



Review article

Extensive comparison of doping and coating strategies for Ni-rich positive electrode materials

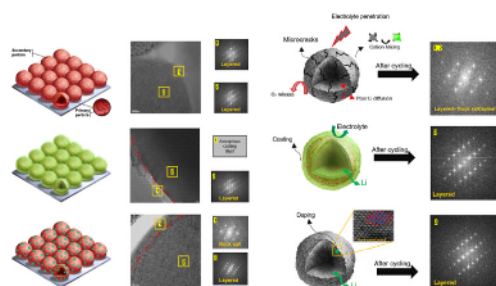
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HIGHLIGHTS

- Nickel rich material confront challenge in structural and electrochemical stability.
- This review covers recent research in synthesis and enhancement of Ni rich materials.
- Different coating and doping materials and mechanisms are discussed.
- Criteria for effective mitigation strategy and optimized materials are proposed.
- Major recommendations to enhance further battery research are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel-rich NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, $x \geq 0.8$) electrode materials are known for their great potential as lithium battery cathode active materials due to their high capacities, low cost, and environment friendliness. However, these materials confront some technical challenges such as structural, surface, and electrochemical instability while different synthesis methods have large influences on NMC morphology, structure, and electrochemical performance. This review summarizes the most common synthesis techniques which have been employed to prepare high-quality Ni-rich positive electrode materials. Besides, recently reported and widely recognized studies on the degradation and mitigation mechanisms of Ni-rich electrodes are outlined in this paper. This review summarizes different studies on doping of Ni-rich materials which are useful for enhancing the capacity and performance and mitigating structural decay of the electrodes. Moreover, surface modifications by thin coatings with metal oxides and Li containing metal oxide layers are also reviewed as those overlayers can enhance stability of NMCs during the long-term cycling. Therefore, the focus of this paper is on fabrication of Ni rich NMC material, as well as reviewing the effect of doping, surface coating and synergistic effect of both for enhancing Ni-rich electrode material performance.

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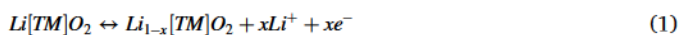
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List of abbreviations

LIB	lithium-ion battery
PHEV	plug-in hybrid vehicle
EV	electric vehicle
NMC	positive electrode material for Li-ion batteries applied to mixed lithiated metal oxide family with formula $\text{Li}[\text{Ni}_a\text{Mn}_b\text{Co}_c]\text{O}_2$ ($a+b+c=1$)
NCA	positive electrode material for Li-ion batteries applied to mixed lithiated metal oxide family with formula $\text{Li}[\text{Ni}_a\text{Co}_b\text{Al}_c]\text{O}_2$ ($a+b+c=1$)
LFP	positive electrode material for Li-ion batteries lithiated iron phosphate with formula LiFePO_4
LNO	positive electrode material for Li-ion batteries lithiated nickel oxide with formula LiNiO_2
LMO	positive electrode material for Li-ion batteries lithiated manganese oxide with formula LiMn_2O_4
LCO	positive electrode material for Li-ion batteries lithiated cobalt oxide with formula LiCoO_2
TM	transition metal
SEI	solid electrolyte interphase formed on negative electrode surface in lithium-ion battery
CEI	cathode electrolyte interphase formed on positive electrode surface in lithium-ion battery
ALD	atomic layer deposition
WC	wet chemistry synthesis method
MPC	Maximum permissible concentration
SOC	State of charge
EIS	electrochemical impedance spectroscopy

1. Introduction

Energy storage devices play an important role in the life of modern society. Nowadays, the rechargeable lithium-ion batteries (LIBs) have been widely used in electronic portable devices, plug-in hybrid vehicles (PHEVs), electric vehicles (EVs), wearable electronics and medical devices due to their high energy storage capability. Generally, a lithium-ion battery consists of two electrodes placed in an electrolyte and divided by a separator layer (Fig. 1a). During charging, the material of the positive electrode is oxidized (eq. (1)) and lithium ions, which belong to the structure of the positive electrode, migrate to the negative electrode. They embed in the structure of the graphite negative electrode where Li is intercalated between the graphite layers. Based on electroneutrality, oxidation state of this system is 0 but smearing of electron density from Li to carbon is possible. (eq. (2)). During the discharge, the reversed reactions proceeds, when the reduced lithium is oxidized to Li^+ ions at the negative electrode and migrate to the positive electrode, where it embeds in its structure [1]. As such, upon applying a potential, a positive electrode material can be reversibly delithiated and lithiated. In this case, the transition metal (TM) atoms inside the lattice are oxidized (eqs. (3) and (4)) [2], and release Li^+ ions in accordance with (eq. (1)).



In modern lithium-ion battery technology, the positive electrode material is the key part to determine the battery cost and energy density [5]. The most widely used positive electrode materials in current

industries are lithiated iron phosphate LiFePO_4 (LFP), lithiated manganese oxide LiMn_2O_4 (LMO), lithiated cobalt oxide LiCoO_2 (LCO), lithiated mixed oxide $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC), such as NMC-111, NMC-523 or NMC-622, and lithiated mixed oxide $\text{LiNi}_a\text{Co}_b\text{Al}_c\text{O}_2$ (NCA) [6]. Each electrode material has its own pros and cons. However, there are several requirements imposed on these materials including final price, ethical production issues, environmental matters, and electrochemical performance. A diagram of the cost versus quantity of the main LiBs elements in the earth's crust is shown in Fig. 1b. The cost is given per element based on the data (<https://metal.com>) in 2021 and the ratio of the atom contents in the earth is given based on references [3]. We consider all form of carbon in the earth's crust for carbon content ratio, while the price is given for graphite (the most used form in LiBs). Based on the diagram (Fig. 1b) a significant part of actively used materials cost up to \$ 20 per kg while Co and Li are more expensive (~\$ 45 and \$ 80 per kg). Besides, the production of Co has ethical and environmental issues. Recently, a significant number of cobalt mines exploit child labor and face safety problems [7]. Moreover, toxicity and environmental hazards are another factor in concern when developing LiB materials. Fig. 1c shows the maximum permissible metal concentrations (MPCs) (for TMs used in LiBs) based on wastewater purity standards in Pennsylvania, USA. The most toxic element in LiBs is Co, which is considered to cause 5–10 times higher pollution effect than Mn, Ni or Fe. Thus, the main disadvantages of cobalt are high prices, ethical production issues, and environmental hazards [7]. One of the most important electrochemical characteristic of LIBs is energy density [8]. LCO and LFP have an outstanding cycling stability, however both materials have a narrow potential range (up to about 3.7 V and 3.3 V, respectively) and low capacities (160 mAhg^{-1} and 140 mAhg^{-1}). LMO has a wider potential range (up to 4.0 V), however this material has poor cycling stability and low capacity (130 mAhg^{-1}). Considering all these factors, Ni-rich materials have low cost, less Co thus are less polluting and possess higher energy density (Fig. 1 d,e and f).

To compare the properties of positive electrode materials with different Ni content, we synthesized the most popular Ni-rich positive electrode materials NMC622 ($x = 0.6$) as well as the higher Ni content material NMC811 ($x = 0.8$) and LNO ($x = 1$). According to the XRD results of the Ni-rich electrode materials represented in Fig. 2a, they do not demonstrate significant differences in crystal structures when Ni content ranges from 1 to 0.6. All these positive electrode materials exhibit strong characteristic peaks corresponding to $R\bar{3}m$ space group that can be indexed to (003), (101), (006), (102), (104), (105), (107), (108), and (110) reflections [9]. However, Rietveld refinements [10] demonstrates significant difference in cationic mixing for both NMC811 and NMC622 comparing to LNO and those are related to defect formation due to presence of Mn and Co atoms, which admittedly affect material functionality. Therefore, to enhance the performance, a deep understanding of chemistry and structural properties of Ni rich positive electrode materials is essential [11].

Cyclic voltammetry of NMC-811, NMC-622 and LNO are also compared at scan rate of $20 \mu\text{s}^{-1}$ (Fig. 2b) to depict the different reactivity of Ni^{4+} in Ni rich materials in the voltage window of 2.5–4.3 V for LNO and 3–4.4 V for the NMC811 and NMC622 [12,13]. The CV curve of the LNO material contains six pairs of peaks, which correspond to the phase changes during delithiation and lithiation, occurring during charge-discharge process. The peaks of the LNO material are reversible, sharp, and well defined. This is due to a large set of phases at various state of delithiation, which corresponds to the oxidation state of the material. Each phase transition has a corresponding pair of a cathodic and anodic peak. With decreasing Ni content, from LNO to NMC811, the peaks of the phase transitions α and β , γ and δ merge, forming four pairs of peaks corresponding to the reactions of $\text{H1} \leftrightarrow \text{M} \leftrightarrow \text{H2} \leftrightarrow \text{H3}$. With a further decrease in the Ni concentration from the LNO material to the sample NMC622, all the peaks merge into one, which correlates with the $\text{H1} \leftrightarrow \text{M}$ phase transition [1,13,14]. Phase transformations during the

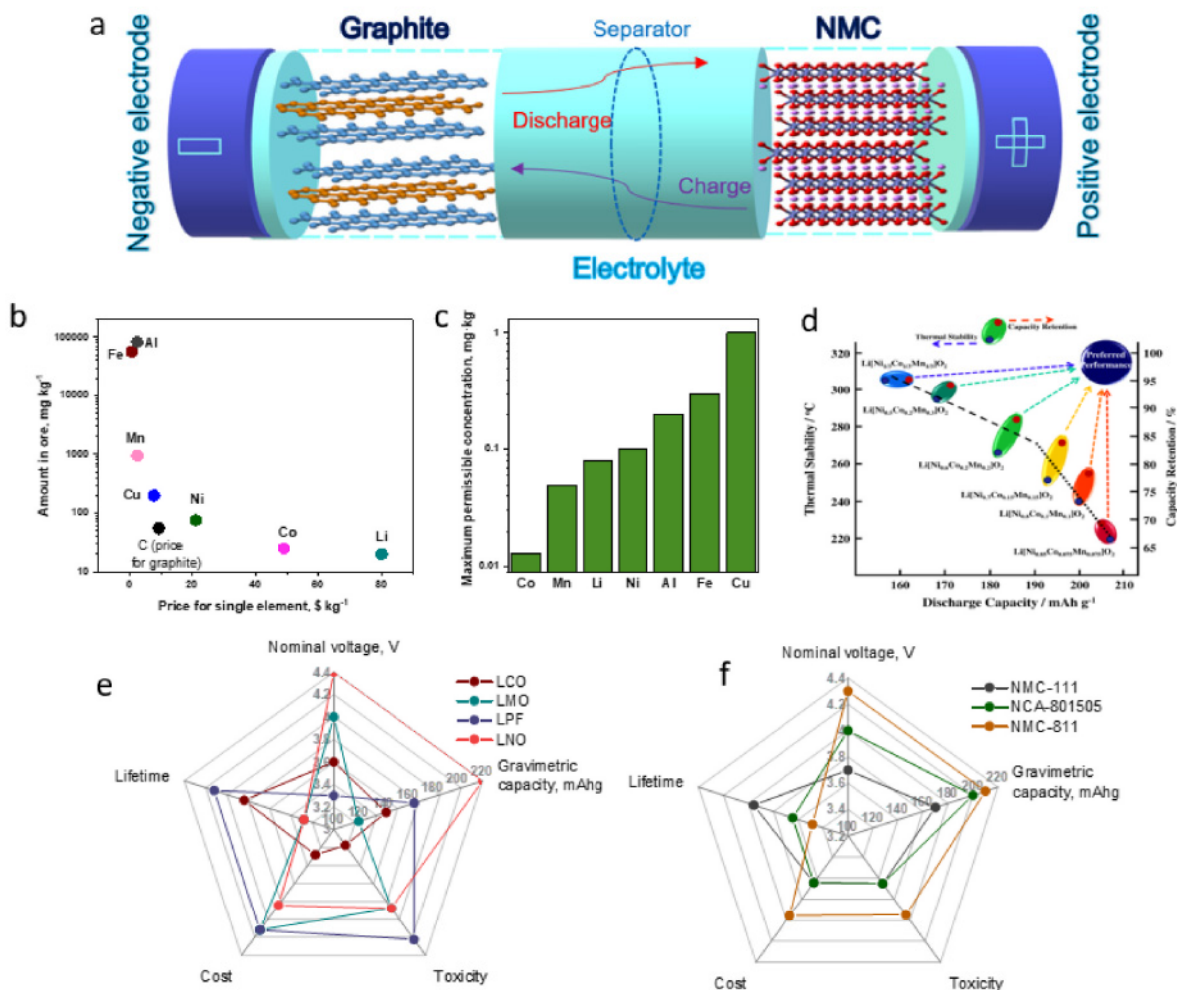


Fig. 1. (a) Schematic illustration of the LiB processes with graphite as an active material for the negative electrode, a layered lithiated Ni rich oxide (NMC) as an active material for the positive electrode, and typically a liquid electrolyte based on organic carbonates as solvents and LiPF₆ as a conducting salt. (b) The content of elements in the earth [3] versus cost for metallic material (according to prices on <https://metal.com>). (c) Maximum permissible concentration of Co, Li, Mn, Ni, Fe and Al in water based on Pennsylvania standards. (d) A map of relationship between discharge capacity, thermal stability and capacity retention of NxMyC₂ ($x < 0.85$), Reprinted with permission from Ref. [4] Copyright © 2013 Elsevier B.V. All rights reserved. (e, f) Comparison of nominal voltage, gravimetric capacity, toxicity, cost, and lifetime of LCO, LiMn₂O₄, NMC-111, LiFePO₄, NCA-801505 and NMC-811.

cycling process cause degradation mechanism in the NMC structure [15]. The formation of H3 (Fig. 2a and b) is one of the reasons for degradation due to volumetric expansion and contraction and, therefore, leading to crack formation. The H2–H3 transition causes detrimental lattice shrinkage along the *c*-direction (Fig. 2c), resulting in volume change and the local stress accumulation, and further leading to microcracks generation and propagation in secondary particles. During the formation of the H3 phase, Li atoms can still participate in the process, but cracks lead to gradual disintegration of the positive electrode materials. Furthermore, side reactions between the highly reactive species Ni⁴⁺ and liquid electrolyte at the interface of the positive electrodes can trigger an irreversible phase transition from the initial layered $R\bar{3}m$ phase to spinel $Fd\bar{3}m$ phase and further to the rock-salt phase [16–20].

A high concentration of Ni in a positive electrode material provides a battery with lower cost and lower environmental impact (comparing to Co rich alternatives), and higher capacitance (comparing to Fe and Mn rich materials), and wide working potential window. Beside these advantages, Ni rich cathodes face some important disadvantages. The primary issue suffered by Ni-rich materials is cationic mixing. There is only one electron in the *e_g* orbital of Ni³⁺ in Ni-rich materials, which is an unstable state in thermodynamics. Therefore, Ni³⁺ is prone to turn into Ni²⁺. Ni²⁺ (0.69 Å) and Li⁺ (0.76 Å) have similar ionic radii, so Ni²⁺

(3a) can easily migrate to Li⁺ site (3b) in the crystal lattice, causing Ni²⁺/Li⁺ cation mixing issue in crystal structure of Ni-rich materials. Besides, a high concentration of Ni in a positive electrode material causes low mechanical stability which causes crack formation during the cell cycling [11]. In addition, high Ni content induces some deficiencies, such as anisotropic volume change, surface reconstruction and phase transformation (Fig. 2d) [4,22]. Therefore, it can provoke progress of cation mixing and impede Li⁺ diffusion into the layered positive electrode structure, resulting in phase transitions, impedance build-up and capacity fading [23,24].

Because of high amount of Ni and, by cases, excess Li on NMC surfaces, Ni rich electrode materials have additional surface reactivity. During NMCs synthesis processes, excessive amount of lithium is used to assure the formation of crystalline and well-ordered layered structure. Excess is required because of lithium loss at the high synthesis temperature. However, unreacted lithium remains on the surface of the positive electrode material and forms Li₂O and Li₂O₂ compounds, which can react with CO₂ and H₂O in ambient conditions to form Li₂CO₃ and LiOH. These compounds cause irreversible capacity, growth of charge transfer resistance, and cation mixing due to lithium-ion diffusion suppression [25–27].

In addition, Li₂CO₃/LiOH can rapidly uptake moisture, upon exposure to air, and form impurities on the surface of positive electrode

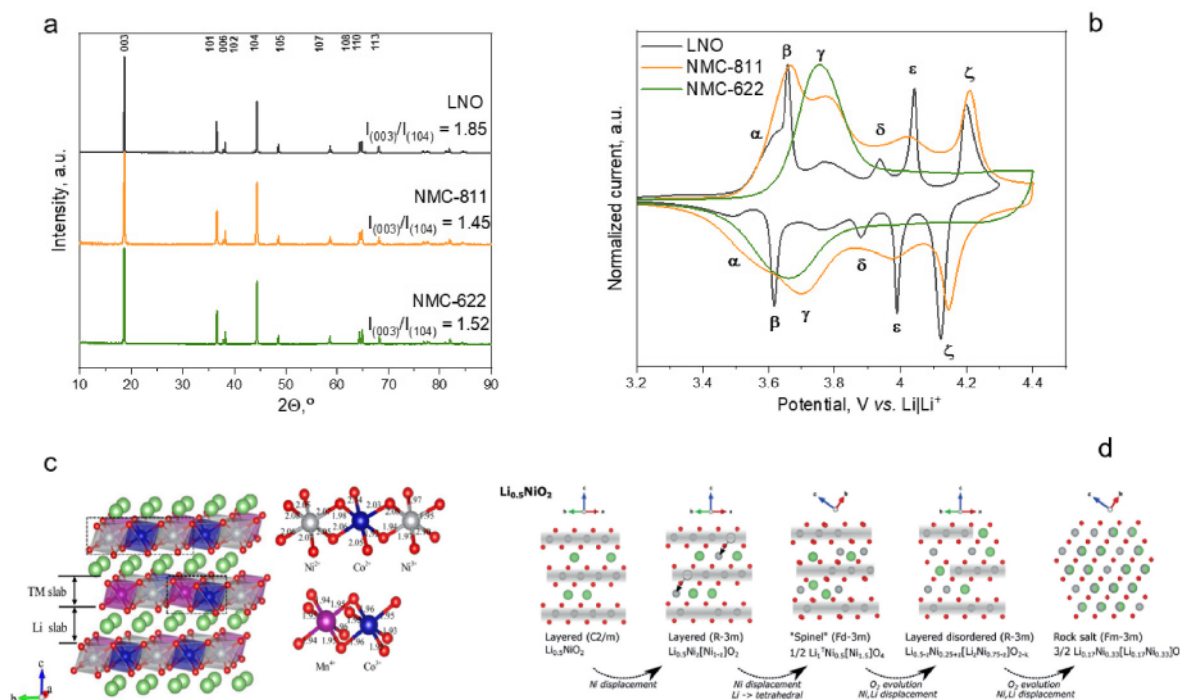


Fig. 2. (a) XRD Cu K α patterns and (b) cyclic voltammograms measures in a three-electrode cell vs. a Li foil in 1 M LPF₆ ethylene carbonate – dimethyl carbonate (volume ratio 1:1) at scan rate 20 $\mu\text{V s}^{-1}$ for LNO, NMC-811 and NMC-622 positive electrode materials ($\alpha - \text{H1} \leftrightarrow \text{H1}'$, $\beta - \text{H1}' \leftrightarrow \text{M}$, $\gamma - \text{M} \leftrightarrow \text{M}'$, $\delta - \text{M}' \leftrightarrow \text{M}''$, $\epsilon - \text{M}'' \leftrightarrow \text{H2}$, $\zeta - \text{H2} \leftrightarrow \text{H3}$). All the experiments were done as described in Refs. [12,13]. (c) TM–O octahedral complexes in NMC and Ni, Mn, and Co places at the octahedral site surrounded by six O atoms, Reprinted with permission from Ref. [21] Copyright © 2017, American Chemical Society. (d) Schematic of phase transition from layered to rock salt structure and possible TM cation migration pathways in charged NMC materials, Reprinted with permission from Ref. [11] © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

materials. Those affect electrochemical properties because of their interaction with the EC and DMC species in the electrolyte which leads to CO₂ formation and CEI growth [25,28]. The reactivity of the Ni rich surfaces is also noticeable due to the increase in number of oxidation state Ni⁴⁺ as a function of state of charge (SOC), which is more intense in Ni rich materials [24]. It has been experimentally proved that Ni⁴⁺–O bonds are unstable in delithiated states and tend to be reduced to more stable form of Ni²⁺ with concomitant release of oxygen in partially delithiated states to keep the overall charge in balance, which results in a degradation of the crystal structure and electrolyte oxidation [22]. Moreover, oxygen loss can generate oxygen vacancies in the positive electrode material structure, which can further induce TMs migration into the Li slabs. We suggest that TM species can be dissolved in the electrolyte in low concentrations which has been confirmed by detecting the TM atoms on the negative electrode surface. TM species agglomerates can also be liberated from an electrode after crack formation.

Cathode electrolyte interphase (CEI) layer is formed on a positive electrode active material surface during the cell cycling and can contribute the diffusion of Li⁺ ions and protection of the Ni rich electrodes against further side reactions. However, additional parasitic electrochemical reactions might occur and reduce the capacity of the battery and its lifetime [29]. These reactions with electrolyte arise with the presence of highly reactive Ni⁴⁺ in the CEI layer, particularly at high potentials.

To increase the reversible capacity, operating the battery at the upper cutoff voltage is beneficial while using Ni rich materials at high potential (beyond 4.6 V vs. Li|Li⁺) exceeds the voltage window of conventional carbonate based LiPF₆ electrolytes and leads to rapid electrolyte decomposition and parasitic side reactions [30]. The unwanted reactions at the positive electrode interface include a series of complicated chemical and electrochemical reactions, which can be initiated by electron transfer reaction between the positive electrode material and the electrolyte. At lower potentials (<4.6 V vs. Li|Li⁺) chemical

reactions between the delithiated positive electrode material and the solvent are the major reactions while at higher potentials electrochemical oxidation of the solvent molecules are dominating. Therefore, at a higher cut off voltage, the oxidized energetically unstable solvent molecules can be generated and locally deposited at the CEI layer. The electrochemical oxidation of solvent not only increases the impedance of the electrodes by thickening the surface film but also generates a highly acidic chemical environment, leading to corrosion of the positive electrode surface and leaching of the TMs from the NMC [24,31]. These decomposition reactions depend on the oxidation state of TMs and chemical bonding between TMs and oxygen at the positive electrode material surface, which consequently affect their electrochemical activity and stability.

In summary, such structural defects as cation mixing, formation of oxygen and lithium vacancies, phase transformations and surface reconstructions, generated by anisotropic volume changes and microcracks, narrow electrochemical stability window of the electrolyte solvents. High reactivity of Ni⁴⁺, interfacial side reactions and TM dissolution, and moisture/air-reactive lithium residues on the surface are responsible for electrochemical shortcomings in Ni rich positive electrode materials. Moreover, all these parasitic reactions either occur at electrode–electrolyte interfaces or compromise the stability of these regions, which further deteriorate the electrochemical performance of the cell. Therefore, designing a stable and robust positive electrode–electrolyte interface is a crucial factor to suppress the interfacial parasitic reactions between a delithiated NMC material and the non-aqueous electrolyte since this can improve the durability of Ni-rich NMCs and regulate the overall efficiency of the cell.

All the challenges mentioned above can be approached by incorporation of modifications into electrode active materials. Doping and/or coating are considered as an effective method to stabilize the surface of layered lithiated Ni-rich oxides and proven to achieve high stability with long-term cyclability [28]. Many electrochemically inert elements has

been reported suitable for increasing bond energy of TM/oxygen and decreasing oxygen evolution and consequently improving structure stability and suppressing capacity fading [9,10,24,28]. This review focuses on summarizing the recent research progress on the Ni rich materials from the synthesis methods towards surface modification methods including coating and doping processes. Firstly, the structures, characters and limitations of Ni rich positive electrode materials are briefly introduced. Then, focus is on the surface technologies of appropriate modifications and the effectiveness of different coating are clarified. At last, the conclusion and prospective challenges about Ni rich positive electrode materials are provided.

2. Synthesis method

Since the appearance of the first lithium ion batteries with layered lithiated TM oxides as a positive electrode material in few decades ago [32], several techniques have been employed to synthesize Ni-rich materials. Different synthesis methods have important effects on the morphology and structure properties of final products. In this section, we summarize several most common synthesis methods for NMC positive electrode materials: solid state, co-precipitation, sol-gel, hydrothermal, combustion and spray. The definition of each method along with their advantages and disadvantages are also summarized in Table 1.

2.1. Solid-state method

For a solid-state method, solid nickel, manganese, cobalt, and lithium precursors are grained, then calcined in a high temperature directly. The morphology of the final product depends on those of the precursor materials. For example, Yoshio et al. [33] employed a simple solid state method to prepare $\text{LiCo}_x\text{Mn}_x\text{Ni}_{1-x-y}\text{O}_2$ by mixing $\gamma\text{-MnOOH}$ (Tohso), Co_3O_4 , LiOH , and $\text{Ni}(\text{OH})_2$, the mixture was pressed at 800 kg cm^{-2} and followed by heating at $700\text{--}900\text{ }^\circ\text{C}$ for 20 h in air. The best performing sample $\text{LiCo}_{0.1}\text{Mn}_{0.2}\text{Ni}_{0.7}\text{O}_2$ reaches discharge capacity only of 156 mAh g^{-1} . This method has low requirements for equipment and simple production processes. However, it needs relatively high calcination temperature, and has risks of uneven mixing and impurity phase formation. Hence, it has been mainly applied in the early days and now it is usually combined with co-precipitation (NMC hydroxide) precursors to synthesize NMC materials with high-performance. Zou et al. [34] investigated the surface transformations during NMC761410 cycling processes using a facile solid-state method by mixing spherical $\text{Ni}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.10}(\text{OH})_2$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ precursor. They were calcined first at $500\text{ }^\circ\text{C}$ for 10 h followed by 20 h at $750\text{ }^\circ\text{C}$ in O_2 atmosphere. The results revealed that the as-prepared NMC761410 exhibits secondary particles with spherical shape and a uniform size diameter of $\sim 10\text{ }\mu\text{m}$ with the initial discharge capacity around 200 mAh g^{-1} between 2.7 and 4.3 V. Chu et al. [35] investigated the influence of Ta doping on NMC622 via a solid state method by ball-milling a commercial hydroxide precursor with $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ and Li_2CO_3 . The as-prepared materials showed spherical or quasi-spherical morphology with diameters of $8\text{--}10\text{ }\mu\text{m}$. The best performing sample has the initial discharge capacity of 196.9 mAh g^{-1} .

2.2. Co-precipitation synthesis

The co-precipitation method is the most commonly used method to synthesize NMC hydroxide precursors. This method is suitable for producing layered NMC materials in large-scale and is already employed in industrial production. First, nickel, manganese, and cobalt precursors (usually sulfates) are dissolved in aspired molar ratios. Then, a precipitant (NaOH solution) and chelating agent (NH_4OH solution) are added. After the reactions are completed, the transition metal hydroxide precipitate is filtered and washed several times to remove impurity ions (Na^+ , SO_4^{2-}). This is followed by mixing the dried co-precipitation precursor with a lithium salt and calcination at high temperature. Ren et al.

Table 1

A comparison of various synthesis methods, their advantages and disadvantages.

Synthesis methods	definition	advantages	disadvantages
Solid state method	According to stoichiometric ratios the raw materials (metal salts, oxides or oxyhydroxides) are mixed, ground and then calcined at a high temperature directly.	1.Easy to control. 2.Low cost. 3.Suitable for large-scale production.	1.High-energy consumption. 2.Low efficiency. 3.Risk for impurities and inhomogeneity.
Co-precipitation method	A precursor is obtained by co-precipitation method. Contains at least two different kinds of cations in an homogeneous solution. Then, a precipitant is add followed by precipitation reactions. Finally, the obtained precursor is mixed with a lithium salt and calcinated in a solid state synthesis step at high temperate.	1.Several chemical compositions of NMC can be obtained. 2.Low cost. 3.Preparation condition is easy to control. 4.Short cycle. 5. Industrial process.	1.Precipitant may cause the too high local concentrations of precursors. 2.Particles agglomeration.
Sol gel method	The starting materials are dispersed in a solvent, and then a complexing agent added, the active monomer is polymerized, and sol starts to form. After further solvent evaporated, a gel is generated. Finally, drying and calcinating to obtain final products.	1. Uniformly mixed reaction system at molecular level. 2.Allows generating close-to-stoichiometric materials. 3.Lower calcination temperature.	1.Raw materials are expensive; some are organic and may be toxic. 2.Long synthesis cycle.
Hydrothermal method	Materials synthesis by dissolving and recrystallizing powders in a sealed pressure vessel to obtain a precursor. Then, mixed with a lithium salt for a solid state synthesis at high temperature.	1.Powder has high purity, good dispersion, and no agglomeration. 2.Easy to control shape of a precursor.	1.Highly dependent on production equipment. 2.Not suitable for large-scale production.
Combustion method	Heating a mixture of metal precursors and a fuel with high combustion enthalpy at low temperature.	1.Low-cost. 2.Simple equipment. 3.Low temperature.	1.Not suitable for large-scale production. 2.Poor controllability
Spray-drying	According to stoichiometric ratio to dissolve raw materials in a solvent, then the resulting solution is dried to form a dry precursor via a spray drier. Last, heating as-prepared precursor at high temperature.	1.Mixing at the atomic level. 2.High efficiency. 3.Continuous production of automatic control.	1.High energy consumption. 2. Need complex equipment. 3. Not suitable for large-scale production.

[36] systematically investigated how the co-precipitation method synthesis parameters influence the final positive electrode products. They have observed that the solution pH value, stirring rate and calcination temperature all play a crucial role in the precursor properties. Because of the synthesis conditions are well controlled, they synthesized the best NMC622 materials reported to date. It has the initial discharge capacities of $205 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C and a remarkable rate capability of $137 \text{ mAh}\cdot\text{g}^{-1}$ at 20C . The pouch-type full cells exhibited exceptional cyclability with a 96% capacity retention at 0.5C after 500 cycles. Their study demonstrates that the synthesis conditions have a significantly effect on NMC properties. Other Ni-rich NMC precursors are also obtained by co-precipitation, $\text{LiNi}_{0.88}\text{Mn}_{0.06}\text{Co}_{0.06}\text{O}_2$, $\text{LiNi}_{0.70}\text{Mn}_{0.22}\text{Co}_{0.08}\text{O}_2$ [37], $\text{LiNi}_{0.901}\text{Co}_{0.051}\text{Mn}_{0.048}\text{O}_2$ [38], $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) [39,40], NMC622 [41,42], $\text{LiNi}_{0.7}\text{Mn}_{0.2}\text{Co}_{0.1}\text{O}_2$ [43]. Most of them have spherical morphology and micron level secondary particle sizes. However, this kind of morphology results in crack formation during the electrochemical processes. Thus, single crystal NMC materials have been prepared by using the same precursor system. The precursors and lithium salts mixture has been calcined at higher temperature or longer time, 900°C for 12 h (NMC622), 955°C for 6 h (NMC622), to increase the growth rate of crystalline NMC materials. The morphology of the obtained NMC materials do not have the spherical secondary particles but primary particles with micron dimensions. The single crystal NMC materials have no grain boundaries, which suppresses crack generation during electrochemical processes significantly improving the cycling stabilities.

2.3. Sol-gel method

Considering the drawbacks related to uniformity of co-precipitate precursors and the impurity phases produced in solid state method synthesis processes, the sol-gel method is an effective strategy to avoid these problems. In a typical sol-gel synthesis processes, nickel, manganese, and cobalt precursors (usually acetates, nitrates, or hydroxides) are dissolved in liquid solvents according to their molar ratios. Then, a chelating agent is added into the solution to obtain a sol. When the solvent is evaporated via stirring, a gel is formed, and it is usually calcined at $400\text{--}600^\circ\text{C}$ in air to remove organic compounds. Last, the obtained powder is heat-treated at an elevated temperature ($680\text{--}900^\circ\text{C}$, depending on the Ni fraction). This method often yields close-to-stoichiometric materials with small nanocrystalline size and narrow particle size distribution. Dong et al. [44] obtained a NMC811 positive electrode material via a sol-gel method with agglomerated primary nanoparticles with an average size of about 500 nm. These nanoparticles have an irregular polygon shape with a smooth surface and sharp edges. This morphology demonstrates high crystallinity and purity typical for sol-gel synthesized materials. Smaller particle size shortens the Li ions transport distances during charge and discharge. The optimized NMC811 can deliver a discharge capacity of $150.0 \text{ mAh}\cdot\text{g}^{-1}$ at 5C rate in a voltage range of $2.7\text{--}4.6 \text{ V}$ with 83.4% capacity retention for up to 500 cycles. Gao et al. [45] have employed a sol-gel method to synthesize a uniform Zr doped NMC811. The as-synthesized NMC811 has cobblestone-like particles, which can reduce the surface area between an electrode and electrolyte. At the best, NCM811 exhibits $100 \text{ mAh}\cdot\text{g}^{-1}$ at 10C with 84.3% capacity retention after 60 cycles. A sol gel method has also been used to synthesize a NMC622 positive electrode material [46,47]. Benefits of sol-gel methods include reduction of the high temperature calcination times and mixing reactants at atomic level. However, it may not be suitable for large-scale production due to long overall synthesis duration and high costs of raw materials.

2.4. Other methods

Beside those common methods mentioned above, other approaches have also been employed to synthesize Ni-rich NMC positive electrode materials. For example, a spray-drying method [48,49], which

wide-spread use is limited by complicated process and high requirements for equipment. For combustion method [50], a mixture consisting of metal precursors and a high combustion enthalpy fuel is heated. Thus, the mixture is calcinated at a relative low temperature. However, this method has such disadvantages as large particle size and difficult controllability. As a third example, hydrothermal method [51] allows control of crystal shape but is not suitable for large-scale production due to equipment requirements.

So far, there is not one synthesis method that can completely replace other methods, co-precipitation method combine with solid state method is already employed in industrial production. However, other methods still play an important role in laboratory-scale research. In addition to several methods mentioned above, some studies show that NMC materials with special morphologies obtained via special synthesis methods, have significantly improved electrochemical properties. For instance, Lee et al. [52] have used a citric acid assisted sol-gel method for synthesizing $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622), which yields a disordered macro porous morphology (Fig. 3a). This method provides good mixing at atomic level, and the citric acid transforms to volatile products upon heating processes. Thus, synthesized microporous NMC622 shows a high discharge capacity of $174 \text{ mAh}\cdot\text{g}^{-1}$ and high rate capability (41% capacity retention at 10C). In another research, Liu et al. [53] have prepared NMC622 with a peculiar hierarchical porous morphology precursor via a facile ammonia-induced method. This hierarchical porous structure can accelerate Li ions transfer due to increased surface area between an electrolyte and active cathode particles. It delivers discharge capacity of $82 \text{ mAh}\cdot\text{g}^{-1}$ at 20C and maintains 91% of its initial discharge capacity after 100 cycles at 1C . A series of multishelled Ni-rich NMC positive electrode materials have been synthesized by Zou et al. [54] using sustainable seaweed (alginate) fiber as a template for synthesis (Fig. 3b). Thus, obtained 1D morphology allows fast Li ion and e^- transport due to effectively increased electrode-electrolyte contact area. Hence, the electrochemical performance is efficiently improved. Liang et al. [55] prepared a quasi-spherical structured NMC622 positive electrode material with a highly ordered microstructure particles via a microfluidic synthetic system. The prepared particles exhibit micrometer sized crystals consisting of uniformly arranged nano-cubes (Fig. 3c). These particles with special morphology deliver a high initial discharge capacity of $195.2 \text{ mAh}\cdot\text{g}^{-1}$ and relatively high capacity retention of 80.83% over 200 cycles.

As a summary, each synthesis method has pros and cons. To synthesize Ni-rich NMC positive electrode materials with good electrochemical performance, it is important to consider the influence of synthesis method on morphology, structure, and the properties of the final product. Besides, the production process, cost, duration, and energy consumption also need to be considered. In this case, the co-precipitation method with the relative homogeneous elements mixing, together with relatively simple, low-cost synthesis conditions and short duration of the solid-state step has been proven out as the most effective method to prepare Ni-rich NMC positive electrode materials in industrial production. However, other methods still have their own value. For instance, special structures, e.g., microporous structure, nanowires, and nanorods, can only be synthesized by some special methods. Hence, fabrication of best performing Ni-rich NMC positive electrode materials might need combination of features from different synthesis methods.

3. Modification by doping

Doping (or substitution) refers to adding of a small number of heteroatoms that are incorporated into the crystal structure of the host, without appearance of additional phases. Doping can be applied to modify lithiated oxides used at LIBs electrodes, including Ni-rich NMC. Usually, the amount of dopant does not exceed 1 at. % comparing to the number of the host TM atoms, although in some cases doping up to 5% can be applied. Despite the low amount of dopant, changes in the structure of lithiated oxide and its electrochemical properties can be

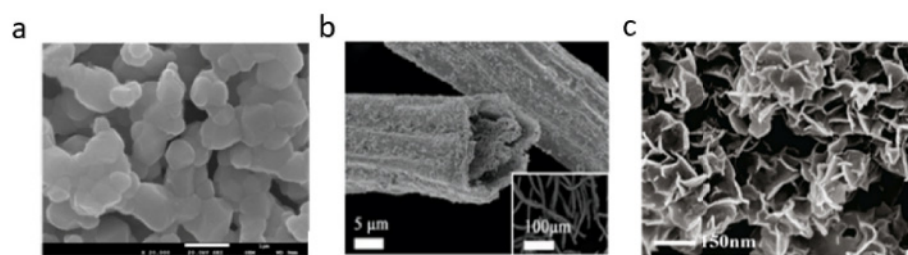


Fig. 3. SEM images of disordered macroporous $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, Reprinted with permission from Ref. [52] © 2016 Elsevier B.V. All rights reserved, (b) the multishelled $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_3$ hollow fibers $x = 0.5$, Reprinted with permission from Ref. [54] © 2016 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, and (c) quasi-spherical structure $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ precursor with uniformly arranged nano-cubes, Reprinted with permission from Ref. [55] © 2016 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

significant, which makes this approach widely applied for controlling active material behavior. An optimal amount of dopants is an important factor to be considered as the side effects overcome the benefits when the doping amount is excessive. For instance, F has been reported to enhance the rate performance, but the achievable discharge capacity reduces for high doping concentrations [56]. Similarly other properties such as electronic conductivity, cation mixing and lithium transfer can be affected adversely by non-optimized doping amount leading to performance deterioration at high C rates or operation voltages.

3.1. Method of doping

Doping can be performed in different ways, during the synthesis or during the lithiation of a TM hydroxide precursor. In the first case, the dopant is added to a mixture of sulfates or other salts, which then form a hydroxide precursor material by coprecipitation [57–59]. As a result of precursor doping, a high homogeneity of the dopant distribution in the lithiated material is achieved. In the second case, the dopant is added together with the Li source to the precursor and then heated up to form a lithiated oxide [60]. A hydroxide precursor can also be coated with a doping agent before mixing with a Li source [61]. In case of solid state synthesis, all the components are mixing together with a dopant and heated up for the lithiation [62]. The main part of the dopant can be concentrated near the surface of the particles or form a concentration gradient from the lithiated oxide core to the surface. In the case of high dopant concentrations near the surface, this modification is close to the coating and mainly affects the surface properties without changing the properties of the particle core.

Based on Section 1 Ni-rich materials with different composition (Ni content) have different optimal synthesis conditions [63]. As the doping leads to different compositions of Ni-rich materials as well, therefore, caution should be applied when concluding the electrochemical performance of undoped and doped NMCs under the same synthesis conditions. Because of such a complex set of parameters, there are no clear patterns of the doping effect on the capacitive behavior of doped materials.

Considering the increased production of LiB materials from recycled electrochemical power sources, doping may be unintentionally due to insufficient purification of recycled compounds. The main contaminants are Cu and Al from current collectors and constitute a significant part of the total mass of LiBs electrodes. For example, electrode materials produced from recycled batteries may content up to 0.3% of Cu [64]. If low amounts of impurity atoms do not affect negatively or have a positive effect on the final active electrode material properties, then lowering the purification requirements for materials obtained from recycling processes will reduce the cost of the final product.

Dopant atoms have a complex effect on the structure and electrochemical behavior of lithiated oxides. When NMC positive electrodes are operated as LiB electrodes, many parallel processes occur. Any additional elements complicates the system even more and hence, positive and negative effects can be initiated by different mechanisms (one or more simultaneously) [65,66]. Therefore, it is important to consider the synthesis conditions besides doping, and the methods for studying the electrochemical properties. Selection of synthesis conditions for doped

and undoped lithium oxides can be also different but this effect is not widely discussed.

3.2. Surface doping sites and approaches

Due to the presence of three types of sites in the NMC material, there are three fundamentally different approaches of doping: the occupation of Li-sites, O-sites, and TM-sites. In addition, doping atoms can form structural defects. TM site doping is more investigated because several atoms can be incorporated in those sites.

The calculated substitution energies suggest that Zr substitution has the highest preference for the Ni sites ($E = -1.82$ eV per dopant), followed by the Co sites ($E = -1.80$ eV per dopant) while the least preferred sites for Zr substitution are the Mn sites ($E = -1.26$ eV per dopant) [67]. A computational study of Al doping demonstrates similar tendencies when Al atoms in Ni sites in the NMC811 positive electrode material are most energetically stable, followed by doping at a Co-, Li-, and Mn-site [68]. W [69], Mo [70], Ce [71], Sn [72], Ti [73], Cr [74] are shown to occupy Ni sites, as well, while Cu replaces Co [75] and Mo can replace Mn sites [76]. In some articles, Mg insertion at the Li-site is shown to be most preferred, followed by doping at the Ni-site in Ni-rich NMC positive electrode materials [68,77]. Other articles demonstrate presence of Mg in TM metal sites [62]. This difference in interpretation can be related to the coordination preferences for Mg, different synthesis methods leading to Mg substitution in the Li or TM slab, or it might be due to experimental error.

The same valence state between Li^+ and alkali metal ions (Na^+ , K^+ , Rb^+) has been suggested to favor alkali metal ions doping into the Li sites [78,79]. However, some caution should be applied here because of the large size those ions, particularly ones larger than Na^+ , can experience steric hindrance at the Li sites. However, we follow the presented classification since it correlates with the results of earlier studies. Ca is larger compared with TMs, so it is an interesting example of different mechanism of interaction with TM layered oxide structure. The lattice parameters of Ca doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are smaller than those of the undoped ones [80]. Because Ca^{2+} ions have larger ionic radius (1.14 Å) the decrease of the lattice parameters is attributed to the formation of defects, which occurs from the partial occupancy of Ca^{2+} ions in the lithium lattice sites and formation of a Ca_{Li} defect and a lithium vacancy (V_{Li}) [80]. Similarly, doping with K promotes the formation of additional vacancies in the Li layer of layered lithiated oxides [73,81]. It is important to notice that the alkali metals doped in the Li sites reduce the amount of electrochemically active Li^+ and can affect capacity of the material [78]. Ta [35,82] is also described as dopant found in Li slab.

For the O sites, F is found to be the most effective replacement [79,83]. Nitrogen can also be introduced to the O sites [84]. B^{3+} has a smaller ionic radius compared to Li and TM ions and hence occupies the tetrahedral interstices and trigonal sites surrounding O atoms between the TM and Li layers, which enlarges the unit cell [85]. It has been suggested that B ions can form polyanions inside the NMC structure [86], but no direct evidences have been reported.

3.2.1. Doping effect on bonding energy

The binding energies of Ni–O, Mn–O and Co–O are 366, 362, and

397 kJ mol⁻¹ [87]. Replacement of TM atoms with Zr [87], Mg [83], Te [88], Al [68], Cr [89], Ti [90], Ce [91], Ca [80] etc. or O atoms with F [92], even in a small amount, leads to the strengthening of the whole system increasing the thermal and surface stability, cyclability, decreasing cation mixing, oxygen release and TM leaching, increasing reaction reversibility and potential window. Hence, this mechanism is most important to improve stability of the NMC system. Zr⁴⁺ is one of the most common dopants due to its promising influence on electrochemical properties by increasing the structural stability of Ni-rich materials. It has been discovered that Zr atoms in the crystal lattice enhances the thermal stability of the positive electrode materials during electrochemical processes [93]. The Al-doped NMC demonstrates lower capacity fading upon aging in a charged state (4.3 V vs. Li|Li⁺) at 60 °C in comparison to their undoped counterparts [94]. Addition of 1 at.% of Cr in the LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ matrix leads to strengthening of metal–oxygen bonds [74]. W substitution enhances the structural stability, hence leading to an improved electrochemical performance [95]. The partial Mo⁶⁺ doping in a Ni-rich material results in improvement of the thermal stability of the doped samples [76] and decreases the total heat evolved during chemical reactions [70]. The higher structural stability is reflected as an enhanced thermal behavior of the Sn-doped material [96]. The enhanced thermal stability described for Mg-substituted Li_{1-x}Ni_{0.8}Co_{0.1}Mn_{0.1-y}Mg_yO₂ can be mainly attributed to the improved structural stability [97] while Ca enhances the stability of the LiNi_{0.8}Co_{0.2}O₂ structure [80]. The Li-site doped Na⁺ can serve as pillar ions to stabilize the structure of the positive electrode materials during Li⁺ intercalation/deintercalation [78].

3.2.2. Doping effect on TMs leaching

Leaching of TMs leads migration of these ions, together with Li ions, from the positive to the negative electrode during the charge process. For Ni ions, Ni cluster formation has been shown to reduce SEI layer on the negative electrode surface and accelerate Li dendrite growth reducing cycle life of batteries [98]. Transition metals, especially Mn²⁺ from dissolved NMC, can cause significant capacity loss due to massive damage to the SEI layer [99]. Doping of both TM sites [94] or O sites [100] can prevent TM dissolution increasing binding energies for whole structure thus stabilizing the material. However, also dopant atoms can be liberated from the NMC structure and migrate from the positive to the negative electrode. For example, in the case of Cu doping of Ni-rich NMC materials, graphite positive electrode surface has been detected to be contaminated by Cu, followed by Mn and with a negligible amount of Co and Ni after cycling [101]. TM dissolution is also related to electrolyte attack which affects metal dissolution and oxygen loss resulting from this process [102].

3.2.3. Ni³⁺ to Ni²⁺ ratio

The high capacity of Ni-rich positive electrode materials is served by the presence of a two-step electrochemical reaction which includes converting of Ni²⁺ to Ni³⁺ and further to Ni⁴⁺, and vice versa. At the same time, Ni²⁺ ions have the greatest ability to migrate, leading to cation mixing and TM dissolution, while Ni⁴⁺ ions have a high reactivity and interact with the electrolyte contributing to the oxygen release, electrolyte attack and rock salt phase formation. Limiting the potential window leads to a noticeable decrease in capacitance and yet cannot completely prevent negative effects due to the overpotential arising because of the inhomogeneity of electrode materials and cells. When performing electrochemical tests, such side reactions are visualized as low reversibility of electrochemical processes during cell charging and discharging. Mechanical stress originating from inhomogeneous spatial Li distribution is assumed to lead to spontaneous reduction of highly reactive Ni⁴⁺ which can be found at high delithiated states of the positive electrode, i.e. at high SoC. The reduction leads to phase transformation from the pristine layered transition metal oxide structure (*R* $\bar{3}m$) to spinel structure (*Fd* $\bar{3}m$) and further to rock-salt structure (*Fm* $\bar{3}m$) [102].

Degraded structures show an oxygen deficit compared to the pristine one. Furthermore, the reduction of Ni⁴⁺ leads to oxygen release from the lattice [102]. It has been calculated that Zr in a Zr doped NMC Ni-rich electrode material migrates from an octahedral site of the TM layer to the tetrahedral site of the Li layer if NMC is fully delithiated. This Zr at the tetrahedral sites suppresses the phase transformations [103,104]. The reversibility of the H2–H3 phase transitions caused by Ti doping decreases the generation of microcracks and structural degradation during prolonged cycling [105]. It is worth mentioning that this effect takes place with x = 0%–1%, when performance of material with x = 2% of Ti is similar to that of an undoped material [16]. K substitution is also shown to prevent the NMC phase transformations during cycling [81]. The partial substitution of manganese by Mo⁶⁺ in a Ni-rich material LiNi_{0.8}Mn_{0.06}Co_{0.1}Mo_{0.04}O₂ results in suppression of the structural transformation from the spinel to rock-salt phase [76]. For the 0.5 at.% W doped NMC positive electrode the H2 → H3 phase transition peak intensity remains stable during 100 cycles unlike for the undoped material [69]. Na substitution has been reported as a potential approach to hinder the transition between the layered and spinel structure [106]. Also Al doping is effective to prevent the expansion of the rock salt phase [59].

The low-valent metal dopants such as Mg [97] or Cu [101] can increase Ni³⁺/Ni²⁺ ratio to maintain electroneutrality of the material which leads to reduce cation mixing via such structural effects as 1) substituting Ni in layered structure and hence reducing Ni²⁺ content in NMC or 2) inducing electrostatic repulsion to prevent Ni²⁺ migration from the TM slab to the Li slab during electrochemical cycling. The high-valent metal dopants such as W [69], Ti, Mo [70] and Nb often decrease Ni³⁺/Ni²⁺ ratio and display more complicated stabilization mechanism including reactions with Mn⁴⁺ [107,108]. To maintain the charge balance when O²⁻ is substituted with F⁻, partial reduction of TMs Mn⁴⁺/Ni³⁺/Co³⁺ occurs to Mn³⁺/Ni²⁺/Co²⁺ [79].

3.2.4. Structural stability

Structural instability issues met in Ni rich layered metal oxides include Li⁺/Ni²⁺ cation disorder. During NMCs synthesis or storing and charging of a battery, Ni²⁺ ions can move readily to Li sites, which results in so called cation mixing problem. Generally, cation mixing occurs because of the similarity between the Li⁺ (0.076 nm) and Ni²⁺ (0.069 nm) radius. Doping suppresses the cation mixing and thereby improves the structural stability of Ni rich layered oxides. Li/Ni disorder not only reduces the amount of Li⁺ participating in the charge–discharge reactions but also decreases the diffusion rate of Li⁺. Thus it contributes to reduced specific capacities and rate capabilities of layered positive electrode materials [109].

Zr⁴⁺ is one of the most common dopants because it decreases the degree of Li⁺/Ni²⁺ cation mixing. Moreover, the Ni²⁺ valence is higher in the doped sample and Li⁺/Ni²⁺ cation mixing decreases after doping, which leads to the superior structural stability of NMC during cycling. In the XRD patterns, Zr doping increases *I*₍₀₀₃₎/*I*₍₁₀₄₎ ratio which correlates with the decreasing Li⁺/Ni²⁺ cation mixing [93]. Theoretical DFT studies have demonstrated higher capacity and stability of Zr doped LiNi_{0.5}Co_{0.25}Mn_{0.25}O₂ materials. It has been calculated that Zr migrates from an octahedral site of the TM layer to the tetrahedral site of the Li layer if NMC is fully delithiated whereas Zr at the tetrahedral sites blocks the migration pathways of Ni-ions from the TM to Li layers [103,104].

Other early transition metals show similar effects to Zr when used as dopants. Ti substitution leads to the reduced Ni²⁺/Li⁺ cation mixing as well as superior capacity performances and faster lithium diffusion kinetics compared with the undoped material [110]. Addition of Cr [74], Cu [111,112], Nb [108], Ta [35] and Sn [113,114] suppresses the cation mixing. Some dopants (for example, W [95]) have been reported to increase cation mixing due to increment of Ni²⁺, but this effect can be also related with unoptimized synthesis conditions.

Like early transition metals, alkaline and alkaline earth elements have favorable effects. In a fully lithiated NMC material, cation

disordering can be suppressed by Mg-doping as Mg blocks tetrahedral voids preventing the migration of nickel ions to the lithium layer [83]. Hence, Mg doping prevents the formation of Ni^{2+} excess in Li^+ sites and Li/Ni exchange as well as Ni migration [68,97]. Li-site dopants (Na [78,115], K [78], Rb [78], Ca [109]) are also found to reduce cation mixing while doping with Na provides the largest effect comparing to K and Rb [78]. In a case of O site doping, decreasing of cation mixing can be also achieved. $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ positive electrode materials doped with 0.005, 0.01 and 0.02 at.% of B allows to reduce Li/Ni ionic mixing [116].

Oxygen release is another instability phenomenon and it takes place during cycling due to the transition of the highly reactive Ni^{4+} containing hexagonal species to the rock salt phase [117]. It can be also supported by interaction of NMC with an electrolyte, the movement of defects from the crystal on its surface. The released oxygen is involved in further electrolyte degradation [14]. The oxygen release can affect the efficiency of the CEI layer which in turn lead to decrease capacity and cycle life of LIBs and even lead to their spontaneous failure, fire, or the thermal runaway. A computational study demonstrates [68] that in the case of fully lithiated NMC811, oxygen vacancies can be effectively prevented by the Al doping. Oxygen stability is improved the most by the Al-doping of the structure, regardless of whether the structure has pre-existing defects or is delithiated [68]. TGA measurements have shown lower mass loss for the charged 2% Sn doped NMC electrodes at temperatures up to 550 °C compared with an undoped NMC material, which indicates a lower amount of oxygen release during thermal decomposition [118]. Also Na and F partially substituted into Li and O sites of the $\text{LiMn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, respectively, enlarge the Li slab, which in turn mitigates oxygen loss [79].

The surface of an active electrode material interacts with the electrolyte to form a CEI layer consisting of electrolyte fragments, Li and TM ions. CEI provides uniform passivation to the positive electrode while maintaining the ionic transport pathway, which suppresses undesirable side reactions between an electrode and electrolyte [119]. Doping ions stabilize the CEI layer, reduce unwanted reactions of the material with the electrolyte, and improve the diffusion of lithium ions through the surface. Performance improvement after Zr doping results from a robust CEI layer formation during cycling of Zr doped NMC. These effects effectively alleviate electrolyte degradation on the positive electrode surface [93]. The electrochemical behavior of Al doped NMC523 electrodes correlates with the lower resistances of the Li^+ migration through the surface. The modified stable and less resistive interface on the Al doped particles comprises of the Li^+ -ion conducting nano-sized centers such as LiAlO_2 , AlF_3 , etc., which promote Li^+ ionic transport to the bulk and therefore facilitate the electrochemical reactions [94]. Furthermore, partial substitution of manganese by Mo^{6+} in a Ni-rich material $\text{LiNi}_{0.8}\text{Mn}_{0.06}\text{Co}_{0.1}\text{Mo}_{0.04}\text{O}_2$ has been reported to suppress exothermic reactions between the positive electrode and electrolyte [76]. The formation of a more stable electrode/electrolyte interface and fewer side reactions of the doped materials with the electrolyte species is also observed for a Mo doped Ni-rich lithiated oxide [70]. For material $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ gradient boracic polyanion $(\text{BO}_3)_x(\text{BO}_4)_y\text{O}_{2-3x-4y}$ ($x + y = 0, 0.01, 0.015, 0.02$) doping results in decreasing surface reactivity inhibiting the decomposition of organic electrolytes [86]. Likewise, Ta doping makes the surface inactive in reactions with electrolyte and suppresses electrolyte-interphase side reactions [35].

3.2.5. Phase transition

During charge and discharge of Ni-rich lithiated based positive electrodes, lithiation/delithiation reactions occur, accompanied by a change in the TM oxidation state and a phase transition. Phase transition is accompanied by a significant change in the crystal lattice parameters (especially c parameter is changing in the range from 14.17 Å to 14.35 Å) [120], which contributes to the formation of cracks in the crystals, primary and secondary particles. The crack formation is also accelerated by defects in the crystal lattice, a high delithiation stages and chemical

degradation.

Ti ions in $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33-y}\text{Ti}_y\text{O}_2$ decrease overall changes in the lithium interstitial volume during cycling, which coincides with a decrease in the intercalation voltages at the lower lithium concentrations. It has been shown that Ti^{4+} is electrochemically inactive while the reduction of Mn^{4+} to Mn^{3+} compensates for the aliovalent substitution of Ti [121]. However, because aliovalent substitution provides an extra electron, for a given delithiation amount, fewer of the Ni/Co redox centers fully oxidized, which aids in volume preservation [122]. The addition of W also contributes to stabilizing the structure and restraining the diffusion of rock-salt phase from surface to the interior, observed from TEM after cycling [95]. W doping structurally modifies the surfaces of the primary particles by forming an ~20-nm-thick spinel-like phase on the primary particle surface stemming from the cation intermixing [69]. In this case the spinel phase on the primary particle surface also increases the cycling stability of the W doped NMC positive electrode. This spinel-like phase on the periphery of the primary particles acts as a buffer phase protecting the particle interior from the electrolyte attack and improves mechanical stability to the NMC particles [69]. The W doping has also been found to enhance the rock-salt phase formation at LiNiO_2 particle surface. This is considered as one of the major reasons for the clearly observed stabilization of W^{6+} doped LiNiO_2 positive electrodes [123]. For Cu [111,112], Al [58,59], Sn [72], W [69] and Mg [68,77] doped Ni-rich lithiated oxides, smaller lattice parameter deformations compared to undoped samples has been related to structure stabilization during cycling. Microcracks resulting from anisotropic volume changes during cycling of the Ni-rich NMCs are observed less often in a case of B doped materials compared to an undoped one, which corroborates materials mechanical stability and hinders electrolyte attack induced chemical degradation [85]. It has been also shown that B modifies the surface energies by producing a highly textured microstructure that can partially relieve the intrinsic internal strain generated during deep charging of a NMC positive electrode material [85].

3.2.6. Morphology and crystal lattice parameters

The crystal lattice parameters for Ni-rich NMC electrode materials differ only slightly but are very important for the electrochemical properties of this material. a parameter determines the distance between TM atoms in the unit crystal cell. c parameter determines the distance between the TMs layers, where the lithium layer is located and in which Li diffusion occurs. A slight increase in the c parameter improves Li diffusion and can be created by larger dopant atoms or decreasing the amount of Ni^{2+} ions. There are no references about effect of a parameter on electrochemical behavior of the Ni-rich NMC positive electrode materials. However, Zr doping [93] has been shown not to affect the a parameter significantly while Al [97] and Mg [97] doping can lead to slight decrease of the a parameter whereas Cr [74], Mo [70], Sn [113,114], Na [78] doping lead to increase of the a parameter. Increase of the c parameter has been confirmed for Zr [93], Ti [105], Al [97], Cr [74], W [69,95], Mo [70], Nb [108], Sn [113,114], Na [78] doping and this provides better Li ion diffusivity during cycling, lower electrochemical impedance, improve Li-ion diffusion, capacity and stability of the materials. Decrease of the c parameter has been found for the Mg doping [97]. Nevertheless, electrochemical properties are reported to improve in this case because of other favorable dopant effects. Na and F co-doping results in reducing of TM atoms with a larger radius, rather than those with a higher oxidation state, conforming to the increase in lattice parameters [78,79]. Contrary, B forms defects in crystals and locates in the interstitial sites of the NMC, causing the expansion of the c axis [124].

Lattice parameters are not the only factor affecting Li diffusion. Other important parameters are defects in the structure and the $\text{Li}^+/\text{Ni}^{2+}$ cationic mixing. Defects can provide better pathways for Li ions, or contrary block them, and the occupation of the Li sites by Ni^{2+} or doping atoms adversely affect the transport of Li^+ ions. Ti [110], Al [94], Cr [74], Nb [107,125], Ca [109], K [81] and Na [115] doping increase Li^+

diffusion promoting faster Li^+ transport, superior capacity performances, decrease resistance for the Li-ion, expand pathways for Li-ion insertion and extraction. Defects in the material produced by Ca substitution decrease the activation energy for the hopping of lithium ions from one site to another improving diffusion, and hence facilitates lithium ions extraction out and insertion into the material [80]. Na, K and Rb dopants introduced into the Li slab with overlarge ionic radii cause lattice distortion and block Li^+ diffusion channels, thus hindering the intercalation of Li^+ and decreasing the initial coulomb efficiency [78]. When both Na and F are partially substituted into Li and O sites in $\text{LiMn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, the Li slab is enlarged and Li diffusion promoted [79] and this effect is higher comparing to separate Na or F substitution in the NMC lattice [92].

Charge transfer resistance can be calculated from EIS analysis and is related to the Li^+ diffusion through the active material lattice structure and surface, electrode volume and electrolyte. High $\text{Li}^+/\text{Ni}^{2+}$ cation mixing, cracks, and defects can increase resistance whereas electrode and battery architecture can also affect resistance. Lower charge-transfer interfacial resistance of Mo-doped electrodes is suggested to result from the formation of additional conduction bands near the Fermi level elucidated from the calculated density of states [70,126]. Ca doping produces defects in the material which increase the conductivity [80] while Na substitution increases the electronic conductivity of the NMC positive electrode material relative to the undoped one which reduces impedance of the former [106]. $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ positive electrode materials doping with 0.005, 0.01 and 0.02 at.% of B allow to reduce interfacial resistance due to the formation of well-ordered lattices structure [116]. EIS results prove that the charge transfer impedance of Ta-0.25% NMC during cycling is clearly less than that of the pristine one [35].

The change in morphology can affect Li^+ diffusion, which directly affects the efficiency of the material. It can be associated with a change in the lattice parameters and the presence of defects. Changes in morphology with doping modification are not often described and the exact effect of such a change is not visualized, since a change in cation mixing or bond strength affects the electrochemical behavior much more significantly. In addition, the surface area of the material available affects the activity of the electrode active material, interactions with the electrolyte and hence electrode degradation. W leads to decreasing primary particle size with increasing W content [69]. No clear differences in the morphology of the secondary particles can be observed after B modification of Ni-rich lithiated oxide, but sizes of the primary particles progressively decrease, became increasingly thinner and elongated in the radial direction with an increase in the B content [85]. Cu doping of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ positive electrode materials contributes to a change in the particle morphology, decreasing the size of the secondary particles and increasing the size of the primary particles and its density with increasing Cu concentration [101].

3.3. Effect of co-doping and different doping elements

In a case of co-doping, synergetic effect is observed increasing stability and capacity even more comparing to the doping with one element only. For example, Al and Zr together significantly enhanced capacity and voltage retention [127]. Ti and B have synergetic effect on the capacity, rate capability and stability [128]. Compared with unsubstituted, Na and F single element substituted samples, the Na-F-substituted $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ shows higher initial coulomb efficiency, enhanced rate capability and superior cycling performance [92].

Not many comparisons of different dopants applied under similar conditions exist but this question is important for the electrode material design. Effect of Sn doping is higher than that of Fe or Al investigated in the same work [96]. Doping of Ni-rich NMC positive electrode materials demonstrates an extremely weak influence of K on NMC electrochemical properties and these are much weaker compared with doping of the same NMC material with Cu or Al [129]. In another work [78], doping of

$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with Na, K and Rb has been compared. Na, K and Rb ions have similar valence but different ion sizes. The Na doped sample has the highest capacity retention and capacity comparing to the K and Rb ones [78]. Enhanced properties are attributed to Li-site doping ions with suitable ionic radii, which are beneficial to improve Li^+ diffusion in the positive electrode materials. Contrary, the lattice distortion and excessive blocking effect of the bigger Li-site doping ions lead to poorer rate performances.

Mostly doping by heteroatoms contribute to an increase in the specific capacity, especially at high C rates. However, a few dopants demonstrate a decrease when they are introduced into the material structure. It can be related with formation of defects, increasing $\text{Li}^+/\text{Ni}^{2+}$ cation mixing and appearance of the dopant atoms in Li^+ pathway. Another issue can be also related with synthesis conditions which are not optimized for investigated positive electrode materials. NMC doping with Zr have been shown to improve the capacitance and stability, while coating with a layer of zirconium oxide leads to an improvement in the electrochemical characteristics during cycling [93,103,104]. Another study [67] indicates that even when Zr is deposited on the surface of NMC811 particles, Zr atoms partially diffuse into the bulk structure. Combination of a ZrO_2 coating with a Zr doping provides a promising synergy leading to an enhanced electrochemical performance of nickel rich NMC811 [67]. Ti is another promising dopant which may improve electrochemical performance and stability [105]. Al has been widely used as one of the LiTMO_2 component systems along with Ni, Mn and Co. Al enhances positive electrode material cyclability, stability and capacity during the charge-discharge processes and is less expensive than Co [94,97,130].

Incorporation of several early transition metals, such as Cr into the TM sites in layered Ni-rich positive electrodes exhibit many favorable characteristics, including structure stability and enhancing cycling performance [74,131]. Also 0.5 at. % W and 1 at.% W doped NMC retains 93.0% and 96.0% of the initial capacity after 100 cycles, respectively, whereas the undoped NMC positive electrode retains only 86.0% of its initial capacity. W doping significantly increases mechanical stability and prevents the formation of cracks during the cycling process. In addition, calendar stability of the NMC material is also improved [69]. Despite a slight cutdown of the initial discharge capacities in W modified materials, performance at high rates as well as cycling stability improve significantly based on the electrochemical characterizations, among which the 0.5% W doped NMC exhibits the optimal electrochemical performance compared with the other W doping contents [95]. Mo-doped electrodes exhibit notably lower irreversible capacity loss in the 1st cycle and lower self-discharge at 4.3 V vs Li^+/Li compared to undoped material [70]. The doped materials have 12%–20% higher discharge capacities compared to undoped ones especially at high rates of 4C and demonstrate higher capacity retention as well as lower voltage hysteresis during cycling [70,126]. Additionally, Nb is a rare element but a promising example of a dopant, which also helps to significantly improve the electrochemical behavior of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [108]. Among late transition metal dopants, Cu doped positive electrode materials show better electrochemical performance, capacity retention and stability than undoped NMC111 [111,112]. Initial charge/discharge capacities gradually decrease with increasing Cu content in positive electrode active materials [101].

Alkaline earth metal Mg is widely used as a dopant for such positive electrode material as LiCoO_2 and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ [132] resulting in enhanced electrochemical performance in the $\text{LiNi}_{1-y}\text{Mg}_y\text{O}_2$ system [77]. The Mg-substituted electrodes $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1-y}\text{Mg}_y\text{O}_2$ ($y = 0.01$ and 0.02) have larger initial capacities compared to the undoped one and show an enhanced capacity retention of 93.3% for $y = 0.02$. Also Ca-doped materials provide a higher initial discharge capacity than the undoped one [80,109]. In this series, the materials doped with 2% and 4% of Ca demonstrate the best stability during cycling while 6% Ca doped NMC811 demonstrate the best rate capability [109]. For NMC materials, doping with alkali metals leads to a slight decrease in the

capacitance values [78]. K doped materials demonstrate better stability and rate capability properties when used as Li-ion battery positive electrodes [81]. Na substitution leads to better efficiency on electrochemical performance [79,106].

Elements belonging to the p block can be also used as dopants. Sn doped NMC material $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.15}\text{Sn}_{0.05}\text{O}_2$ shows improved rate-capability and cycle life despite a drop in the specific capacity compared to the undoped material [96,113,114]. It has been shown that doping of a positive electrode material with 1–2 at.% of Sn is most effective for capacity and stability improvement [118]. B^{3+} concentrations of 0.4 at.% and 1.0 at.% allows to increase the mechanical and cycling stability of $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$. As a result, the 1.0 at.% doped NMC sample delivers a discharge capacity of 237 mAh g^{-1} with an outstanding capacity retention of 91% after 100 cycles at 55°C ; this percentage is 15% higher than that of the undoped NMC positive electrode material [85]. A high initial specific capacity of 194.7 mAh g^{-1} at 0.1 C for 0.01 at.% B doped NMC811 is reported instead of 173.8 mAh g^{-1} for the undoped one while a capacity retention of 98.2% after 100 cycles for 0.01 at.% B doped NMC811 is maintained instead of 77.27% for the undoped one [116]. The boracic polyanion-doped oxides exhibit a more stable discharge capacity and much less potential drop even under high cut-off potential and elevated temperatures [86]. Partial replacement of oxygen (O^{2-}) by fluorine (F^-) leads to the formation of $\text{M}-\text{F}$ bonds, which stabilizes the structure during cycling, enabling high potential cycling [83]. Thus, doping by heteroatoms appears to be a promising and perspective method for improving the electrochemical performance of NMC positive electrode materials tough method of synthesis and doping process is affecting the electrochemical behavior of doped NMC.

Recent studies show that introducing of additional atoms into the NMC structure can help to overcome difficulties which cause a decrease in the electrochemical, structural, and thermal stability. At the same time, additional atoms strengthen the structure due to stronger inter-atomic interactions, prevent the migration of atoms, increase diffusion, contribute to the mechanical strength of the particle, change the morphology, and inhibit oxygen evolution reactions. Fig. 4 shows effects of doping agents on the Ni-rich positive electrode materials. In all cases, there is an increase in electrochemical stability during cycling, which is very important for Ni-rich positive electrode materials. This effect can be

provided both by strengthening the bonds of the crystal lattice, and by stabilizing phase transformations during the charging and discharging of electrodes. Reducing the $\text{Li}^+/\text{Ni}^{2+}$ cationic mixing plays an extremely important role in increasing the efficiency of NMC materials. Most dopants initiate this effect, but heteroatoms with a high oxidation state can increase cation mixing or have no effect. Another important parameter is the migration of Li^+ ions, which can be improved by the creation of defects, an increase the lattice parameter and a decrease $\text{Li}^+/\text{Ni}^{2+}$ cationic mixing. On the other hand, the occupation of the Li sites by doping atoms can also adversely affect the transport of Li^+ ions. Other parameters, for example, particle size, surface diffusion, and concentration gradient of elements in a particle can also play an important role in lithiation and delithiation of the NMC positive electrode material. Due to such a complex set of parameters, there are no clear patterns of the doping effect on the capacitive behavior of doped materials. Mostly doping by heteroatoms contribute to an increase in the specific capacity, especially at high C rates. However, a few dopants demonstrate a decrease in capacity when they are introduced into the material structure. Thus, doping by heteroatoms appears to be a promising and perspective method for improving the electrochemical performance of NMC positive electrode materials.

4. Surface modification by coating

Beside doping, surface modification methods have been used in order to enhance the low conductivity and suppress the fast capacity fading of the positive electrode materials during cycling [24,133,134]. One of the most direct approaches to avoid undesirable electrode-electrolyte interactions is provided by protecting the surface by a coating [134,135]. These coatings can improve the thermal and structural stabilities of the positive electrode materials, as well as their chemical and mechanical properties [134]. The desirable coating layer should possess the following general characteristics: 1. Chemical stability within the working voltage window in order to suppress side reactions between a coated active electrode material and electrolyte [136]. 2. Having a high redox potential in order to function as a “buffer” layer and decrease the oxygen release during cycling at high voltages to prevent electrolyte degradation [137]. 3. Protect the electrode surface with a uniform layer with a controlled thickness in order to avoid blocking the Li ion diffusion

	$\text{Li}^+/\text{Ni}^{2+}$ cationic mixture	Ni^{2+} concentr- ation	The strength of bonds	Structural stability	Li diffusion	Resistan- ce	c parameter	a parameter	Surface stability	Stable phase transformati- on	Defect and vacancies	Size of particles	Capa- city	Electroche- mical stability
Zr	↓	↑	↑	↑	↑	↓	↑		↑	↑	↑		↑	↑
Ti	↓			↑	↑	↓	↑			↑			↑	↑
Al	↓		↑	↑	↑	↓	↑	↓	↑		“O” vacancies		↑	↑
Cr	↓	↓	↑	↑	↑	↓	↑	↑	↑				↑	↑
W	↑	↑		↑	↑		↑	↑	↑	↑		↓ - primary particles	↑	↑
Mo		↑		↑	↑	↓		↑	↑	↑			↓	↑
Cu	↓	↓					↓					↑ primary particles secondary part.	↑	↑
Nb	↓				↑		↑						↑	↑
Sn			↑	↑	↑		↑	↑					↓	↑
Mg			↑	↑			↓	↓					↑	↑
Ca	↓		↑	↑	↑	↓	↓	↓			↑		↑	↑
Na	↓	↓		↑	↓		↑	↑					↓	↑
B	↓				↑			↑	↑			↓ - primary particles	↑	↑
F	↓	↑	↑	↑	↑		↑	↑					↑	↑

Fig. 4. Summary of different dopants effect on Ni rich electrode electrochemical or structural behavior.

and increase the resistance at electrode/electrolyte interface [138,139].

4. Highly conformal, pinhole free, with high electron throughput, and high coverage area coating in order to have safe positive electrode-electrolyte interface and retard TM dissolution [140]. Adverse effects of a coating include limiting the rate of lithium-ion and electron transportation which occurs particularly when the coating is too thick and dense. This blocking of the active particles surface deteriorates the initial capacity and increase the cell polarization highlighting the need for optimizing the functional properties of the coating.

According to the above requirements, a wide variety of suitable compounds and methods can be chosen as coating candidates. Nevertheless, it is essential to utilize an appropriate coating material and employ a suitable technique to generate high performance electrode materials, since different choices might change the physicochemical properties of the coating and result in different effects on the electrochemical performances of the positive electrode materials [24]. Most common methods currently used form three main categories: Deposition techniques [141], Wet chemistry routes [142], and Dry chemistry [93]. The coating parameters, such as high temperature, stirring and dissolution, and sintering, might destroy the surface of active electrode materials. Therefore, uniformity and controllability of electrode materials coatings have a significant influence on their performances [143]. For example, Han et al. performed a systematic comparison between atomic layer deposition (ALD) and wet chemistry (WC) coating protocols to demonstrate how the coating method could influence the chemistry and structure of a coated electrode, and consequentially affect the electrochemical performance. The results show that the ALD-coated samples have much higher capacities and much lower impedances than the WC-coated samples. They concluded that the ALD method provides better initial quality of the coatings than the WC method and that the ALD-coated sample do not suffer from cyclability loss due to better coating uniformity [144]. Therefore, for similar positive electrode materials coated by different methods, electrochemical properties such as specific capacity, cycle life, and high temperature performance can show

clear differences. To find the optimal coating on the surface of Ni rich electrode materials, several methods have been introduced to investigate their various effects.

4.1. Coating methods

4.1.1. Deposition techniques

ALD and chemical vapor deposition (CVD) are deposition techniques, and they have gained attention in the battery application to modify electrode surfaces. Both are thin film deposition techniques which utilizes gaseous or liquid reactants in specific atmosphere to enable surface chemical reactions between the volatile precursors and the material to be coated. These techniques can be widely used to form suitable conformal coatings on electrode materials to reduce the electrolyte-electrode side reactions, reduce self-discharge reactions, improve thermal and structural stability, increase the conductivity of electrodes, and thus further enhance the battery performance. However, it should be noted that the improvement in electrochemical performance is mainly dependent upon the correct thickness and the selection of a proper coating material (Fig. 6c). As such the improvement in electrochemical performance is dependent on the type, amount, and thickness of the coating obtained [134,141,145]. The ALD technique is similar to CVD, however, it exposes the substrate to the precursors separately and there is no interaction between the precursors in the reaction chamber before reacting with the surface of the sample. Besides, ALD controls thickness by considering the number of self-limiting reaction cycles at the substrate surface while in CVD the thickness is controlled the dose of precursors, flow rate and temperature. This surface modification technique can mainly prevent electrode-electrolyte side reactions and improve electrochemical cycling performance. However, these processes are slow and expensive as they need clean substrates [145–148].

Sputtering is a physical vapor deposition (PVD) method to grow thin films mainly on the surface of electrodes and has also gained significant attention in energy and battery applications. In this technique, a target

Coating	U ³⁺ /Ni ²⁺ cationic mixture	wt%/mol%	Bonding energy kJmol ⁻¹	Structural stability	conductivity scm ⁻¹	Li diffusivity	acidity	NiO-O release	physical parameter (morphology and thickness dependence)	initial D-capacity	Capacity retention	electrochemical stability	polarization
ZrO ₂			159	↓	10 ⁻⁶	↑	acidic		low porosity	↓		↓	↑
TiO ₂		↓	666.5	↑	10 ⁻¹²	↓	amphoteric	↓	high surface coverage	↓	↑	↑	↑
Al ₂ O ₃		↓	511	↑		↓	amphoteric		high porosity/high surface coverage	↑		↑	↓
Cr ₂ O ₃			461				amphoteric						
WO ₃	↓	↓	720	↑	↑	↑	acidic-HF			↓	↑	↑	↓
MnO ₃	↓		502	↑	↑	↑	acidic	↓	full coverage diffuse between grain boundaries	↑	↑	↑	↓
CdO	↓	↓	236	↑	↑	↑	basic	↓		↑	↑	↑	↓
MnO ₂	↓	↓	362	↑	↑	↑	amphoteric	↓		—	↑	↑	—
Ce ₂ O ₃	↓	↓	790	↑	↓	↓	amphoteric	↓		↓	↑	↑	↓
LiNbO ₃	↓		726.5	↑		↑	amphoteric	↓		↑	↑	↑	
SnO ₂	↓		528	↑	↑	↑	amphoteric			—	↑	↑	↓
MgO			363.2	↓	↓	↓	basic			—	↑	↑	↓
CaF ₂			527			↑		↓		↓	↑	↑	
AlPO ₄	↓		216.7 (Al-P)	↓	↓	↑	acidic		high thickness, dense, full coverage	↑	↑	↑	↓
LiF	↓	↓	577	↑	↓	↑	amphoteric	↓		↑	↑	↑	↓
Li ₂ O-2B ₂ O ₃	↓		340.5-809	↑	↓	↑	amphoteric			↑	↑	↑	↓
Li ₂ TiO ₃	↓	↓		↑	↓	↑	amphoteric			↑	↑	↑	↓
Li ₂ SiO ₃	—	—		↑	↓	↑	acidic-HF			↓	↑	↑	
Li ₃ PO ₄	—			↑	↓	↑	acidic	↓		↑	↑	↑	↓
N-doped LiAlO ₂	↓			↑			basic	↓				↑	
Li ₂ ZrO ₃	—	↓		↑	3.3 × 10 ⁻³	↑		↓	full coverage	↓	↑	↑	↓

Fig. 5. Summary of different coating effect on Ni rich electrode electrochemical or structural behavior.

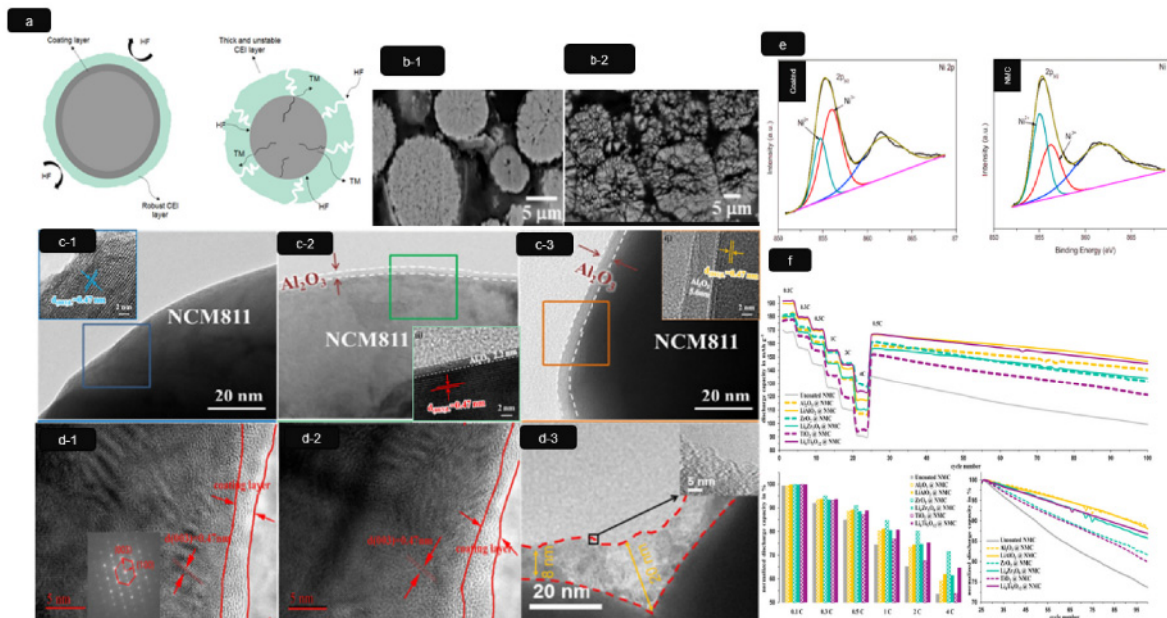


Fig. 6. (a) Schematic difference between CEI layers with and without coatings. (b) SEM images of cross sections of cycled NMCs coated and uncoated, Reprinted with permission from Ref. [173] Copyright © 2021, American Chemical Society. (c) Al_2O_3 ALD-coating with a uniform and nanoscale layer on NMC811 [133]. (d) Li_3PO_4 (LPO) and $(\text{Li}_4\text{Ti}_5\text{O}_{12})$ LTO non-uniform WC-coating on NMC with high thickness, Reprinted with permission from Ref. [189] © 2018 Elsevier Ltd and Techna Group S. r.l. All rights reserved. (e) XPS spectra of Ni 2p and reduction of $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio due to the presence of a coating on a NMC surface Reprinted with permission from Ref. [164] © 2018 Published by Elsevier Ltd. (f) Effect of physical and chemical parameters of metal oxide and Li containing metal oxide coatings on their cycling performances, Reprinted with permission from Ref. [173] Copyright © 2021, American Chemical Society.

of the desired coating material is bombarded with high-energy ions, and the atoms ejected deposit onto the electrode surface forming thin films. The ejected target atoms travel through plasma in the line-of-sight and physically deposit on the material. The reaction between the deposited target atoms and the substrate surface is physical. Sputtering can deposit all kinds of metals as well as metal oxides, metal carbides, metal nitrides, etc. This technique is simple, fast and can be utilized to modify the surface of positive electrode materials while achieving a nanometer scale protective coating is not expected [134,149].

4.1.2. Wet chemistry

Wet chemical routes, such as co-precipitation, sol gel and hydrothermal, have been widely used for positive electrode material coatings. These methods are generally believed to be low-temperature, low-cost and more easily upscaled. Therefore, it is the most commercially employed coating technique offering high purity and high adhesion coatings. Wet coating is a common thin film deposition technique in which the material is dispersed in a liquid precursor solution, followed by heat treatment, which results in a crystalline and non-uniform coating on the surface of positive electrode materials. The coating produced by such a wet chemistry method as sol gel are often affected by large shrinkage and cracking upon drying which can affect the electrochemical performance of electrode materials during the cycling. Moreover, it requires a high-temperature post-treatment to finalize the surface coating growing crystalline layers. This also may affect the phase composition and bring more defects in the structure of coated electrode materials [26,149].

4.1.3. Dry coating

Dry coating techniques, such as ball milling, are one approach to produce surface coatings on the positive electrode materials. In this method, a coating additive is mechanically mixed with positive electrode active material particles to form a thin surface layer. It is simple and low-cost compared to other coating techniques while unable to produce very conformal layer with controlled thickness. The thickness may vary in nano to submicron range. This technique requires a high-

temperature post-treatment to finalize the coating and grow crystalline compounds at the surface of the particles, which can hinder Li^+ ion diffusion at the electrode electrolyte interface. Therefore, amorphous like phase is requested for preventing a high migration barrier. Amorphous structures have higher diffusion coefficient which can provide higher Li intercalation than crystalline compounds [143,150,151]. Dry coating methods are applicable to provide coating on the surface of different positive electrode particles whereas the ratio of the positive electrode material and coating components and the size ratio of these materials are determining factors in forming an efficient coating layer. The thickness uniformity and control are major concerns in this method [93,143].

Table 2 contains a summary of different coating methods employed for modification of positive electrode materials with their advantages and disadvantages. A conclusive explanation for the differences in performance of positive electrode materials with coatings made with different approaches cannot be provided as the varying conditions under which the coating is synthesized may also affect the properties of the material subjected to the coating. However, the properties of these coating methods can be compared to find out the most suitable one. Some factors, which can be ascribed to the methods, can be summarized as follows: thickness of the coatings, defects and impurities in coatings and coverage, which all affect the electrochemical performance of final active materials (Fig. 6a and b). Compared to other coating methods, surface modification via the deposition technique improves the structural stability of electrode materials with minimal loss of available specific capacity due to significantly thinner coating. Consequently, it can provide electrochemical improvement in performance of the coated electrode materials including coulombic efficiency in the first cycle, capacity retention, rate capability, and overcharge tolerance [145]. A layer grown with high purity can effectively reduce defects and impurities of deposited coatings, which leads to lower dissolution of TMs into the electrolyte [145,152].

Han et al. studied the influence of ALD and wet chemistry (WC) coating of alumina (Al_2O_3) on an NMC532 electrode. Their results show that the ALD-coated samples demonstrate much higher capacities and

Table 2
A comparison of various coating methods with their advantages/disadvantages.

Coating method	Advantages	Disadvantages	Schemes of typical layer uniformity and smoothness
Deposition techniques: ALD, CVD, PVD, etc.	Uniform, continuous and nanoscale coating on particle surface Dense and void-free coating Coating different substrate (particles, electrode)	Expensive Complex process	
Wet chemistry: sol gel, coprecipitation	Simple and economical preparation Easy to scale up	Non-uniform and non-continuous coating on particle surface Long-term instability High thickness Complex process	
Dry chemistry: ball milling	Simple preparation Easy to scale up	Non-uniform coating on particle surface Long-term instability Formation of cracks	

much lower impedance than the wet chemistry-coated samples. However, no cyclability loss has been observed on thin ALD-made coatings which might be related to lower uniformity of the coating obtained with the WC in comparison to ALD-made coating (Fig. 6c and d) [144].

These results imply that the coatings formed by different surface modification methods may have very different morphology which can directly affect the positive electrode properties and electrochemical performances. It has been accepted that coating methods (wet chemistry, dry chemistry) leave part of the electrode surface exposed to the electrolyte (Table 2). Therefore, the uncovered areas of the electrode are susceptible to dissolution via reactions with the electrolyte and consequently lead the electrode-electrolyte interface and electrode structure degradation during cycling. Deposition methods avoid this problem, as they are known to deposit continuous films over the entire surface [144, 153]. Besides, coatings provided by different method can behave differently, which could be due to different transportation of Li^+ as well as electrons through coatings [154]. Ultrathin layers provided by the deposition techniques do not block lithium-ion diffusion into the electrode particles. However, other methods such as wet chemistry methods need multiple complex steps, and the resulting coatings lack conformity, uniformity, and full coverage on an electrode material surface (Table 2).

4.2. Surface coating materials (metal oxides)

The choice of the coating material is another effective factor in producing ideal coatings [154]. Commonly used coatings for positive electrode modifications include numerous oxides, phosphates, fluorides, lithium-containing composites and carbon materials [134,143,155]. Various metal oxide coatings such as Al_2O_3 [133], ZrO_2 [139], V_2O_5 [156], MgO [157], ZnO [158], and TiO_2 [159] have been reported to have a positive effect on cycling performance and rate capability.

Electrode surface modifications with different metal oxides (with similar thicknesses), can result in dissimilar electrochemical performances, implying that the characteristics of the coating itself has large influence on electrode properties [144,157]. Metal oxide deposition, including ZrO_2 , MgO and Al_2O_3 , on NMC622 show that the Li ion diffusivity for oxide coatings differs at different current densities [160]. Because of this, MgO coated NMC delivers higher capacity and energy at higher C-rates while Al_2O_3 coated NMC has longer lifetime at low C-rates. Among these materials, the Al_2O_3 -coated sample delivers the highest capacity retention, while it suffers from decreased initial capacity and unsolved problems of rate property and voltage decay. Performance of titanium dioxide coated NM622 at high cut off voltages show electrochemical improvement [12]. TiO_2 coating protects the electrode surface by inhibiting parasitic reactions with the electrolyte. However, due to low conductivity of TiO_2 , rate capability is not enhanced [12]. In contrast, tungsten oxide has a good conductivity, and can be used as a coating on Ni rich electrodes to overcome hydrogen fluoride (HF) attack. Moreover, WO_3 can react with lithium and help to remove some lithium residues on the surface of NMC material. Thus, different coatings can enhance the electrochemical and structural stability of NMC differently. Below, we summarize the most important coating effects (specially for metal oxides) affecting the Ni rich positive electrode materials (Fig. 5) [161].

4.2.1. Ni^{3+} to Ni^{2+} ratio

Metal oxide coatings can prevent the phase transformations by retarding the reduction of surface Ni^{3+} . The reduction from Ni^{3+} to Ni^{2+} can take place on the Ni rich surfaces spontaneously when the electrode surface is exposed to air, or during the cell charging at high cut of voltages (Fig. 6e). This results in the formation of a NiO-like layer which is electrochemically inert and hinders the Li diffusion significantly. Besides, formation of Li_2CO_3 is partially derived from the reaction between excess lithium residues with atmospheric CO_2 or H_2O . Li_2CO_3 and LiOH on the electrode surface have a low ionic conductivity and hence impede the charge-transfer reactions at the interface. As an example, CdO [162] coating can inhibit the reduction of Ni^{3+} to Ni^{2+} and reduce the Li/Ni mixing. It causes more balanced charge distribution at the electrode-electrolyte interface due to the presence of Cd^{2+} in the coating [162]. Moreover, the same effect has been detected for a NCA electrode coated by MnO_2 [163] which yields excellent electrochemical performances due to the delaying spontaneous reduction of Ni^{3+} to Ni^{2+} on the electrode surface [163]. CeO_2 [164] is also used as an electrode coating due to its highly oxidizing effect which can inhibit the mixing and phase transition of $\text{Li}^+/\text{Ni}^{2+}$. Due to CeO_2 oxidizing effect, a stronger bond between the oxygen and the TMs is formed which leads to increase in the lattice oxygen ratio on the surface and results in stronger $\text{M}-\text{O}$, $\text{Co}-\text{O}$, and $\text{Ni}-\text{O}$ bonds. Besides, the formation of LiOH and Li_2CO_3 on the surface of an electrode can be effectively inhibited by reduced oxygen absorption which can help to stabilize the Ni rich cathode material [164]. WO_3 coating [165] confirms the positive effect on retarding the aggravate side reactions between an electrolyte and positive electrode material. When comparing the XPS results of the coated NMC with the uncoated one, the surface oxygen peaks of the sample modified by tungsten oxide are slightly weakened, indicating that there is more reactive oxygen on the surface of the uncoated NMC sample [165]. As such tungsten oxide modification can reduce the polarization of a NMC material to a certain extent and improve the electrochemical properties.

4.2.2. Crystallinity and amorphous nature of the coating

Crystalline or amorphous nature of a coating can affect its properties. Transformation of the crystalline coating into an amorphous surface layer has been studied for LiNbO_3 coatings on NMC [166]. The results show that the ionic conductivity is higher in the amorphous than crystalline layer [166]. The higher conductivity of the amorphous layer is accompanied with the lowered activation energy for the Li ion conduction in the mixture, facilitating Li ion conduction [167]. This could

be due to the behavior of the ion conduction in solid as it takes place by jumping of the ions to the adjacent vacancies or interstitial sites. Thus, the structural evolution at the interface strongly influences the activation energy required for Li migration. An amorphous layer at the electrode-electrolyte interface can contribute to formation of defects and increasing the number of mobile Li ions as well as promote the migration of Li ions [168].

4.2.3. Acidity of a coating

Acidity of a coating can be another factor affecting its efficiency as coatings can provide stronger corrosion resistance against the parasitic reactions at an electrode-electrolyte interface. WO_3 is an acidic oxide and hence it can well resist hydrogen fluoride (HF). It also can react with lithium and consume the alkali residues on the surface of a NMC material [165] so that its rate performance and cycle stability can be significantly improved. CrO_3 [169], ZrO_2 [170] and MoO_3 [171] are other acidic oxides which have been used as coatings for Ni rich positive electrode materials.

4.2.4. Coating thickness

Generally, metal oxides are known as electrochemically inert materials. Thus, electrodes coated with metal oxides can hinder the conductivity of Li ions at the electrode-electrolyte interface. TiO_2 has a poor electronic conductivity in the range of 10^{-12} to $10^{-7} \text{ S cm}^{-1}$ and slow Li^+ diffusion rate, restricting the rate capability and storage capacity of TiO_2 . Designing different nanostructured TiO_2 – with different technique such as ALD, sputtering or liquid-phase deposition – can be used to form more open channels and active sites for Li-ion transport, as well as increasing the intrinsic electrical conductivity of the coating [168]. To maximize the electrochemical performance of Ni-rich materials coated by a non-conductive oxide material, control of the coating thickness is necessary.

NMC622 electrode has been coated by Al_2O_3 with thicknesses varying from 1 to 4 nm. The results show that Al_2O_3 coatings on a NMC622 composite electrode increase the capacity retention while a thicker coating has a negative effect on the initial discharge capacity and rate capability. Therefore, in terms of optimum capacity and kinetics, the coating should be as thin as possible but yet uniform [172]. Moreover, conformity and uniformity of the thin film Al_2O_3 coating has been studied on the surface of NMC811 particles [133]. Uniform coating and nanoscale thickness significantly affect charge transfer and ion diffusion through the electrode-electrolyte interface, and consequently suppress phase transitions and electrochemical polarity of the Ni-rich core during reversible lithiation/delithiation [133,154].

4.2.5. Physical parameters

Apart from the chemical composition, physical properties of a coating, such as porosity, have a significant effect on the NMC rate capability. Herzog et al. [170] have used a dry coating method to cover $\text{N}_{0.7}\text{M}_{0.15}\text{Co}_{0.15}$ by different oxides. They conclude that although ZrO_2 has better Li diffusivity in comparison to Al_2O_3 , its lower porosity or surface coverage caused by the preparation method decreased its rate performances. They showed that the BET surface area of the Al_2O_3 -coated NMC is significantly higher than that of the ZrO_2 -coated sample and consequently a higher porosity is achieved with the Al_2O_3 coating. These results indicate a strong influence of the coating physical properties, on the Li diffusivity behavior as the liquid electrolyte easily penetrates a porous coating enhancing the apparent lithium diffusion coefficients [170].

A comparison of metal oxide and Li containing metal oxide coated NMC811 [173] has confirmed that a high coating porosity favors increased rate capability, while a high coverage of the surface enhances long-term cycling stability and decrease the crack generation in NMC particles. The comparison of coated NMCs shows the following trend for coatings to increase in rate performance: $\text{TiO}_2 < \text{Al}_2\text{O}_3 < \text{Li}_4\text{Zr}_3\text{O}_8 < \text{LiAlO}_2 < \text{Li}_4\text{Ti}_5\text{O}_{12} < \text{ZrO}_2$ (Fig. 6f). Zr-containing coatings possess the

best lithium diffusion for high-rate performances, however, the rate capability of the $\text{Li}_4\text{Zr}_3\text{O}_8$ -coated NMC is limited due to the reduced porosity of the coating, which results in lower surface area. In that study, aluminum-containing coatings indicate superior surface coverage in comparison to other coatings and superior chemical nature to protect high-nickel NMCs. Thus, the best long-term cycling stability with the highest absolute capacity has been obtained for the NMC coated with LiAlO_2 [173].

4.3. Surface coating materials (other coatings)

Alongside metal oxides, metal fluorides, metal phosphates, metal oxyfluorides, metal hydroxides and organic compound have been studied as coatings [99,137]. Phosphates are thermodynamically stable at the operation window of Ni rich cathode materials [174]. The chemical bonds between PO_4^{3-} group and metal ions have strong covalence property hindering reactions between the electrode and the electrolyte. Hence, this stable coating can improve the positive electrode material stability. For example, a MnPO_4 coating on NMC622 enhances the rate capability, cycling performance and thermal stability [175]. After 100 charge-discharge cycles the coated material has exhibited excellent cycling stability with 97.7% capacity retention at 10 C which is notably higher than that for the uncoated NMC622. Moreover, phosphate coatings on the surface of a positive electrode material can influence the formation and thickness of the electrode-electrolyte interface film due to their strong chemical bonds [175].

An ALD technique has been used to coat aluminum phosphate (AlPO_4) on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode material [176]. The surface of the electrode is coated using 10 ALD cycles to provide an ultrathin coating. The nano-scale layer with improved thermal stability effectively impedes the side reactions occurrence at high voltages, resulting in significantly improved safety and electrochemical performances. The capacity retention of the bare and coated sample after 100 cycles are 69% and 94%, respectively. Furthermore, AlPO_4 is also found to be more effective in improving the thermal stability of the cathode.

Fluoride compounds are also widely used coatings for modifying the surface of Ni rich cathode materials. Fluoride compounds have superior chemical stability at the interface when compared with other chemical compositions as they are hardly attacked by trace amounts of H_2O and HF in the electrolyte [137,177,178]. It is found that the addition of fluoride compounds can reduce the charge transfer resistance, improve the conductivity, and thus improve the rate performance and cyclability of Ni rich cathode materials [137,178]. The improved electrochemical performance has been achieved by an AlF_3 coating, through which the extracted oxygen has reduced activity and hence suppress the electrolyte decomposition at voltages above 4.5 V. Based on the results, the irreversible capacity produced by Li loss during the initial cycling, has been reduced due to the AlF_3 coating. This coating induces phase transformation at the beginning and reduces the initial irreversible capacity. The results confirm that the improvement of the first cycle efficiency is consistent with the extent of the structural transformation observed in TEM, and electrochemical data [179]. CoF_2 nano-coating has been found to enhance electrochemical performances as well as providing high protection for an active electrode material. The result show also enhancement of electrochemical reaction kinetics with higher electron transfer and Li^+ diffusion. Furthermore, the layered-spinel phase transition is inhibited by decreasing the migration of TM ions into Li layers [180]. Another fluorine compound, calcium fluoride (CaF_2), possess better thermodynamically stability due to its higher bond energy ΔH_f ($\text{Ca-F} = 527 \text{ kJ mol}^{-1}$ compared to other coating materials (ΔH_f ($\text{Zr-O} = 159 \text{ kJ mol}^{-1}$, ΔH_f ($\text{Mg-O} = 363.2 \text{ kJ mol}^{-1}$, ΔH_f ($\text{Mg-F} = 461.9 \text{ kJ mol}^{-1}$, ΔH_f ($\text{Si-O} = 460 \text{ kJ mol}^{-1}$ and ΔH_f ($\text{Al-O} = 511 \text{ kJ mol}^{-1}$). This is the main reason for the improved stability of the positive electrode material during Li^+ intercalation/deintercalation [181]. Furthermore, the octahedral structure of CaF_2 provides octahedral gap and empty

spaces, which offers more diffusion paths for Li-ions and thus improves the rate performance [132].

Composite materials also used to coat NMC show synergistic effects. LBO ($\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$) coating has shown a good ionic conductivity, which makes the coated NMC materials more conducive to lithium ions, thus leading to better electrochemical properties. Besides, it has a good wetting properties which facilitates the even coverage of the coating on the electrode surface [142]. A $\text{C}-\text{Al}_2\text{O}_3$ composite coating has been implemented by Kong et al. [133] on NMC622. The insulating behavior of Al_2O_3 is alleviated by the conducting network of sp^2 -graphitic carbon in the $\text{C}-\text{Al}_2\text{O}_3$ composite and the final electrical conductivity is enhanced. Moreover, the synergistic effect of Al_2O_3 and carbon results in improved electrochemical kinetics for Li-ion transport. As such, the conformal, uniform, and continuous Al_2O_3 layer protects the electrode from corrosion, whereas carbon can improve the electrical conductivity of the composite electrode [133]. Al_2O_3 and AlPO_4 single-coated and double-coated NMC532 materials have been synthesized by a wet-coating method [134]. When comparing with corresponding single-coated or uncoated samples, the double-coated one exhibits superior thermal stability as well as electrochemical properties. The possible reason is the dense and uniform coating as well as the formation of Li_3PO_4 and LiAlO_2 on the positive electrode material surface. Besides, the dense and uniform coatings on the double coated sample can prevent the attack of O_2 and H_2O in air as well as HF in an electrolyte, resulting in more stable electrochemical properties. Previous studies have shown that an Al_2O_3 coating for a Ni rich material can mitigate side reactions between the active material and electrolyte [134], while an AlPO_4 coating is beneficial for forming a more stable CEI film on the surface of the electrode. An amorphous state of both coatings on an electrode surface can provide Li^+ transportation path from the bulk material to the electrolyte, making the composite exhibit superior cycling performance and rate properties.

Lithium-containing coating have also received much attention for surface modification. As an example, LiF-modified NMC811 shows significantly enhanced performance in rate capability and cycling retention in comparison to bare NMC811. The rate capability analysis also confirms the positive effect of LiF coating as it enhances the capacity retention at higher current density and decreased charge transfer resistance during cycling [135]. Although the LiF coating helps to inhibit the parasitic side reactions between the electrolyte and active material, it is not conducive. Hence, it does not improve the electrochemical performance of NMC811 and has an adverse effect on lithium-ion transport.

As such the Li containing coatings with higher porosity (more available Li pathways) could be more effective even at higher thicknesses. At present, these type of materials are mainly lithium-containing composite oxides, including LiAlO_2 [136], Li_2SiO_3 [136], Li_2TiO_3 [137], and Li_2ZrO_3 [138]. A $\text{Li}_x\text{Nb}_y\text{O}_z$ coating has been deposited on the surface of NMC811 through a wet chemistry method [137]. This coating provides a protective surface coating on NMC811 and helps to enhance the electrochemical behavior of the positive electrode. The coating shows stable thermodynamical behavior in the entire electrochemical window for NMC811 cycling. The $\text{Li}_x\text{Nb}_y\text{O}_z$ coated and uncoated electrode deliver average capacity of 135 and 158 mAh g^{-1} (at 2C), respectively, at the first stage of cycling while the coated sample possess higher capacity retention (89.6% after 60 cycles) in comparison to the uncoated NMC811 (81.60% after 60 cycles) [137]. Moreover, Li_2SiO_3 coated NMC811 materials, obtained by wet chemistry methods, show lower initial specific discharge capacities than an uncoated sample. This is attributed to the properties of the coating that produces a negative influence on the capacity of the electrode materials. However, with an increasing cycle number the importance of the coating becomes more evident and after 50 cycles the capacity retention of the pristine and Li_2SiO_3 -coated electrodes are 57.6 and 77.7% indicating superior cycling stability at high voltages after Li containing-surface modification [136].

5. Synergistic effect of coating and doping

Ni rich electrode materials modification is a key to improve the electrochemical performance of future LIBs. Decreasing oxygen loss, alleviating electrode-electrolyte interfacial reactions, maintaining internal structure, and decreasing crack or defects formation are essential for improving cycling performance and safety behavior for LIBs. As discussed in previous sections, lattice doping, and surface coating are very effective strategies to enhance nickel-rich NMCs properties. The latter is an efficient technique to increase cycle life and safety performance for the batteries and it can suppress surface deterioration caused by side reactions at an electrode-electrolyte interface, resulting in reducing the gas release. During long-term cycling, coating can stabilize the phase structure and enhance the thermal security.

Doping of NMC (Fig. 7c) can diminished $\text{Li}^+/\text{Ni}^{2+}$ cation mixing and oxygen loss [190]. Furthermore, dopants easily occupy either the Li^+ or TM sites and enhance the internal structural stability by hindering the formation of microcracks and transformation of Ni^{2+} ions to the Li layer (Fig. 7a and b). However, doping cannot remarkably restrain the gas release and oxygen loss neither improve the cycle life by diminishing the surface parasitic reaction between an electrode and electrolyte. Moreover, the amount of dopant should be optimized since unoptimized amount may induce capacity decay and cycling deterioration. Hence, as doping and coating have different benefits, their combination always generated multifunctional effects to greatly improve the electrochemical performance of LIBs (Fig. 7 a, b, d, and e).

For instance, the coating with nano-scale thickness as well as bulk doping in nickel-rich materials often exhibit superior electrochemical performance. For example, WO_3 modified NMC811 [161] shows significantly enhanced behavior as the content of Ni^{2+} and Ni^{3+} in the samples are different and in particularly the number of Ni^{3+} on the coated NMC811 is smaller than for uncoated NMC811. It indicates that the WO_3 modification changes the valence states distribution of nickel at the NMC surface. This research concludes that the coating promotes the NMC crystal structure to maintain the electroneutrality because of W penetration into its crystals structure. This generates larger layer space and results in the smooth insertion/extraction of Li^+ from the NMC materials. As such, WO_3 coating and W doping can reduce the degree of polarization during the NMC electrochemical reactions and enhance the structural stability of a Ni rich electrode material [161].

Likewise to W, bulk penetration of Ce^{4+} in $\text{Ce}_{0.8}\text{Dy}_{0.2}\text{O}_{1.9}$ coated NMC811 structure has been confirmed as this causes enlarged lattice parameters and leads to suppressed cation mixing and increased coulombic efficiency (Fig. 7e). Besides, the oxygen vacancies in the $\text{Ce}_{0.8}\text{Dy}_{0.2}\text{O}_{1.9}$ coating help to decrease oxygen loss from the NMC structure during charging. Thus, the synergistic effect of coating and doping enhances the structural stability of NMC [191].

A Li-Nb-O coating has been deposited on the surface of NMC811 through a wet chemistry method [137]. The coating shows thermodynamically stable behavior in the entire electrochemical window of NMC811 cycling while Nb^{5+} incorporation into the bulk structure also enhances the positive electrode capacity. The Li-Nb-O coated and uncoated electrode deliver average capacity of 135 and 158 mAhg^{-1} (at 2C), respectively, at the first stage of the cycling while the coated-doped sample possess higher capacity retention (89.6% after 60 cycles) in comparison to uncoated NMC811 (81.6% after 60 cycles).

Zr^{4+} doping and coating of NMC622 has been carried out by an ALD method [192]. The incorporation of the dopant in the NMC structure, substitute Li or Ni-sites, which is favorable for inhibiting the cation mixing of Li^+ and Ni^{2+} . Besides, it provides strong Zr-O bonding and decreased lattice oxygen release especially at high voltage which result in preserving the NMC layered structure. Moreover, ZrO_2 coating is chemically inert which prevent electrolyte decomposition. As the results shows (Fig. 7a), higher annealing temperature results in some Li_2ZrO_3 particles formation on the surface of NMC particles. However, it provides non-uniform coating which cannot protect the entire cathode

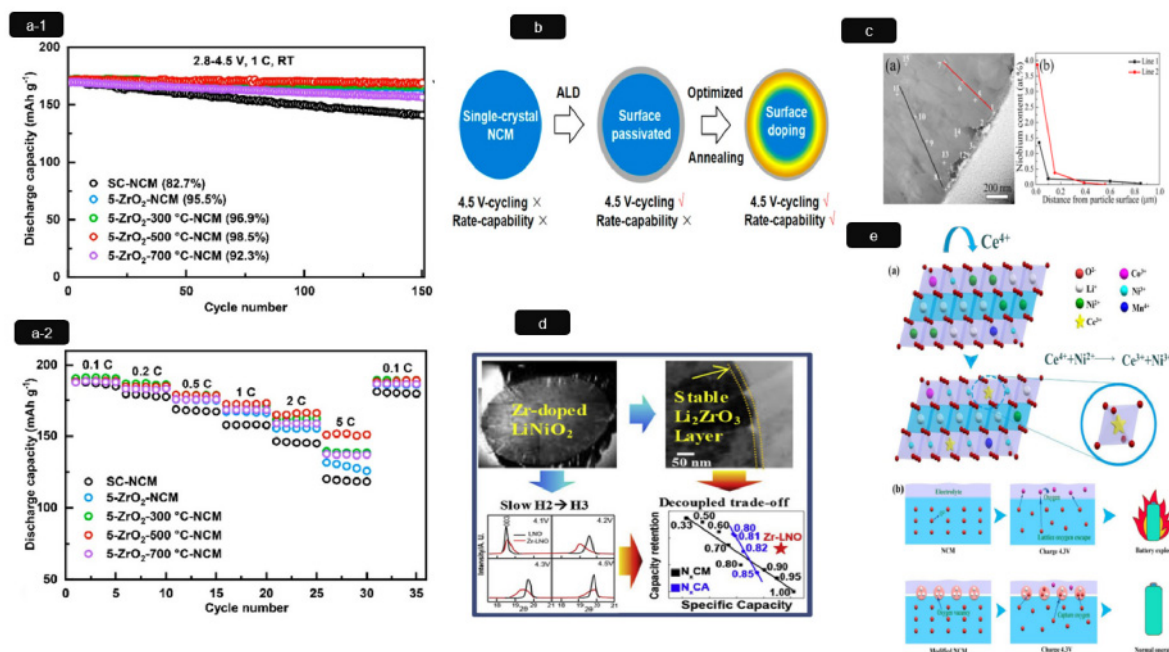


Fig. 7. (a-1,2) Cycle performance and rate performance of NMC, NMC-doped, NMC-coated and NMC-doped and coated annealed at different temperatures (between 2.8 and 4.5 V), Reprinted with permission from Ref. [192] Copyright © 2020, American Chemical Society. (b) Schematic illustration of the synergistic effect of coating and doping at high cut-off voltage, Reprinted with permission from Ref. [192] Copyright © 2020, American Chemical Society. (c) Depth of doping elements diffusion and EDS results for 1% Li-Nb-O-modified NMC 811 sample, Reprinted with permission from Ref. [190] Copyright © 2019, American Chemical Society. (d) A thin protective layer of ZrO₂ or Li₂ZrO₃ with synergistic effect of doping on the surface of LNO, Reprinted with permission from Ref. [193] Copyright © 2018, American Chemical Society. (e) Schematic diagram of cation disorder and doping in NMC and schematic illustration of the oxygen vacancies in a modified sample, Reprinted with permission from Ref. [191] Copyright © 2019, American Chemical Society.

materials from electrolyte attack. Thus, the synergetic effect of doping and coating at lower annealing temperature can provide is clearer and provide better stability during the cycling.

The coating and doping of Zr element in LiNiO₂ exhibit enhanced electrochemical behavior (Fig. 7d) [193]. A thin protective layer of ZrO₂ or Li₂ZrO₃ with a thickness of 5–10 nm covers the LNO surface protecting against electrolyte attract. Besides, Zr substituted to Li or Ni sites increments Li⁺ diffusion rate while maintaining the surface structure and decreasing the charge transfer resistance.

Li₃PO₄ forms an efficient coating on NMC due to the strong bonding energy of polyanion [194] while coating material penetration into NMC particle grain boundaries occurs during post annealing steps. As Li₃PO₄ is a conductive material, its penetration into the NMC structure can provide a fast channel for Li diffusion while protecting the secondary particles from side reaction with an electrolyte. Consequently, Li₃PO₄ coated NMC displays a good long-term cycling stability and diminished voltage fade during cycling.

Combination of a nano-thickness coating and doping facilitates multifunctional improvements. Fig. 8 summarized the representative doping elements and coating materials for NMC electrode materials. NMC degradation is induced by the surface reactions between the active material and electrolyte as well as the cationic Li/Ni mixing. Thus, the combination of a thin protective layer and doping by partial substitution for the lithium sites or Ni sites can stabilize the surface and interior structure.

6. Conclusion and perspectives

In this review, we summarize common synthesis and modification methods used for Ni rich positive electrode materials. Different synthesis methods have their own pros and cons. Among all the approaches, the coprecipitation method with the relative homogeneous element mixing, together with relatively simple, low-cost synthesis conditions and short duration has been considered as the most effective method to prepare

NMC precursors. Modification methods such as doping, and coating improve NMC electrode materials structure and electrochemical properties. Doping can change NMC structure by adding atoms into NMC structure. These dopants strengthen the structure due to stronger interatomic interactions, prevent the migration of atoms, increase diffusion and mechano-chemical strength of the particles, change the morphology, and inhibit oxygen evolution reactions. Coating of the electrode can enhance ionic/electronic conductivity and stability of positive electrode materials. Each coating method or material shows its own advantages, disadvantages, and different coating protocols can greatly affect the chemical or physical composition and structures of a coating on electrode materials.

Undoubtedly, the work is still in progress, and more needs to be done to fulfil the expected performance requirement for advanced, next-generation lithium-ion batteries. Research on doping and coating of nickel-rich materials for lithium-ion batteries have been performed for many years but lacks deeper comprehension and more extensive theoretical insight. Therefore, more intrinsic mechanisms need to be systematically investigated and analyzed to disclose the relationship between electrochemical behavior and doping/coating modification. These are related to batteries capacity and cycling behavior, safety, shelf-life and so on. Especially, developing high-performance batteries with lifespan above ten years for EVs and stationary energy storage are urgently needed in future. As such, some of the most important issues which are missing in the literature are listed in this review and they can be considered for the next research in this filed:

- Computational analysis reported in the literature explain accurately the effects while, unfortunately, these analyses are not always practically confirmed. Even though computational studies can bring further insight, complexity of the studied systems should be beard in mind and limitations of the used methods considered more. However, there is clear difference between ideal computational structure and actual materials containing defects, crystal disordering, local

Sample	Initial capacity	Structural stability	Coulombic efficiency
Zr	↑	↑	↑
ZrO ₂ -LiZrO ₂	↓	↑	↓
Ti	↑	↑	↑
TiO ₂ -Li ₂ TiO ₃	↓	↑	↑
Al	↑	↑	↑
Al ₂ O ₃ -LiAlO	↓	↑	↑
W	↑	↑	↑
WO ₃	↑	↑	↑
Ce	↑	↑	↑
CeO ₂	↓	↑	↓
B	↑	↑	↑
Li ₂ O-2B ₂ O ₃	↑	↑	↑
Nb	↓	↑	↑
LiNbO ₃	↑	↑	↑
Mo	↓	↑	↑
MoO ₃	↑	↑	↑

Fig. 8. Co-effects of doping and coating on nickel-rich positive electrode materials.

inhomogeneity, etc which affect the material properties. In cases calculations can show doubtful structures, for example, large size ions (for example, Rb⁺) in the Li sites but in practice those can experience steric hindrance and rather occupy TM sites or form defects in the structure. Another example is Ni²⁺/Li⁺ cation mixing calculations using Rietveld refinement or similar approaches when many other effects (vacancies, orientation of crystals, contamination) lead to notable error in analysis and yet those cannot be included into computational experiment. Naturally, validating computational results with experimental analysis is essential for future research.

- Reproducibility of experiments is another issue. Only few studies have demonstrated statistically validated results for the electrochemical measurement while for synthesis such validation is lacking. Yet, several parameters, including particle size and concentration gradient of elements in a particle, can also play an important role in electrochemical performance of the NMC positive electrode materials. As such, having enough knowledge about the synthesis condition effects on Ni rich materials is essential for improving the electrochemical performance and reproducibility of the results.

- One important issue is comparison of modified and unmodified NMC samples which have been synthesized under conditions optimized for only one particular sample. Based on our recent results, optimal synthesis conditions for undoped and doped Ni-rich NMC materials are different and hence comparison of materials synthesized under similar conditions does not reveal the full potential of each material composition. Even small changes in synthesis conditions affect differently in the structure and properties of unmodified and modified NMC positive electrode materials. Yet, the optimization conditions in laboratories are done usually once and the same conditions are used for synthesizing all the electrode materials. As such, all the samples whether they are coated, doped or unmodified are suggested to be optimized individually.
- Beside understanding the effect of synthesis conditions, the future works should also focus on identifying effective coating/doping methods, conditions, and material(s). Studies carried out under comparable conditions to conclude effect of different coating/doping methods and materials are still largely missing. Generally, different doping elements or coating materials affect differently on NMC electrodes. Each coating material or dopant has unique interactions with Ni rich chemistries resulting in differing power and aging

performances and having enough knowledge about their mechanism for most common ones is essential.

- The future coating/doping synthesis method should provide a controllable uniform or gradient coating/doping modification with the merits of low cost and ease for scaling-up. Besides, the effect of doping and coating modification on aging the cells is suggested to be clearly discussed in the future research. Even if there are many research on doping or coating modifications on Ni-rich NMC materials, there is still no clear conclusions on best performing dopants or coatings. Different coating or doping techniques have been used for Ni rich samples in a laboratory scale. Considering the large-scale application of lithium-ion batteries, long-term cycling performance studies paired with in-situ or in-operando analysis in full cells with Ni rich electrodes coated/doped with different techniques/material are needed to enable comparison of various methods/materials and understand their functioning.
- One common issue in most of the recent research is the absence of detailed description of the experimental protocols which is essential for the understanding of electrochemical tests. Having standardized protocols decrease difficulties in comparison of the results.
- Finally, a large number of studies on the NMC materials have mainly focused on the cycling stability improvement. However, one more important property is the safety of the NMC materials and effects of doping and coating on thermal stability and safety. In this regard, investigations on batteries subjected to unexpected condition such as overcharge, over-discharge, high and/or low operation temperatures is highly recommended.

CRediT authorship contribution statement

Zahra Ahaliabadeh: Conceptualization, Methodology, Resources, Writing – original draft. **Kong Xiangze:** Methodology, Writing – original draft. **Fedorovskaya Ekaterina:** Methodology, Resources, Writing – original draft. **Tanja Kallio:** Supervision, Resources, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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