneous thermal catalysis: recent progresses and challenges Chin. Chem. Lett. 32 3307–21

[110] Jiang B, Li J R, Luo B, Yan Q Z, Li H, Liu L H, Chu L H, Li Y F, Zhang Q B and Li M C 2021 LiPO_2F_2 electrolyte additive for high-performance Li-rich cathode material J. Energy Chem. 60 564–71

[111] Zhang D, Li L, Zhang W Z, Cao M H, Qiu H W and Ji X H 2022 Research progress on electrolytes for fast-charging lithium-ion batteries Chin. Chem. Lett. accepted (https://doi.org/10.1016/j.clet.2022.01.015)

[112] Alvarado J, Wei C X, Nordlund D, Kroll T, Sokaras D, Tian Y C, Liu Y J and Doeff M M 2020 Thermal stress-induced charge and structure heterogeneity in emerging cathode materials Mater. Today 35 87–98

[113] Steiner J D, Mu L Q, Walsh J, Rahman M M, Zydlewski B, Michel F M, Xin H L, Nordlund D and Lin F 2018 Accelerated evolution of surface chemistry determined by temperature and cycling history in nickel-rich layered cathode materials ACS Appl. Mater. Interfaces 10 23842–50
[114] Bak S M, Hu E Y, Zhou Y N, Yu Q Q, Senanyake S D, Cho S J, Kim K B, Chung K Y, Yang X Q and Nam K W 2014 Structural changes and thermal stability of charged LiNi_{0.5}Mn_{0.2}Co_{0.3}O_{2} cathode materials studied by combined in situ time-resolved XRD and mass spectroscopy ACS Appl. Mater. Interfaces 6 22594–601

[115] Zheng J X et al 2016 Tuning of thermal stability in layered Li[Ni_{0.5}Mn_{0.2}Co_{0.3}]O_{2} J. Am. Chem. Soc. 138 13326–34

[116] Wang C H, Shao L, Guo X, Xi X M, Yang L S, Huang C H, Zhou C X, Zhao H H, Yin D L and Wang Z C 2019 Air-induced degradation and electrochemical regeneration for the performance of layered Ni-rich cathodes ACS Appl. Mater. Interfaces 11 44306–45

[117] Duan Y D, Yang L Y, Zhang M J, Chen Z H, Bai J M, Amine K, Pan F and Wang F 2019 Insights into Li/Ni ordering and surface reconstruction during synthesis of Ni-rich layered oxides J. Mater. Chem. A 7 513–9

[118] Freiberg A T S, Sickling J, Solchenbach S and Gasteiger H A 2020 Li_{2}CO_{3} decomposition in Li-ion batteries induced by the electrochemical oxidation of the electrolyte and of electrolyte impurities Electrochim. Acta 346 126271

[119] Huang Z et al 2019 Carbon dioxide directly induced oxygen vacancy in the surface of lithium-rich layered oxides for high-energy lithium storage J. Power Sources 432 8–15

[120] Hatsukade T, Schiele A, Hartmann P, Brezesinski T and Janek J 2018 Origin of carbon dioxide evolved during cycling of nickel-rich layered NCN cathodes ACS Appl. Mater. Interfaces 10 38892–9

[121] Wandt J, Freiberg A T S, Ogrodnik A and Gasteiger H A 2018 Singlet oxygen evolution from layered transition metal oxide cathode materials and its implications for lithium-ion batteries Mater. Today 21 825–33

[122] Streich D, Erk C, Guéguen A, Müller P, Brezesinski T and Janek J 2018 Improved surface stability and ordered surface layered structure and better electrochemical performance for lithium-ion batteries J. Electrochem. Soc. 167 120514

[123] Lee Y, Kim H, Yim T, Lee K Y and Choi W 2018 Compositional core-shell design by nickel leaching on the surface of Ni-rich cathode materials for advanced high-energy and safe rechargeable batteries J. Power Sources 400 87–95

[124] Maeng S, Chung Y, Min S and Shin Y 2020 Enhanced mechanical strength and electrochemical performance of core–shell structured high-nickel cathode material J. Power Sources 448 227395

[125] Yoon S J, Park K J, Lim B B, Yoon C S and Sun Y K 2015 Improved performances of Li[Ni_{0.65}Co_{0.28}Mn_{0.07}]O_{2} cathode material with full concentration gradient for Li-ion batteries J. Electrochem. Soc. 162 13059–63

[126] Noh H J, Myung S T, Lee J Y and Sun Y K 2014 High-energy layered oxide cathodes with thin shells for improved surface stability Chem. Mater. 26 5973–9

[127] Wang D W et al 2017 Synthetic control of kinetic reaction pathway and cathionic ordering in high-Ni layered oxide cathodes Adv. Mater. 29 1606715

[128] Zhang Y, Su Y F, Chen L, Bao L Y, He T, Li J H and Chen S 2015 Effect of Ni^{2+} content on lithium/nickel disorder for Ni-rich cathode materials ACS Appl. Mater. Interfaces 7 7702–8

[129] Ding Y, Mu D B, Wu B R, Zhao Z K and Wang R 2020 Controllable synthesis of spherical precursor NiO_{0.7}CoO_{0.3}MnO_{2}(OH) for nickel-rich cathode material in Li-ion batteries Ceram. Int. 46 9436–45

[130] Su Y F, Zhang Q Y, Chen L, Bao L Y, Lu Y, Shi Q, Wang J, Chen S and Wu F 2020 Improved stability of layered and porous nickel-rich cathode materials by relieving the accumulation of inner stress ChemSusChem 13 426–33

[131] Kim K J, Jo Y N, Lee W J, Subburaj T, Prasanna K and Lee C W 2014 Effects of inorganic salts on the morphological, structural, and electrochemical properties of preparednickel-rich Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_{2} J. Power Sources 268 349–55

[132] Kalluri S, Cha H, Kim J, Lee H, Jang H and Cho J 2020 Building high-rate nickel-rich cathodes by self-organization of structurally stable macrovoid Adv. Sci. 7 1902844

[133] Xiang W, Liu W Y, Zhang J, Wang S, Zhang T T, Yin K, Peng X, Jiang Y C, Liu K H and Guo L D 2019 Controlled synthesis of nickel-rich layered cathode oxides with preferentially exposed [010] active facets for high rate and long cycling stable lithium-ion batteries J. Alloys Compd. 775 72–80

[134] Zheng J M, Yan P F, Estevez L, Wang C M and Zhang J G 2018 Effect of calcination temperature on the electrochemical properties of nickel-rich LiNi_{0.79}Mn_{0.14}Co_{0.07}O_{2} cathodes for lithium-ion batteries Nano Energy 49 538–48

[135] Li H Y, Li J, Ma X W and Dahn J R 2018 Synthesis of single crystal LiNi_{0.83}Mn_{0.17}O_{2} with enhanced electrochemical performance for lithium-ion batteries J. Electrochem. Soc. 165 A1038–45

[136] Peng P P, Tan X X, Wang Z, Cai Z J, Nan J M, Xing Z Y and Li H 2021 Crack-free single-crystal LiNi_{0.83}Co_{0.17}Mn_{0.007}O_{2} as cycling/stable cathode materials for high-voltage lithium-ion batteries Electrochem. Acta 365 137380

[137] Fan X M, Hu G R, Zhang B, Ou X, Zhang J F, Zhao W G, Jia H P, Zou L F, Li P and Yang Y 2020 Crack-free single-crystalline Ni-rich layered NCN cathode enable superior cycling performance of lithium-ion batteries Nano Energy 70 104450

[138] Yang W W, Jia X B, Yang Y, Huang Y Y, Yang Y and Yuan G H 2020 Synthesis of single crystal LiNi_{0.83}Co_{0.17}Mn_{0.007}O_{2} cathode materials with superior electrochemical performance for lithium-ion batteries J. Electrochem. Soc. 167 120514

[139] Lee Y, Kim H, Yim T, Lee K Y and Choi W 2018 Compositional core-shell design by nickel leaching on the surface of Ni-rich cathode materials for advanced high-energy and safe rechargeable batteries J. Power Sources 400 87–95

[140] Maeng S, Chung Y, Min S and Shin Y 2020 Enhanced mechanical strength and electrochemical performance of core–shell structured high-nickel cathode material J. Power Sources 448 227395

[141] Yoon S J, Park K J, Lim B B, Yoon C S and Sun Y K 2015 Improved performances of Li[Ni_{0.65}Co_{0.28}Mn_{0.07}]O_{2} cathode material with full concentration gradient for Li-ion batteries J. Electrochem. Soc. 162 13059–63

[142] Noh H J, Myung S T, Lee J Y and Sun Y K 2014 High-energy layered oxide cathodes with thin shells for improved surface stability Chem. Mater. 26 5973–9

[143] Wang D W et al 2017 Synthetic control of kinetic reaction pathway and cathionic ordering in high-Ni layered oxide cathodes Adv. Mater. 29 1606715

[144] Zhang Y, Su Y F, Chen L, Bu L Y, He T, Wang J, Chen R J, Tan J and Wu F 2018 Pre-oxidizing the precursors of nickel-rich cathode materials to regulate their Li^{+}/Ni^{2+} cation ordering towards cyclability improvements J. Power Sources 396 734–41

[145] Zhang C C, Liu M M, Pan G J, Liu Y Y, Liu D, Chen C G, Su J M, Huang T and Yu A S 2018 Enhanced electrochemical performance of LiNi_{0.83}Co_{0.17}Mn_{0.007}O_{2} cathode for lithium-ion batteries by precursor preoxidation ACS Appl. Energy Mater. 1 4374–84

[146] Tang Z F, Bao J J, Du Q X, Shao Y, Gao M H, Zou B K and Chen C H 2016 Surface surgery of the nickel-rich cathode material LiNi_{0.83}Co_{0.17}Fe_{0.00}Mn_{0.00}O_{2}: toward a complete and ordered surface layered structure and better electrochemical properties ACS Appl. Mater. Interfaces 8 34879–87

[147] Sun H H, Choi W, Lee J K, Oh I H and Jung H G 2015 Control of electrochemical properties of nickel-rich layered cathode materials for lithium ion batteries by variation of the manganese to cobalt ratio J. Power Sources 275 877–83

[148] Zheng J M, Kang W H and Manthiram A 2015 Role of Mn content on the electrochemical properties of nickel-rich layered LiNi_{0.8}Co_{0.14}Mn_{0.0}O_{2} (0.0 ≤ x ≤ 0.08) cathodes for lithium-ion batteries ACS Appl. Mater. Interfaces 7 6926–34
[145] He K, Ruan Z W, Teng X G and Zhu Y M 2017 Facile synthesis and electrochemical properties of spherical LiNi₀.₅₀Co₀.₅₀O₂ with sodium aluminum via co-precipitation Mater. Res. Bull. 90 131–7

[146] Liang J N, Lu Y, Wang J, Liu X P, Chen K, Ji W H, Zhu Y and Wang D L 2020 Well-ordered layered LiNi₀.₅₀Co₀.₅₀Mn₀.₀₂O₂ submicron sphere with fast electrochemical kinetics for cathodic lithium storage J. Energy Chem. 47 188–95

[147] Wu K, Li Q, Dang R B, Deng X, Chen M M, Lee Y L, Xiao X L and Hu Z B 2019 A novel synthesis strategy to improve cycle stability of LiNi₀.₅₀Mn₀.₅₀Co₀.₀₂O₂ at high cut-off voltages through core-shell structuring Nano Res. 12 2460–7

[148] Ma Y T, Li L, Wang L C, Luo R, Xu S W Y, Wu F and Chen R J 2019 Effect of metal ion concentration in precursor solution on structure and electrochemical performance of LiNi₀.₅₀Co₀.₅₀Mn₀.₀₂O₂ J. Alloys Compd. 778 643–51

[149] Seo J S and Lee J W 2017 Fast growth of the precursor particles of Li[Ni₀.₅₀Co₀.₅₀Al⁺₀.₁₀O₂] via a carbony co-precipitation route and its electrochemical performance J. Alloys Compd. 704 703–9

[150] Liu W M, Qin M L, Gao C W, Yu D H and Yue Y Z 2019 Green and low-cost synthesis of LiNi₀.₅₀Co₀.₁₅Al₀.₅₀O₂ cathode material for lithium-ion batteries Mater. Lett. 246 153–6

[151] Song B H, Li W D, Yan P F, Oh S M, Wang C M and Manthiram A 2016 A facile cathode design combining Ni-rich layered oxides with Li-rich layered oxides for lithium-ion batteries J. Power Sources 325 620–9

[152] Zhou K, Huang B H, Qin X Y, Zhang L H, Wang W, Lv F Z, Zhang S C, Kang F Y and Li B H 2019 Application of nano Al₂O₃ particles as precipitate nucleus for preparation of high rate nickel-rich cathode materials J. Power Sources 439 227038

[153] Li Q, Dang R B, Chen M M, Lee Y, Hu Z B and Xiao X L 2018 Synthesis method for long cycle life lithium-ion cathode material: nickel-rich core-shell LiNi₀.₃₀Co₀.₅₀O₂ ACS Appl. Mater. Interfaces 10 17850–60

[154] Lei Y K, Ai J J, Yang S, Jiang H Y, Lai C Y and Xu Q J 2019 Effect of flower-like Ni(OH)₂ precursors on Li⁺/Ni²⁺ cation mixing and electrochemical performance of nickel-rich layered cathode J. Alloys Compd. 797 421–31

[155] Fu C C, Li G S, Luo D, Li Q, Fan J M and Li L P 2014 Nickel-rich layered microspheres cathodes: lithium/nickel disordering and electrochemical performance ACS Appl. Mater. Interfaces 6 15822–31

[156] Tian J, Su Y F, Wu F, Xu S Y, Chen F, Chen R J, Li Q, Li J H, Sun F C and Chen S 2016 High-rate and cycling-stable nickel-rich cathode materials with enhanced Li⁺ diffusion pathway ACS Appl. Mater. Interfaces 8 8582–7

[157] Shi Y, Zhang M H, Fang C C and Meng Y S 2018 Urea-based hydrothermal synthesis of LiNi₀.₃₀Co₀.₇₀O₂ cathode material for Li-ion battery J. Power Sources 394 114–21

[158] Zuo Y X, Xu G D, Yin Q, Sun Y Z, Huang B and Liang G C 2020 Hydrothermally synthesized rugby-like LiNi₀.₆₀Co₀.₄₀Mn₀.₀₂O₂ cathode materials with micro-nano structure for high performance Li-ion batteries J. Electroanal. Chem. 878 114660

[159] Zhang J T, Tan X H, Guo L M, Jiang Y, Liu S N, Wang H F, Kang X H and Chu W G 2019 Origin of performance differences of nickel-rich LiNi₀.₅₀Mn₁₀O₂ cathode materials synthesized in oxygen and air Energy Technol. 7 1800752

[160] Zhang J T, Tan X H, Guo L M, Jiang Y, Liu S N, Wang H F, Kang X H and Chu W G 2019 Controllable formation of lithium carbonate surface phase during synthesis of nickel-rich LiNi₀.₅₀Mn₁₀O₂ in air and its protection role in electrochemical reaction J. Alloys Compd. 771 42–50

[161] Yang X K et al 2013 Layered Li[Ni₀.₅₀Co₀.₃₀Mn₀.₂₀]O₂-Li₃Mn₂O₄ core-shell structured cathode material with excellent stability J. Power Sources 242 589–96

[162] Zhang M L, Shen J T, Li J, Zhang D Y, Yan Y X, Huang Y X and Li Z M 2020 Effect of micron sized particle on the electrochemical properties of nickel-rich LiNi₀.₆₀Co₀.₄₀Mn₁₀O₂ cathode materials Ceram. Int. 46 4643–51

[163] Li Y, Li X H, Wang Z X, Guo H J and Wang J X 2018 Spray pyrolysis synthesis of nickel-rich layered cathodes LiNi₁−xCoₓMn₁₀O₂ (x = 0.075, 0.05, 0.025) for lithium-ion batteries J. Energy Chem. 27 447–50

[164] Xi Z, Wang Z X, Yu G C, Guo H J, Li X H, Hu Q Y, Peng W J and Wang J X 2019 Hydrometallurgical production of LiNi₀.₃₀Co₁₅Al₀.₅₀O₂ cathode material from high-grade nickel matte Hydrometallurgy 186 30–41

[165] Zhu J, Zheng J C, Cao G L, Li Y J, Zhou Y, Deng S Y and Hai C X 2020 Flux-free synthesis of single-crystal LiNi₀.₅₀Co₀.₂₀Mn₁₀O₂ boosts its electrochemical performance in lithium batteries J. Power Sources 464 228207

[166] Liu W M, Hu G R, Peng Z D, Du K, Cao Y B and Liu Q 2011 Synthesis of spherical LiNi₀.₃₀Co₁₅Al₀.₅₀O₂ cathode materials for lithium-ion batteries by a co-oxidation-controlled crystallization method Chin. Chem. Lett. 22 1099–102

[167] Jiang L-W, Du K, Peng Z-D, Cao Y-B and Hu G-R 2014 Synthesis and electrochemical performance of LiNi₀.₃₀Co₀.₂₀Mn₁₀O₂ as a concentration-gradient cathode material for lithium batteries Chin. Chem. Lett. 25 883–6

[168] Lian J L et al 2022 Design of hierarchical and mesoporous FeₓFᵧ/GO hybrids as cathodes for superior lithium-ion batteries Chin. Chem. Lett. 33 3931–5

[169] Liu L L, Du C J, Wang S L and Chen S M 2018 Three new bifunctional additives for safer nickel-cobalt-aluminum based lithium ion batteries Chin. Chem. Lett. 29 1781–4

[170] Jamali S, Ran Q W, Yang L, Huang Y, Cao S, Yang X K and Wang X Y 2021 Improved high-voltage performance of LiNi₀.₅₀Co₀.₄₀Al₀.₁₀O₂ by Li⁺-conductor coating Chem. Eng. J. 407 126442

[171] Yasmin A, Shehzad M A, Wang J R, He X-D, Ding X, Wang S, Wen Z Y and Chen C H 2020 Li₃AlₓNi₁−xO₂ shielded layered cathode materials for emerging high-performance safe batteries ACS Appl. Mater. Interfaces 12 826–35

[172] Li W J et al 2020 Regulating the grain orientation and surface structure of primary particles through tungsten modification to comprehensively enhance the performance of nickel-rich cathode materials ACS Appl. Mater. Interfaces 12 47513–25

[173] Kim N Y, Yim T, Song J H, Yu J-S and Lee Z 2016 Microstructural study on degradation mechanism of layered Li[Ni₁−xCoₓMnₓ]O₂ cathode materials by analytical transmission electron microscopy J. Power Sources 307 641–8

[174] Jung S H, Kim U-H, Kim J-H, Jun S, Yoon C S, Jung Y S and Sun Y-K 2020 Ni-rich layered cathode materials with electrochemo-mechanically compliant microstructures for all-solid-state Li batteries Adv. Energy Mater. 10 1903360

[175] Kim U-H, Park G-T, Son B-K, Nam G W, Liu J, Kuo L-Y, Kaghazchi P, Yoon C S and Sun Y-K 2020 Heuristics solution for achieving long-term cycle stability for Ni-rich layered cathodes at full depth of discharge Nat. Energy 5 860–9

[176] Yu Z L, Qu X Y, Wan T, Dou A C, Zhou Y, Peng X Q, Su M R, Liu J Y and Chu D W 2020 Synthesis and
mechanism of high structural stability of nickel-rich cathode materials by adjusting Li-excess ACS Appl. Mater. Interfaces 12 40393–403

[177] Liu T C et al 2021 Understanding Co roles towards developing Co-free Ni-rich cathodes for rechargeable batteries Nat. Energy 6 277–86

[178] Hua W B, Zhang J F, Zheng Z, Liu W Y, Peng X H, Guo X-D, Zhong B H, Wang Y-J and Wang X L 2014 Na-doped Ni-rich LiNi0.8Co0.15Mn0.15O2 cathode material with both high rate capability and high tap density for lithium battery Dalton Trans. 43 14824–32

[179] Wang Y-Y, Sun Y-Y, Liu S, Li G-R and Gao X-P 2018 Na-doped LiNi0.8Co0.15Al0.15O2 with excellent stability of both capacity and potential as cathode materials for Li-ion batteries ACS Appl. Energy Mater. 1 3891–9

[180] Xu T T, Liu C, Guo Z X, Li W L, Li Y H and Yang G 2021 Improved rate and cyclic performance of potassium-doped nickel-rich ternary cathode material for lithium-ion batteries J. Mater. Sci. 56 2399–411

[181] Bai X, Wei A J, He R, Li W, Li X H, Zhang L H and Liu Z F 2020 The structural and electrochemical performance of Mg-doped LiNi0.8Co0.15Al0.15O2 prepared by a solid state method J. Electroanal. Chem. 858 112771

[182] Laskar M R, Jackson D H K, Xu S Z, Hamers R J, Morgan D and Kuech T F 2017 Atomic layer deposited MgO: a lower overpotential coating for Li[Ni0.85Mn0.15]O2 cathode materials ACS Appl. Mater. Interfaces 9 11231–9

[183] Chen M M, Zhao E Y, Chen D F, Wu M M, Han S B, Huang Q Z, Yang L M, Xiao X L and Hu Z B 2017 Decreasing Li/Na disorder and improving the electrochemical performances of Ni-rich LiNi0.75Co0.1Mn0.15O2 by Ca doping J. Electrochem. Sci. 56 8355–62

[184] Ryu H-H, Park N-Y, Seo J H, Yu Y-S, Sharma M, Mücke R, Kagahachi P, Yoon C S and Sun Y-Y 2020 A highly stabilized Ni-rich NCA cathode for high-energy lithium-ion batteries Mater. Today 36 73–82

[185] Li Q, Zhuang W D, Li Z, Wu S J, Li N, Gao M, Li W J, Wang J T and Lau S G 2020 Realizing superior cycle stability of a Ni-rich layered LiNi0.8Co0.15Mn0.15O2 cathode with a B2O3 surface modification ChemElectroChem 7 998–1006

[186] Hashigami S, Yoshimi K, Kato Y, Yoshida H, Inagaki T, Wang Y-Y, Sun Y-Y, Liu S, Li G-R and Gao X-P 2018 Stability of a Ni-rich layered LiNi0.75Co0.1Mn0.15O2 cathode for high-energy lithium-ion batteries Solid State Ions. 338 31–38

[187] Wu J D et al 2019 Improvement of electrochemical performance of nickel rich LiNi0.8Co0.15Mn0.15O2 cathode by lithium aluminates surface modifications Energy Technol. 7 209–15

[188] Tong W J, Chen Z X, Xiong F, Chen F, Huang C, Gao Q, Wang T Z, Yang Z H and Zhang W X 2019 An effective etching-induced coating strategy to shield LiNi0.8Co0.15Mn0.15O2 electrode materials by LiAlO2 J. Power Sources 412 246–54

[189] Duan J G, Dong P, Wang D, Li X, Xiao Z W, Zhang Y J and Hu G R 2018 A facile structure design of LiNi0.8Co0.15Al0.05O2 as advanced cathode materials for lithium-ion batteries via carbonation decomposition of NaAl(OH)4 solution J. Alloys Compd. 739 335–44

[190] Vaidivel S, Phatharasupakun N, Wuttiprom J, Duangdangchote S and Sawangphruk M 2019 High-performance Li-ion batteries using nickel-rich lithium nickel cobalt aluminium oxide-nanocarbon core-shell cathode: in operando x-ray diffraction ACS Appl. Energy Interfaces 11 30719–27

[191] Tian X H, Zhu Y B, Tang Z H, Xie P F, Natarajan A and Zhou Y K 2019 Ni-rich LiNi0.8Co0.15Mn0.15O2 nanoparticles enwrapped by a 3D graphene aerogel network as a high-performance cathode material for Li-ion batteries Ceram. Int. 45 22233–40

[192] Son I H, Park J H, Kwon S, Mun J and Choi J W 2015 Self-terminated artificial SEI layer for nickel-rich layered cathode material via mixed gas chemical vapor deposition Chem. Mater. 27 7370–9

[193] Son I H, Park K and Park J H 2017 Improvement in high-voltage and high rate cycling performance of nickel-rich layered cathode materials via facile chemical
vapor deposition with methane. *Electrochim. Acta* **230** 308–15

[207] Shim J-H, Kim Y-M, Park M, Kim J and Lee S 2017 Reduced graphene oxide-wrapped nickel-rich cathode materials for lithium ion batteries *ACS Appl. Mater. Interfaces* **9** 18720–9

[208] Chen R, Zhang H Y, Xie J, Lin Y X, Yu J L and Chen L G 2018 Preparation, lithium storage performance and thermal stability of nickel-rich layered LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode materials by SbO_2 coating *J. Power Sources* **282** 45–50

[209] Dai H, Cao H S, Du F H, Zhou Q, Adkins J, Sun P P, Hu D and Zheng J W 2020 A novel ultra-thin Si-O layer endowing significant improvement of interface properties for nickel-rich cathode materials in lithium-ion batteries *Energy Technol.* **8** 2000204

[210] Hashigami S et al 2019 Effect of lithium silicate addition on the microstructure and crack formation of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode particles *ACS Appl. Mater. Interfaces* **11** 39910–20

[211] Hashigami S, Kato Y, Yoshimi K, Yoshida H, Inagaki T, Hashinokuchi M, Doi T and Inaba M 2018 Influence of lithium silicate coating on retarding crack formation in LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode particles *Electrochim. Acta* **291** 304–10

[212] Chen Z W, Liu Y X, Lu Z C, Hu R Z, Cui J, Xu H Y, Qiuang Y P, Zhang Y and Zhu M 2019 Plasma-assisted coating of nano-sized SnO_2 on LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathodes for enhanced cyclic stability of lithium-ion batteries *J. Alloys Compd.* **803** 71–79

[213] Xie Z C, Zhang Y Y, Yuan A B and Xu J Q 2019 Effects of lithium excess and SnO_2 surface coating on the electrochemical performance of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material for Li-ion batteries *J. Alloys Compd.* **787** 429–39

[214] Zhu H L, Shen R, Tang Y W, Yan X Y, Liu J, Song L B, Fan Z Q, Zheng S L and Chen Z Y 2020 Sn-doping and Li_2SnO_3 nano-coating layer Co-modified LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode with improved cycle stability at 4.6 V cut-off voltage *Nanomaterials* **10** 6868

[215] Jo C-H, Cho D-H, Noh H-J, Yashiro H, Sun Y-K and Myung S T 2015 An effective method to reduce residual lithium compounds on Ni-rich Li[Ni_{0.8}Co_{0.15}Al_{0.05}O_2 active material using a phosphoric acid derived Li_2PO_4 nanolayer *Nano Res.* **8** 1464–79

[216] Lee S-W, Kim M-S, Jeong J H, Kim D-H, Chung K Y, Roh K C and Kim K-B 2017 Li_3PO_4 surface coating on Ni-rich LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 by a citric acid assisted sol-gel method: improved thermal stability and high-voltage performance *J. Power Sources* **360** 206–14

[217] Zhao Z K, Chen S, Mu D B, Ma R, Li C L, Wu B R, Wu F, Cheng K L and Xie C X 2019 Understanding the surface decoration on primary particles of nickel-rich layered LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material with lithium phosphate *J. Power Sources* **431** 84–92

[218] Wang M, Zhang R, Gong Y Q, Su Y F, Xiang D B, Chen L, Chen Y B, Luo M and Chu M 2017 Improved electrochemical performance of the LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 material with lithium-ion conductor coating for lithium-ion batteries *Solid State Ion.* **312** 53–60

[219] Yuan H, Song W B, Wang M, Gu Y J and Chen Y B 2019 Lithium-ion conductive coating layer on nickel rich layered oxide cathode material with improved electrochemical properties for Li-ion battery *J. Alloys Compd.* **784** 1311–22

[220] Hofmann M, Nagler F, Kapuschniski M, Guntow U and Giffin G A 2020 Surface modification of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 particles via Li_3PO_4 coating to enable aqueous electrode processing *ChemSusChem* **13** 5962–71

[221] Kim J, Lee J, Bae C and Kang B 2020 Sublimation-induced gas-reacting process for high-energy-density Ni-rich electrode materials *ACS Appl. Mater. Interfaces* **12** 11745–52

[222] Ding G Y, Li Y H, Gao Y, Wang Q L, Zhu Z, Jing X G, Yan F Q, Yue Z L, Li X M and Sun F G 2020 Uniform coating of se on selenophenic surfaces of nickel-rich layered oxide cathode materials for high performance Li-ion batteries *ACS Sustain. Chem. Eng.* **8** 9632–40

[223] Huang Y, Liu X, Yu R Z, Cao S, Pei Y, Luo Z G, Zhao Q L, Chang B B, Wang Y and Yang X Y 2019 Tellurium surface doping to enhance the structural stability and electrochemical performance of layered Ni-rich cathodes *ACS Appl. Mater. Interfaces* **11** 40022–33

[224] Liu K, Zhang Q Q, Dai S, Li W, Liu X J, Ding F and Zhang J L 2018 Synergistic effect of F doping and LiF coating on improving the high-voltage cycling stability and rate capacity of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode materials for lithium-ion batteries *ACS Appl. Mater. Interfaces* **10** 34153–62

[225] Liu J et al 2022 Chloro-free synthesis of LiPF_6 using the fluorine-oxide exchange technique *Chin. Chem. Lett.* **33** 4061–3

[226] Sathiramunicy M C, Celio H, Shiva K, Gao H C, Goodnough J B, Liu H K and Dou S X 2017 Long stable cycling of fluorine-doped nickel-rich layered cathodes for lithium batteries *Sustain. Energy Fuels* **1** 1292–8

[227] Wang J P, Du C Y, Yan C Q, Xu X, He X S, Yin G P, Zuo P J, Cheng X Q, Ma Y L and Gao Y Z 2016 Role of fluorine surface modification in improving electrochemical cyclability of concentration gradient Li[Ni_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material for Li-ion batteries *RSC Adv.* **6** 26307–16

[228] Li C L et al 2019 Inducing favorable cation antisite by doping halogen in Ni-rich layered cathode with ultrahigh stability *Adv. Sci.* **6** 1801406

[229] Huang J L, Du K, Peng Z D, Cao Y B, Xue Z C, Duan J G, Wang F, Liu Y and Hu G R 2019 Enhanced high-temperature electrochemical performance of layered nickel-rich cathodes for lithium-ion batteries after LiF surface modification *ChemElectroChem* **6** 5428–32

[230] Zhao B, Si J, Cao C H, Zhang J, Xia B J, Xie J W, Li B B and Jiang Y 2019 Enhanced electrochemical performance of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode by reducing lithium residue with low-temperature fluorination treatment *Solid State Ion.* **339** 114998

[231] Dai S C, Yuan M L, Wang L, Luo L M, Chen Q C, Xie T F, Li Y P and Yang Y T 2019 Ultrathin-Y_2O_3-coated LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 as cathode materials for Li-ion batteries: synthesis, performance and reversibility *Ceram. Int.* **45** 674–80

[232] Wu F, Li Q, Chen L, Lu Y, Su Y F, Bao L Y, Chen R J and Chen S 2019 Use of Ce to reinforce the interface of Ni-rich LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode materials for lithium-ion batteries under high operating voltage *ChemSusChem* **12** 935–43

[233] He R, Wei A J, Zhang L H, Li W, Bai X and Liu Z F 2019 Studies on the electrochemical properties of nickel-rich Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2 materials for lithium-ion batteries via cerium modifications *Solid State Ion.* **337** 56–62

[234] Yan C, Yang X F, Zhao H T, Zhong H, Ma G M, Qi Y F, Koele B E and Ju Y G 2021 Controlled Dy-doping to improve the electrochemical cyclability of concentration gradient Li[Ni_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material for Li-ion batteries *J. Power Sources* **430** 113849

[235] Koel B E and Ju Y G 2021 Controlled Dy-doping to improve the electrochemical cyclability of concentration gradient Li[Ni_{0.8}Co_{0.15}Al_{0.05}O_2 cathode material for Li-ion batteries *ACS Electrochem. Lett.* **9** 984–8
nickel-rich cathode materials in high temperature aerosol synthesis Proc. Combust. Inst. 38 6623–30

[236] Wu F et al 2019 Improving the reversibility of the H2-H3 phase transitions for layered Ni-rich oxide cathode towards retarded structural transition and enhanced cycle stability Nano Energy 59 50–57

[237] Steiner J D et al 2019 Targeted surface doping with reversible local environment improves oxygen stability at the electrochemical interfaces of nickel-rich cathode materials ACS Appl. Mater. Interfaces 11 37885–91

[238] Nurpeissova A, Choi M H, Kim J-S, Myung S-T, Kim S-S and Sun Y-K 2015 Effect of titanium addition as nickel oxide formation inhibitor in nickel-rich cathode material for lithium-ion batteries J. Power Sources 299 425–33

[239] Li X, Shi H B, Wang B, Li N, Zhang L Q and Lv P P 2019 Controllable TiO2 coating on the nickel-rich layered cathode through TiCl4 hydrolysis via fluidized bed chemical vapor deposition RSC Adv. 9 17994–9

[240] Chen Y P, Zhang Y, Chen B J, Wang Z Y and Lu C 2014 An approach to application for LiNi0.8Co0.15Mn0.05O2 cathode material at high cutoff voltage by TiO2 coating J. Power Sources 256 20–27

[241] Gao H et al 2018 Modifying the surface of a high-voltage lithium-ion cathode ACS Appl. Energy Mater. 1 2254–60

[242] Qin C C, Cao J L, Chen J, Dai G L, Wu T F, Chen Y B, Tang Y F, Li A D and Chen Y F 2016 Improvement of electrochemical performance of nickel rich LiNi0.8Co0.15Mn0.05O2 cathode active material by ultrathin TiO2 coating Dalton Trans. 45 9699–75

[243] Gao H, Cai J Y, Xu G-L, Li L X, Ren Y, Meng X B, Amine K and Chen Z H 2019 Surface modification for suppressing interfacial parasitic reactions of a nickel-rich-lithium-ion cathode Chem. Mater. 31 2723–30

[244] Li Y et al 2020 Toward a high-voltage fast-charging pouch cell with TiO2 cathode coating and enhanced battery safety Nano Energy 71 104643

[245] Subburaj T, Jo Y N, Prasanna K, Kim K J and Lee C W 2017 Titanium oxide nanofibers decorated nickel-rich cathodes as high performance electrodes in lithium ion batteries J. Ind. Eng. Chem 51 223–8

[246] Dai G L, Du H J, Wang S S, Cao J L, Yu M, Chen Y B, Tang Y F, Li A D and Chen Y F 2016 Improved electrochemical performance of LiNi0.8Co0.15Al0.05O2 with ultrathin and thickness-controlled TiO2 shell via atomic layer deposition technology RSC Adv. 6 100841–8

[247] Wu N T, Wu H, Kim J-K, Liu X M and Zhang Y 2018 Restoration of degraded nickel-rich cathode materials for long-life lithium-ion batteries ChemElectroChem 5 78–83

[248] Kim D, Lim J-M, Lim Y-G, Yu J-S, Park M-S, Cho M and Cho K 2015 Design of nickel-rich layered oxides using d electronic donor for redox reactions Chem. Mater. 27 6450–64

[249] Sim S-J, Lee S-H, Jin B-S and Kim H-S 2019 Improving the electrochemical performances using a V-doped Ni-rich NCM cathode Sci. Rep. 9 8952

[250] Sun C C, Chen W X, Gao P, Hu H L, Zheng J G and Zhu Y M 2022 Investigation of structure and cycling performance of Nb-doped nickel-rich single-crystal ternary cathode materials Ionics 28 747–57

[251] Xin F X, Zhou H, Chen X B, Zuba M, Chernova N, Zhou G W and Whittingham M S 2019 Li–Nb–O coating/substitution enhances the electrochemical performance of the LiNi0.5Mn0.3Co0.2O2 (NMC 811) cathode ACS Appl. Mater. Interfaces 11 54889–94

[252] Jamil S, Yu R Z, Wang Q, Fasehullah M, Huang Y, Yang Z H, Yang X K and Wang Y 2020 Enhanced cycling stability of nickel-rich layered oxide by tantalum doping J. Power Sources 473 228597

[253] Xu Y-D, Zhang J, Wu Z-G, Xu C-L, Li Y-C, Xiang W, Wang Y, Zhong Y-J, Guo X-D and Chen H 2020 Stabilizing the structure of nickel-rich lithiumated oxides via Cr doping as cathode with boosted high-voltage/temperature cycling performance for Li-ion battery Energy Technology 8 1900408

[254] Xue L L, Li Y J, Xu F, Chen Y X, Cao G L, Li J G, Deng S Y, Chen Y J and Chen J 2018 Effect of Mo doping on the structure and electrochemical performances of LiNi0.8Co0.2Mn0.2O2 cathode material at high cut-off voltage J. Alloys Compd. 748 561–8

[255] Piskin B, Uygur C S and Aydinol M K 2018 Mo doping of layered Li(Ni,Mn)0.5Co1−x−yMxCyO2 cathode materials for lithium-ion batteries Int. J. Energy Res. 42 3888–98

[256] Chen M H, Zhang Z P, Savilov S, Wang G M, Chen Z and Chen Q G 2020 Enhanced structurally stable cathodes by surface and grain boundary tailoring of Ni-rich material with molybdenum trioxide J. Power Sources 478 229051

[257] Becker D, Börner M, Nölle R, Diehl M, Klein S, Rodehorst U, Schmich R, Winter M and Placke T 2019 Surface modification of Ni-rich LiNi0.8Co0.15Mn0.05O2 cathode material by tungsten oxide coating for improved electrochemical performances in lithium-ion batteries ACS Appl. Mater. Interfaces 11 18404–14

[258] Shang G Z, Tang Y W, Lai Y Q, Wu J, Yang X, Li H X, Peng C, Zheng J F and Zhang Z A 2019 Enhancing structural stability unto 4.5 V of Ni-rich cathodes by tungsten-doping for lithium storage J. Power Sources 423 246–54

[259] Song G W, Zhong H, Dai Y Y, Zhou X Y and Yang J 2019 WO3 membrane-encapsulated layered LiNi0.8Co0.15Mn0.05O2 cathode material for advanced Li-ion batteries Ceram. Int. 45 6774–81

[260] Xu C-L, Xiang W, Wu Z-G, Xu Y-D, Li Y-C, Chen M-Z, Xiaodong G, Lv G-P, Zhang J and Zhong B-H 2018 Constructing a protective pillaring layer by incorporating gradient Mn4+ to stabilize the surface/interfacial structure of LiNi0.815Co0.15Al0.03O2 cathode ACS Appl. Mater. Interfaces 10 27821–30

[261] Li W J, Zhuang W D, Gao M, Zhou Y N, Zhang J, Li N, Liu X H, Huang W and Lu S G 2020 New insight into the role of Mn doping on the bulk structure stability and interfacial stability of Ni-rich layered oxide ChemNanoMat 6 451–60

[262] Du F H, Zhou Q, Cao H S, Dai H, Hu D, Sun P P, Adkins J and Zheng J W 2020 Confined growth of primary grains towards stabilizing integrated structure of Ni-rich materials J. Power Sources 478 228737

[263] Cho W, Lim Y J, Lee S-M, Kim J H, Song J-H, Yu J-S, Kim Y-J and Park M-S 2018 Facile Mn surface doping of Ni-rich layered cathode materials for lithium ion batteries ACS Appl. Mater. Interfaces 10 38915–21

[264] Huang B, Wang M, Zhao Z Y, Chen L and Gu Y J 2019 Effects of the strong oxidant treatment of precursor on the electrochemical properties of LiNi0.8Co0.2Mn0.2O2 for lithium-ion batteries J. Alloys Compd. 810 151800

[265] Huang B, Wang M, Wang Y X, Wu G D and Gu Y J 2019 Enhanced electrochemical performance of the layered nickel-rich oxide cathode by KMnO4 treatment precursor J. Alloys Compd. 808 151683

[266] Huang B, Wang M, Zhang X W, Zhao Z Y, Chen L and Gu Y J 2020 Synergistic coupling effect of single crystal morphology and precursor treatment of Ni-rich cathode materials J. Alloys Compd. 832 156077

[267] Liu Y, Shan Y Y and Pang H 2020 Design and synthesis of nitrogen-doped hexagonal NiCoO nanoparticles derived from Ni-Co-MOF for high-performance electrochemical energy storage Chin. Chem. Lett. 31 2280–6
[268] Yang C-K, Shao R W, Wang Q, Zhou T Y, Lu J, Jiang N, Gao P, Liu W, Yu Y and Zhou H H 2021 Bulk and surface degradation in layered Ni-rich cathode for Li-ion batteries: defect proliferation via chain reaction mechanism Energy Storage Mater. 35 62–69

[269] Wu F, Tian J, Liu N, Lu Y, Yu Y F, Wang J, Chen R J, Ma X, Bao L, Yang Y, Chen S 2017 Alleviating structural degradation of nickel-rich cathode material by eliminating the surface Fm3m phase Energy Storage Mater. 8 134–40

[270] Meng K, Wang Z X, Guo H J and Li X H 2017 Enhanced cycling stability of LiNi0.8Co0.1Mn0.1O2 by reducing surface oxygen defects Electrochim. Acta 234 99–107

[271] Park S, Jo C, Kim H J, Kim S, Myung S-T, Kang H-K, Kim H, Song J, Yu J S and Kwon K 2020 Understanding the role of trace amount of Fe incorporated in Ni-rich Li[Ni1−y−z,Co2,Mn]O2 cathode material J. Alloys Compd. 835 155342

[272] Du F H, Chen R F, Zhuang Y, Zhu L L, Cao H S, Dai H, Adkins J, Zhou Q and Zheng J W 2019 Effect of substitution of cobalt with iron on electrochemical behavior and solid electrolyte interface of LiNi0.8Co0.1Al0.1O2 Appl. Surf. Sci. 484 374–82

[273] Kim J, Ma H, Cha H, Lee H, Sung J, Seo M, Oh F, Park M and Cho J 2018 A highly stabilized nickel-rich cathode material by nanoscale epitaxy control for high-energy lithium-ion batteries Energy Environ. Sci. 11 1449–59

[274] Tao F, Yan X-L, Liu J-J, Zhang H-L and Chen L 2016 Effects of PVP-assisted CoO2 coating on the electrochemical and storage properties of LiNi0.8Co0.2Mn0.2O2 at high cut-off voltage Electrochim. Acta 210 548–56

[275] Liu W M, Hu G R, Du K, Peng Z D, Cao Y B and Liu Q 2012 Synthesis and characterization of LiCoO2-coated LiNi0.8Co0.2Al1−xO2 cathode materials Mater. Lett. 83 11–13

[276] Liu W M, Hu G R, Du K, Peng Z D and Cao Y B 2013 Surface coating of LiNi0.8Co0.15Al0.05O2 with LiCoO2 by a molten salt method Surf. Coat. Technol. 216 267–72

[277] Liu W M, Hu G R, Du K, Peng Z D and Cao Y B 2013 Enhanced storage property of LiNi0.6Co0.15Al0.05O2 coated with LiCoO2 J. Power Sources 230 201–6

[278] Lu Y et al 2020 Insights on the activation and stabilization of NCA cathode interface: surface chemical state modulations of aluminum-mediated Li[Co,1−x]O2 coatings ACS Sustain. Chem. Eng. 8 14975–84

[279] Xiong X H, Yang C H, Wang G H, Lin Y W, Ou X, Wang J H, Zhao B T, Liu M L, Lin Z and Huang K 2017 SnS2 nanosheets electrostatically anchored on three-dimensional N-doped graphene as an active and durable anode for sodium-ion batteries Energy Environ. Sci. 10 1757–63

[280] Yang C H, Ou X, Xiong X H, Zheng F H, Hu R Z, Liu M L and Huang K 2017 V2S3–graphite hybrid nanosheets as a high rate-capacity and stable anode material for sodium-ion batteries Energy Environ. Sci. 10 107–13

[281] Yanxia S et al 2020 Improved lithium ion diffusion and stabilization of LiNi0.8Co0.1Mn0.1O2 cathode via the synergistic effect of Na and mg dual-metal cations for lithium ion battery J. Electrochem. Soc. 167 020522

[282] Lipson A L et al 2020 Improving the thermal stability of NMC 622 Li-ion battery cathodes through doping during coprecipitation ACS Appl. Mater. Interfaces 12 18512–8

[283] Choi J, Kim J, Lee K-T, Lim J, Lee J and Yun Y S 2016 Effect of Na2SO4 coating layer on nickel-rich Li[Ni0.6Co0.2Mn0.2O2 cathode material for lithium-ion batteries Adv. Mater. Interfaces 3 1600784

[284] Woo S-G, Han J-H, Kim K J, Kim J-H, Yu J-S and Kim Y-J 2015 Surface modification by sulfated zirconia on high-capacity nickel-based cathode materials for Li-ion batteries Electrochim. Acta 153 115–21

[285] Levartovsky Y, Wu X J, Erik C, Maiti S, Grinblat J, Taliaferro M and Aurbach D 2021 Enhancement of structural, electrochemical, and thermal properties of Ni-rich LiNi0.65Co0.3Mn0.05O2 cathode materials for Li-ion batteries by Al and Ti doping Batter. Supercaps 4 221–31

[286] Ren Z M, Shen C, Liu M, Liu J, Zhang S Q, Yang G, Hua L Y, Liu X S, Wang D Y and Li H 2020 Improving LiNi0.9Co0.08Mn0.02’s cyclic stability via abating mechanical damages Energy Storage Mater. 28 1–9

[287] Li J J, Xu M, Yao Q, Chen Z Y, Song L B, Zhang Z A, Gao C H, Wang P, Yu Z Y and Lai Y Q 2016 Alleviating surface degradation of nickel-rich layered oxide cathode material by encapsulating with nanoscale Li-ions/electrons superionic conductors hybrid membrane for advanced Li-ion batteries ACS Appl. Mater. Interfaces 8 30879–89

[288] Feng Z, Huang X B, Rajagopalan R, Tang Y G, Peng Z G and Wang H Y 2019 Enhanced electrochemical properties of LiNi0.8Co0.1Mn0.1O2 at elevated temperature by simultaneous structure and interface regulating J. Electrochem. Soc. 166 A1439–48

[289] Lee Y-S, Shin W-K, Kannan A G, Koo S M and Kim D-W 2015 Improvement of the cycling performance and thermal stability of lithium-ion cells by double-layer coating of cathode materials with Al2O3 nanoparticles and conductive polymer ACS Appl. Mater. Interfaces 7 13944–51

[290] Xu L P, Zhou F, Zhou H B, Kong J Z, Wang Q Z and Yan G Z 2018 Ti2C2(OH)4 coated Li[Ni0.8Co0.2Mn0.2]O2 cathode material with enhanced electrochemical properties for lithium ion battery Electrochim. Acta 289 120–30

[291] Weigel T, Schirner F, Erickson E M, Susai F A, Markovsky B and Aurbach D 2019 Structural and electrochemical aspects of LiNi0.8Co0.1Mn0.2O2 cathode materials doped by various cations ACS Energy Lett. 4 508–16

[292] Ou X et al 2022 Enabling high energy lithium metal batteries via single-crystal Ni-rich cathode material co-doping strategy Nat. Commun. 13 2319

[293] Nanthagopal M, Santhoshkumar P, Shaji N, Praveen S, Kang H S, Senthil C and Lee C W 2019 Nitrogen-doped carbon-coated Li[Ni0.6Co0.2Mn0.2]O2 cathode material for enhanced lithium-ion storage Appl. Surf. Sci. 492 871–8

[294] Chen X, Ma F, Li Y Y, Liang J S, Matthews B, Sokolowski J, Han J T, Wu G, Lu X and Li Q 2018 Nitrogen-doped carbon coated LiNi0.6Co0.2Mn0.2O2 cathode with enhanced electrochemical performance for Li-ion batteries Electrochim. Acta 284 526–33

[295] Nanthagopal M, Santhoshkumar P, Shaji N, Sim G S, Park J W, Senthil C and Lee C W 2020 An encapsulation of nitrogen and sulphur dual-doped carbon over Li[Ni0.3Co0.7Mn0.1]O2 for lithium-ion battery applications Appl. Surf. Sci. 511 145580

[296] Jeng S E, Chang B, Shin H, Kim H, Lee T, Char K and Choi J W 2020 Pyrazine-linked 2D covalent organic frameworks as coating material for high-nickel layered oxide cathodes in lithium-ion batteries ACS Appl. Mater. Interfaces 12 10597–606

[297] Huang Y et al 2020 Conductive cyclized polycarboxylitrile coated LiNi0.6Co0.2Mn0.2O2 cathode with the enhanced electrochemical performance for Li-ion batteries Electrochim. Acta 332 135505

[298] Chen Z Y, Cao K F, Zhu H L, Gong X L, Liu Q M, Duan J F and Li L J 2019 Improved electrochemical performance of surface coated Li[Ni0.6Co0.15Mn0.2]O2 with polypyrrole Front. Chem. 6 648

[299] Xu G-L et al 2019 Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes Nat. Energy 4 484–94
trapping transition-metal components in lithium-ion batteries ACS Sustain. Chem. Eng. 6 8547–53

[316] Wang W Z, Wu L Y, Li Z W, Ma S, Dou H and Zhang X G 2020 Rational design of a piezoelectric BaTiO3 nanodot surface-modified LiNi0.8Co0.18Mn0.12O2 cathode material for high-rate lithium-ion batteries ChemElectroChem 7 3646–52

[317] Xu M, Fei L F, Zhu S-C, Lu W, Lai Y Q, Zhang Z A, Lam C-H and Huang H T 2018 Multifunctional NiTiO3 nanocoating fabrication based on the dual-Kirkendall effect enabling a stable cathode/electrolyte interface for nickel-rich layered oxides J. Mater. Chem. A 6 2643–52

[318] Zhang J F, Ren T, Duan G J, Li X, Dong P, Zhang Z Y and Wang D 2019 Enhanced high-voltage cycling stability of nickel-rich cathode materials by surface modification using LaFeO3 ionic conductor JOM 71 1975–80

[319] Huang W, Zhuang W D, Li N, Gao M, Li W X, Xing R and Lu S G 2019 Nanoscale Y-doped ZrO2 modified LiNi0.88Co0.09Al0.12O2 cathode material with enhanced electrochemical properties for lithium-ion batteries Solid State Ion. 343 115087

[320] Wang L F, Liu J Y, Ding X N, Zhan C and Wang X D 2019 Simultaneous coating and doping of a nickel-rich cathode by an oxygen ion conductor for enhanced stability and power of lithium-ion batteries ACS Appl. Mater. Interfaces 11 33901–12

[321] Bui T T, Yun B, Darko K, Shin S B, Kim J, Hong J, Lee M, Park S K and Kim M-G 2021 Solution processing of lithium-rich amorphous Li-La-Zr-O ion conductor and its application for cycling durability improvement of LiCoO2 cathode as coating layer Adv. Mater. Interfaces 8 2001767

[322] Yasmin A, Shehzad M A, Ding X, Wang J R, Yu R, Deng M M, Tan Z F and Chen C H 2020 A first report on ex-situ synthesis and utilization of pure La0.15Li0.85O2 in emerging high-performance safe batteries J. Alloys Compd. 821 153208

[323] Zhang R X, Wang Y Y, Song X, Li G R, Liu S and Gao X P 2020 Enhanced electrochemical and thermal stabilities of Li[Li0.25Na0.05Al0.15]O2O2 cathode material by La2Ni2O8 coating for Li-ion batteries ChemElectroChem 7 2042–7

[324] Wang M, Gong Q Y, Gu J Y, Chen Y B, Chen L and Shi H 2019 Effects of fast lithium-ion conductive coating layer on the nickel rich layered oxide cathode material Ceram. Int. 45 3177–85

[325] Qiu L et al 2019 Polyanion and cation co-doping stabilized Ni-rich Ni-Co–Al material as cathode with enhanced electrochemical performance for Li-ion battery Nano Energy 63 103818

[326] Song H J, Oh S H, Lee Y, Kim J and Yim T 2021 Dually modified cathode-electrolyte interphases layers by calcium phosphate on the surface of nickel-rich layered oxide cathode for lithium-ion batteries J. Power Sources 483 229218

[327] Chen Z, Kim G-T, Huang Y, Bresser D, Diemant T, Huang Y Z, Copley M, Behm R J, Passerini S and Shen Z X 2018 Manganese phosphate coated Li[Ni0.8Co0.2Mn0.12]O2 cathode material: towards superior cycling stability at elevated temperature and high voltage J. Power Sources 402 263–71

[328] Cho W, Kim S-M, Lee K-W, Song J H, Jo Y N, Yim T, Kim H, Kim J-S and Kim Y-J 2016 Investigation of new manganese orthophosphate Mn5(PO4)3 coating for nickel-rich LiNi0.8Co0.18Mn0.12O2 cathode and improvement of its thermal properties Electrochem. Acta 198 77–83

[329] Lee D-J, Scrosati B and Sun Y-K 2011 Ni5(PO4)3–coated Li[Ni0.8Co0.18Al0.05]O2 lithium battery electrode with
improved cycling performance at 55 °C. J. Power Sources 196 7742–6

[330] Tong H, Dong P Y, Zhang J F, Zheng J C, Yu W J, Wei K, Zhang B, Liu Z M and Chu D W 2018 Cathode material LiNi0.8Co0.1Mn0.1O2/LaPO4 with high electrochemical performance for lithium-ion batteries J. Alloys Compd. 764 44–50

[331] Hu G R, Zhang Z Y, Li T F, Gan Z F, Du K, Peng Z D, Xia J, Tao Y and Cao Y B 2020 In situ surface modification for improving the electrochemical performance of Ni-rich cathode materials by using ZrP2O7 ChemSusChem 13 1603–12

[332] Zhu L, Yan T-F, Jia D, Wang Y, Wu Q, Gu H-T, Wu Y-M and Tang W-P 2019 LiFePO4-coated LiNi0.5Co0.2Mn0.3O2 cathode materials with improved high voltage electrochemical performance and enhanced safety for lithium ion pouch cells J. Electrochem. Soc. 166 A5437–44

[333] Chen J C et al 2019 LiNi0.8Co0.15Al0.05O2 cathodes exhibiting improved capacity retention and thermal stability due to a lithium iron phosphate coating Electrochim. Acta 312 179–87

[334] Wang Z, Zhong H and Song G W 2020 Enhancing high-voltage performance of LiNi0.4Co0.1Mn0.5O2 by coating with NASICON fast ionic conductor Li1.5Al0.5Zr1.5(PO4)3 J. Alloys Compd. 849 156467

[335] Xiao Z L, Chi Z Z, Song L B, Cao Z and Li A A 2020 LiTa2PO5 coated nickel-rich cathode material for improved electrochemical performance at high voltage Ceram. Int. 46 8328–33

[336] Binder J O, Culver S P, Pinedo R, Weber D A, Friedrich M S, Gries K I, Volz K, Zeier W G and Janek J 2018 Investigation of fluorine and nitrogen as anionic dopants in nickel-rich cathode materials for lithium-ion batteries ACS Appl. Mater. Interfaces 10 44452–62

[337] Lee S-H, Yoon C S, Amine K and Sun Y-K 2013 Improvement of long-term cycling performance of Li[Ni0.8Co0.15Al0.05]O2 by AlF3 coating J. Power Sources 234 201–7

[338] Gutierrez A, Choudhury D, Sharifi-Asl S, Yonemoto B T, Shahbazian-Yassar R, Mane A U, Elam J W and Croy J 2020 Multifunctional films deposited by atomic layer deposition for tailored interfaces of electrochemical systems J. Electrochem. Soc. 167 140541

[339] Xie J et al 2017 Atomic layer deposition of stable LiAlF4 lithium ion conductive interfacial layer for stable cathode cycling ACS Nano 11 7019–27

[340] Wang H Q, Chu Y Q, Pan Q C, Yang G C, Lai A J, Liu Z H, Zheng F H, Hu S J, Huang Y G and Li Q Y 2021 Enhanced interfacial reaction interface stability of Ni-rich cathode materials by fabricating dual-modified layer coating for lithium-ion batteries Electrochim. Acta 366 137476

[341] Liu W M, Tang X, Qin M L, Li G L, Deng J Y and Huang X W 2016 FeF3-coated LiNi0.8Co0.15Al0.05O2 cathode materials with improved electrochemical properties Mater. Lett. 185 96–99