REVIEW ARTICLE

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Challenges and opportunities using Ni-rich layered oxide cathodes in Li-ion rechargeable batteries: the case of nickel cobalt manganese oxides

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This review provides an overview of recent advances in the utilization of Ni-rich nickel–cobalt–manganese (NCM) oxides as cathode materials for Li-ion rechargeable batteries (LIBs). In the past decade, Ni-rich NCM cathodes have been extensively investigated because of their rational capacity and easy accessibility of constituent elements. However, huge capacity fading and irreversible structural disorder, associated with oxygen release, are the major limitations which hinder the desired electrochemical performance of these cathodes. The LIB performance can be improved through several strategies such as doping, coating, composite formation, microstructure manipulation and replacing the Mn ions. Attempts are also made to amend the crystal orientation and achieve additive-induced surface engineering of NCM cathodes. However, the practical application of high-performance LIBs demand an effective modification of the intrinsic properties of NCMs. Substandard thermal stability is another safety aspect to be resolved in the Ni-rich NCMs. However, efforts in this context are not enough. Apart from designing NCM cathodes, there are major issues such as cost-effectiveness, supply and demand for constituent elements, and the reuse of spent batteries, which hinder the realisation of LIBs with high electrochemical performance. Keeping in mind the current research interests, this review article presents concise and in-depth strategies to design NCM cathodes for future energy demands of mankind by considering the cost and Co abundance-related issues.

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Introduction

Rechargeable batteries have emerged as an alternative to fulfill the future energy demands of society.[1–3] In the past 15 years, the use of rechargeable batteries for mobile and other portable electronic devices has been well established.[4,5] Their role in the utilization of electrical vehicles (EVs)[6–9] together with other high-energy applications such as grid-scale storage systems[10,11] needs to be proven. Despite their higher cost and unsafe nature compared to internal combustion engines (ICEs),[11] rechargeable batteries are getting optimized in terms of energy capacity, safety and cost-effectiveness before their practical applications.[12,13] Hence, extensive research efforts have been made to develop rechargeable batteries with higher energy density, reversibility[14,15] and cycling efficiency[16,17] to compete with the existing ICEs.

Numerous rechargeable batteries are designed for fulfilling the required parameters of high electrochemical performance.[18] Some of these batteries, which have drawn significant attention, are Pb-acid,[19] aqueous rechargeable,[20] Mg-ion,[21] Ca-ion,[22] K-ion[23] and Al-ion batteries.[24] Various parameters such as specific energy, energy density, charging/discharging efficiency and life of several batteries are collated in Table 1.[25–28] The comparative analysis presented in Table 2 conveys the superiority of Li-ion batteries (LIBs) over other rechargeable batteries. Thus, LIBs show potential to compete with ICEs in terms of performance.[29,30] Work done to date has

depicted an advancement in battery parameters for better functionality by engineering cathode[31–35] and anode[36–39] properties. Thus, LIBs are classified into different categories with regard to the nature of their components such as cathodes, anodes and electrolytes.[40,41] Table 3 summarizes the various types of LIBs based on these components.[42–59] Among these, LIBs based on NCM, commonly termed as NCM batteries, have received considerable attention in recent years because of their high lithium diffusion coefficient.[60,61] Thus, NCM batteries, especially those with excess Ni contents (Ni-rich),[62–64] received great attention for scientific research to make their commercialization successful. This is reflected in the recent reviews on various aspects of NCM cathodes such as commercialization,[65] electrochemical performance,[66–68] cost-effectiveness,[69] and recovery[70] independently. Though these reviews provide authenticated and independent analyses of these aspects, there

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Table 1 Characteristic parameters of various rechargeable batteries. Values of different parameters are adopted from the description available at https://circuitdigest.com/article/different-types-of-batteries

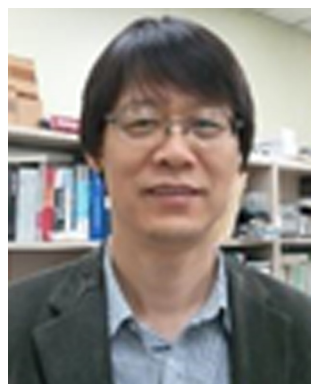| Battery	Characteristic parameters					
	Specific energy (W h kg^{-1})	Energy density (W h L^{-1})	Specific power (W kg^{-1})	Charge/discharge efficiency (%)	Self-discharge rate (% month)	Life (cycles)
Ni–Cd[25]	40–60	50–150	150	70–90	10	2000
Ni–MH[26]	60–120	140–300	250–1000	66–92	1.3–2.9	180–2000
Li-ion[27]	265	693	340	80–90	—	1200
Zn-ion[28]	250	450	—	80	—	1000

is lack of a comprehensive review combining all aspects at one place. Thus, this review is an attempt to fill this gap, by combining most of the challenges associated with NCM cathodes in a concrete and concise manner by providing an understanding of the layered structure and Li-migration in NCM materials.

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Layered oxide cathodes

The advanced pedagogical developments of layered oxide cathode materials have opened up new avenues to offer high cumulative capacity of batteries designed for high-energy applications. These layered oxides are successfully used in various batteries such as LIBs,[71,72] Na-ion batteries,[73–76] K-ion batteries[77,78] and Ca-ion batteries.[79,80] Thus, numerous layered oxide cathodes are investigated for LIBs to optimize their performance.[81–86] The chemical formula of layered oxides is LiMO$_2$, where M is a transition metal (TM). Most common metals are iron, manganese, cobalt, nickel, titanium and vanadium. Layered LiMnO$_2$ and Li$_2$MnO$_3$, as LIB cathodes, are known for significant values of theoretical capacities.[86,87] Other oxides with similar values of cumulative capacity are LiCoO$_2$, LiNiO$_2$ and LiVO$_2$.[88] Among these oxides, layered LiNiO$_2$ has a theoretical capacity of 275 mA h g^{-1} [89,90] but it is not preferred because of low electrochemical stability. Another major issue related to this cathode is the presence of local John Teller distrotions[91,92] and is responsible for phase transition.[93]

These drawbacks are proposed to be minimized by doping the cathodes[94,95] with similar elements and developing other layered oxides such as LiNi$_{1-x}$M$_x$O$_2$ (M–Co, Fe, Mn, Ti, Mg and Al), LiNi$_{1-x-y}$Mg$_x$M$_y'$O$_2$ (M$'$ = Ti and Al) and LiNi$_{1-x-y}$Co$_x$Al$_y$O$_2$ (NCA).[96] The growth of layered oxides such as NCA and NCM is the result of such efforts. Table 4 depicts the characteristics of selected layered oxides along with their cumulative capacities.[97–112] Thus, it is clear from Table 4 that layered

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Sangsul Lee

Table 2 General components of electric batteries. Permission obtained from C Iclodean et al., IOP Conf. Ser.: Mater. Sci. Eng. **252** (2017) 012058

Name	Value for battery type				Unit
	Li-ion	Na–NiCl$_2$	Ni–MH	Li–S	
Maximum charge	75	84	85	80	A h
Nominal voltage	323	289	288	305	V
Stored energy	24.2	24.2	24.2	24.2	kW h
Maximum/minimum voltage	339/308	275/304	274/302	290/320	V
Initial charge	100	100	100	100	%
Number of cells per cell-row	12	12	20	26	—
Number of cell-row	17	30	20	1	—
Internal resistance charge/discharge	1/1	1/1	1/1	1/1	Ω
Operating temperature	33	270	36	30	°C
Specific heat transition	0.4	6	0.4	0.08	W K^{-1}
Specific heat capacity	795	950	677	1650	J kg^{-1} K^{-1}
Mass of battery	318	457	534	173	kg
Battery price	300	500	400	250	£

Table 3 Various types of Li rechargeable batteries and their abbreviations based on cathodes, anodes and the nature of electrolytes

Type	Abbreviation	Basis
Lithium ion cobalt oxide battery[42]	LCO	LiCoO$_2$
Lithium ion manganese oxide battery[43,44]	LMO	LiMnO$_2$
Lithium ion nickel oxide battery[45]	LNO	LiNiO$_2$
Lithium iron phosphate battery[46,47]	LFP	LiFePO$_4$
Lithium nickel manganese battery[48]	LNMO	LiNi$_{0.5}$Mn$_{1.5}$O$_4$
Lithium nickel cobalt aluminium oxide[49]	NCA	LiNiCoAlO$_2$
Lithium nickel cobalt manganese oxide[50]	NCM	LiNiCoMnO$_2$
Lithium–titanate battery[51]	LTO	Li$_4$Ti$_5$O$_{12}$
Lithium–sulphur battery[52]	Li–S	Li as anode and Li$_2$S as cathode
Lithium–air battery[53]	Li–air	
Lithium-ion polymer battery[54,55]	LIP	Polymer as electrolyte
Thin film lithium-ion battery/microbattery[56–58]		Based on the nature of electrolyte and thickness of electrodes
Lithium ceramic battery/solid state battery[59]		Based on nature of electrolyte

structures, in which, M has a combination of two or more TMs, exhibit improved electrochemical performance, thereby deeming the NCM cathodes to be effective for a typical LIB.

Nickel cobalt manganese oxide (NCM)

The widespread use of NCM cathode materials in the current scenario is evident from Table 4 as well as the work reported by research groups working in this direction.[113–116] The electrochemical performance of the NCM cathode can be optimized by altering the chemical compositions[117] as observed from compositions such as LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM333),[118] Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$,[119] LiNi$_{0.4}$Co$_{0.4}$Mn$_{0.2}$O$_2$ (NCM442),[120] LiNi$_{0.5}$Co$_{0.3}$Mn$_{0.2}$O$_2$ (NCM532),[121] LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$ (NCM622),[122,123] and LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811).[124,125] As a result, several investigations are

Table 4 Characteristics of selected layered oxide cathode materials

| Cathode material	Cumulative capacity (mA h g^{-1})	Capacity retention (%)/cycle/charging rate	Discharge voltage (V)
LiNiO$_2$[97]	183.4	91.9/20 cycle	3.8
LiNi$_{0.92}$Co$_{0.08}$O$_2$[98]	212.8	75.4/100 cycle/0.1C	2.75–4.3
LiNi$_{1-x}$Fe$_x$O$_2$[99]			
LiNi$_{0.5}$Mn$_{0.5}$O$_2$[100]	186.3	87.5 (100 cycle/20 mA g^{-1})	2.5–4.7
LiNi$_{0.975}$Ti$_{0.025}$O$_2$[101]	171	95.9/30 cycle/0.2C	4.3
LiNi$_{1-x}$Mg$_x$O$_2$[102]	—	—	—
LiNi$_{0.995}$Al$_{0.005}$O$_2$[103]	164	0.65 mA h per g per cycle	
LiNi$_{0.8}$Co$_{1.9}$Ti$_{0.05}$Mg$_{0.05}$O$_2$[104]	120	93/40 cycle/0.4C	2.5–4.4
LiNi$_{0.90}$Al$_{0.05}$Mg$_{0.05}$O$_2$[105]	180	—	—
LiNi$_{0.9}$Co$_{0.06}$Ti$_{0.04}$O$_2$[106]	214	98.7/50 cycle/0.1C	4.3
LiNi$_{0.84}$Co$_{0.14}$Al$_{0.02}$O$_2$[107]	190	96.8/30 cycle/0.1C	4.3
LiNi$_{0.7}$Co$_{0.2}$Mn$_{0.1}$O$_2$[108]	148	95.2/14 cycle/0.2C	
LiMnO$_2$[109]	270		
Li$_2$MnO$_3$[110]	400		
Li$_2$Mn$_{0.9}$Al$_{0.1}$O$_3$[111]	99.4	97.1/40 cycles/0.1C	2.0–4.8
LiNi$_{0.90}$Co$_{0.07}$Mg$_{0.03}$O$_2$[112]	228.3	84.3/300 cycle/0.1C	4.2

continuing on NCM cathodes, particularly those with excess Ni ions and surpassing Ni content to 0.8.[126,127] In effect, NCM cathodes with excess Ni contents in the range of 0.8 to 0.99 are being designed by researchers in order to increase the cumulative capacity.[128–130] Some cathodes in this range of Ni content are LiNi$_{0.88}$Mn$_{0.06}$Co$_{0.06}$O$_2$,[131] LiNi$_{0.91}$Co$_{0.06}$Mn$_{0.03}$O$_2$,[132] Li$_{1+x}$-(Ni$_{0.88}$Mn$_{0.06}$Co$_{0.06}$)$_{1-x}$O$_2$ (NMC88),[133] LiNi$_{0.83}$Co$_{0.11}$Mn$_{0.06}$O$_2$,[134] LiNi$_{0.895}$Co$_{0.085}$Mn$_{0.02}$O$_2$[135] and LiNi$_{0.96}$Co$_{0.03}$Mn$_{0.01}$O$_2$.[136] Interestingly, among different compositions, the NCM811 cathode material is seen to offer an amazing value of cumulative capacity (200 mA h g^{-1}) and is therefore deemed the most effective Ni-rich composition of the NCM cathode.[137,138]

For the understanding of the layered structure of NCM oxides, the unit cell of NCM111 cathode material (hexagonal α-NaFeO$_2$ layered structure the with $R\bar{3}m$ space group) is shown in Fig. 1a.[139] In this structure, oxygen atoms form a cubic close-packed (ccp) lattice with rhombohedral distortion along the c-direction, resulting in layers formed by edge-sharing octahedra. The octahedral sites of the somewhat thinner layer (Wyckoff position 3a) are occupied mainly by TM layers, whereas those of the somewhat thicker layer (Wyckoff position 3b) are occupied mainly by lithium (Li layer), yielding [Li]$_{3b}$[TM]$_{3a}$[O$_2$]. Especially, in the presence of manganese, the material becomes Li rich, which leads to fractional occupancy of 3a sites by the Li ions. Hence, NCM is frequently denoted as Li$_{1+z}$(Ni$_{1-x-y}$Co$_x$Mn$_y$)$_{1-z}$O$_2$. By contrast, LNO tends towards Li deficiency, meaning that nickel occupies some of the 3b sites. In case of layered oxides, this type of structure is often referred to as H$_1$-type structure.[140–143] The structure is stable for various compositions of NCM oxides.[144] The atomic models of crystal structure for NCM811 in different planes are depicted in Fig. 1b and c. With the change in composition, the unit cell parameters of the NCM structure vary (Table 5).[145] The TM and Li layer distances for various compositions are shown in Fig. 1d.

Fig. 2 shows a schematic of the Li intercalation process in the NCM cathode.[146] Delithiated NCM materials experience crystalline structure change at elevated temperatures. Although the detailed phase transition process differs in various reports, most studies agree that the delithiated NCM cathodes experience a three-stage transition with the increase in temperature: from layered structure ($R\bar{3}m$) to spinel phase ($Fd\bar{3}m$), and then to rock salt phase (MO-type).[147,148] The spinel phase can split into two sequential stages: spinel phase I (LiMn$_2$O$_4$-type) and II (M$_3$O$_4$-type).[149] Only a few research studies reported metallic phases (nickel or cobalt) as the final products, which might be generated under extremely high pressures or temperatures (above 900 °C).[150,151] The three-stage phase transition reactions release heat and oxygen. The oxygen reacts with electrolytes and lithiated anodes[152–155] and is chiefly responsible for the thermal runway (TR) in Ni-rich oxide cathodes.[156,157] The thermal stability of NCM cathodes is intricately linked to the composition of Ni, Mn, and Co. Notably, the presence of Mn^{4+} plays a pivotal role in enhancing the thermal stability as it remains electrochemically inert, providing stabilization to the oxide matrix even in a deep delithiated state.[158,159] Conversely, higher concentrations of Ni in delithiated NCM lead to a lower onset
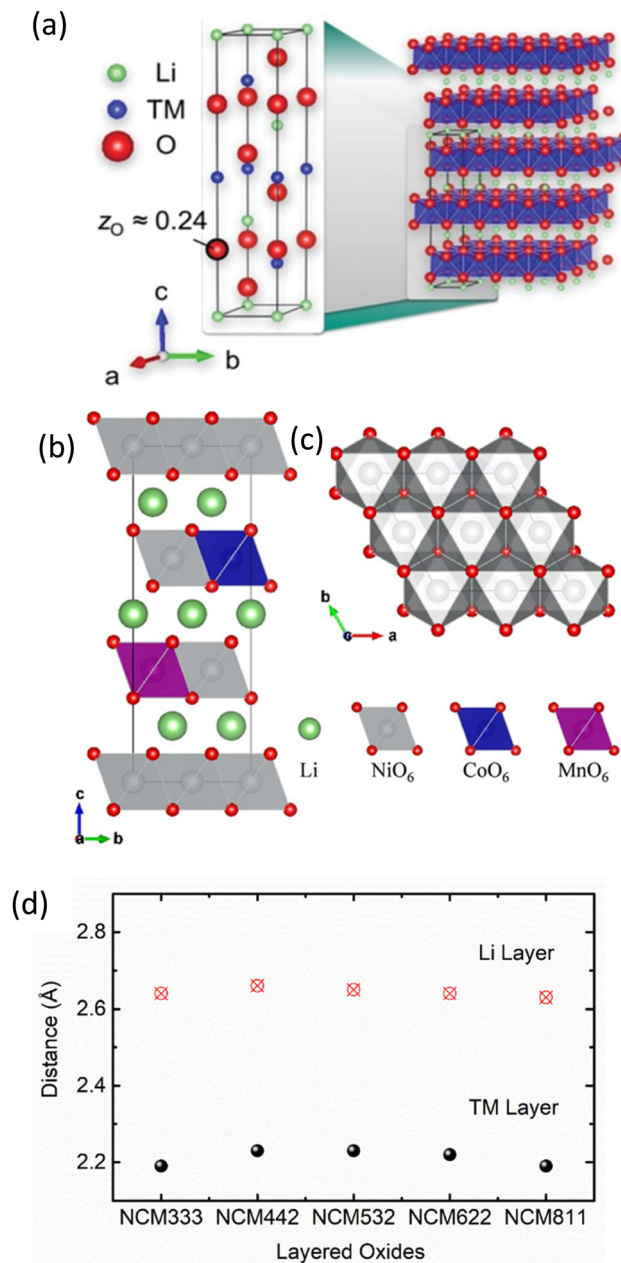
Fig. 1 Structure of layered oxides: (a) layered crystal structure of NCM. Reprinted with permission from L. de Biasi, A. O. Kondrakov, H. Geßwein, T. Brezesinski, P. Hartmann and J. Janek, *J. Phys. Chem. C*, 2017, **121**, 26163.[139] Atomic models of Ni-rich LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) layered oxides ($R\bar{3}m$) projected onto the (b) *bc* and (c) *ab* planes. Reprinted with permission from J.-M. Lim, T. Hwang, D. Kim, M.-S. Park, K. Cho and M. Cho, *Sci. Rep.*, 2021, **7**, 39669.[144] (d) Distance of the TM and Li layer with various compositions of cathodes. Values are adopted from H. Sun and K. Zhao, *J. Phys. Chem. C*, 2017, **121**, 6002.[145]

temperature for phase transitions towards spinel and rock salt phases, accompanied by an increased release of oxygen.[127] This liberated oxygen contributes to solvent combustion and heat generation. Consequently, formulations with elevated Ni contents and reduced levels of Mn and Co generally exhibit higher self-heating rate values, coupled with lower temperatures for

Table 5 Average bond length (Å) of TM–TM and TM–O pairs

Composition	Ni–Mn	Mn–Co	Ni–Co	Mn–O	Ni–O	Co–O
NCM333	2.93	2.89	2.92	1.95	2.06	1.99
NCM442	2.93	2.91	2.92	1.95	2.07	1.99
NCM532	2.91	2.91	2.92	1.94	2.05	1.98
NCM622	2.91	2.88	2.91	1.94	2.02	1.97
NCM811	2.91	2.85	2.88	1.94	2.00	1.94

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exothermic reactions to initiate. The phase stability in Ni-rich cathode materials also shows the manifestation of structure with temperature.[127,146]

Challenges with NCM cathodes

NCM cathodes represent a pivotal component in the advancement of LIB technology, owing to their commendable energy density and cycling stability, as discussed in the previous section. However, this section delves into the multifaceted challenges that confront the design and application of NCM cathodes. Notably, the cation disorder within the crystal lattice poses a significant hurdle, as it disrupts the ordered arrangement of nickel, manganese, and cobalt ions, leading to compromised electrochemical properties. Additionally, the delicate balance in material composition, particularly in mitigating the reliance on cobalt, necessitates intricate optimization strategies. Furthermore, the intricacies of surface coatings and modifications, as well as the understanding of voltage fade mechanisms, demand meticulous investigations. Thermal stability and safety concerns, which become paramount in applications exposed to elevated temperatures, represent another substantial research avenue. Following are some recent literature highlights of these challenges and overcoming of these

may pave the way for enhanced NCM cathodes that drive the evolution of high-performance lithium-ion batteries.

Cation disorder

The phenomenon of cation disorder within the crystal lattice presents a significant challenge to NCM optimization. This disorder leads to variations in the electronic structure and local environments around the transition metal sites, affecting the key electrochemical parameters. In layered NCM oxide cathodes, there is existence of Ni^{2+} ions at the Li^+ site and *vice versa*,[160] which is termed cation disorder/mixing (Fig. 3a). This factor affects Li mobility in these materials,[161–163] which consequently influences the capacity of LIBs.[164] Fig. 3b shows that intermixing decreases with the increase of Mn ions.[161] Studies have shown that the disorderly distribution of cations in NCM cathodes can result in reduced capacity, voltage fade, and deteriorated cycling stability,[165] which ultimately affects the electrochemical performance of batteries. Hence, efforts are made to control cation ordering through tailored synthesis techniques and doping strategies[166,167] for the improvement of NCM cathode performance.

Cumulative capacity and retention

These materials have the potential to be utilized for EV applications due to their high theoretical capacity of 230 mA h g^{-1}.[11,169,170] The composition of NCM cathodes plays a crucial role in determining both the cumulative capacity and capacity retention of a battery. On the contrary, higher nickel contents can reduce the thermal stability of the cathode material, potentially affecting capacity retention over extended cycling (Fig. 3c).[168] An optimal Mn content ensures a balance between capacity and structural stability. It also plays a crucial role in stabilizing the crystal structure of the cathode material. This can enhance the cathode's ability to retain capacity over repeated cycles. Cobalt contributes to the overall capacity of the cathode. However, it is
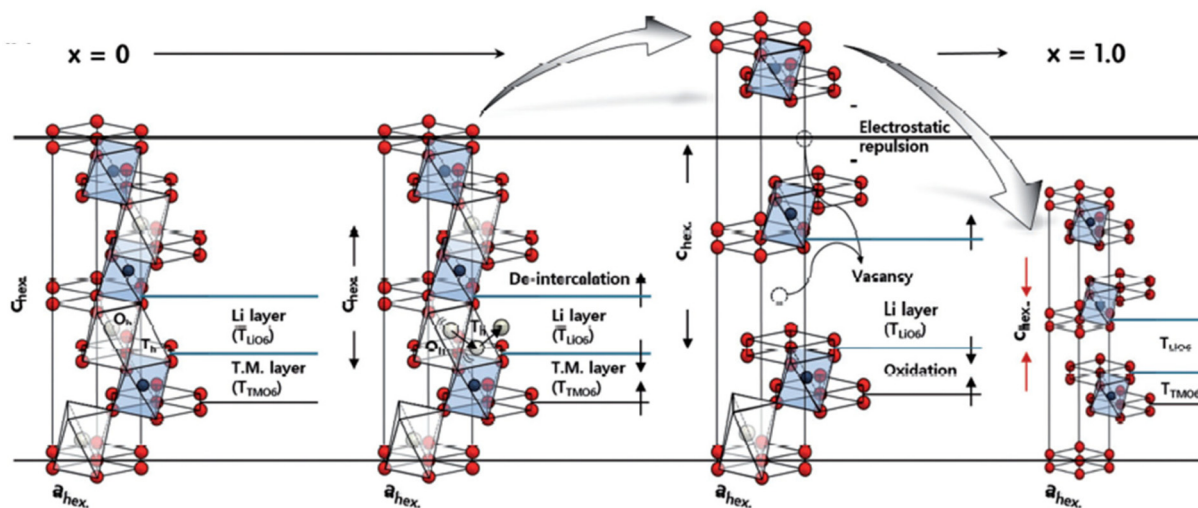
Fig. 2 De-intercalation process in the NCM cathode: structural description of the NCM622 cathode material during the first de-intercalation process (*x* = 0 to *x* = 1.0). Reprinted with permission from W. Lee, S. Muhammad, T. Kim, H. Kim, E. Lee, M. Jeong, S. Son, J.-H. Ryou and W.-S. Yoon, *Adv. Energy Mater.*, 2018, **8**, 1701788.[146]
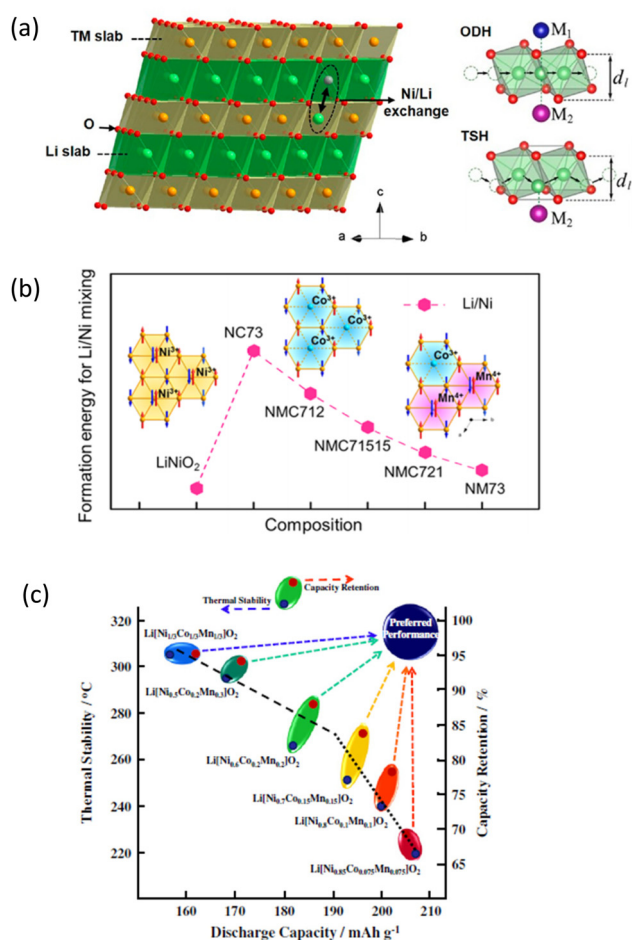
Fig. 3 Issues related to NCM cathodes: (a) α-NaFeO$_2$-type structure of layered NMC materials with one pair of Ni/Li exchange (left panel) and illustration of the ODH (oxygen dumbbell hopping) and TSH (tetrahedral site hopping) types of Li-ion diffusion pathways (right panel). Permission obtained from J. Zheng, Y. Ye, T. Liu, Y. Xiao, C. Wang, F. Wang and F. Pan, *Acc. Chem. Res.*, 2019, **52**, 2201.[160] (b) Variation of Ni/Li exchange in various compositions of NCM oxides Permission obtained from D. Wang, C. Xin, M. Zhang, J. Bai, J. Zheng, R. Kou and J. Y. P. Ko *et al.*, *Chem. Mater.*, 2019, **31**, 2731.[161] (c) Thermal stability, capacity retention and discharge capacity of various Ni-rich cathode materials. Permission obtained from H.-J. Noh, S. Youn, C. S. Yoon and Y.-K. Sun, *J. Power Sources*, 2013, **233**, 121.[168]

often limited due to cost and ethical considerations. Reduced cobalt content may not significantly affect the initial capacity but can influence capacity retention. Further, the disordered distribution of Ni, Mn, and Co ions within the crystal lattice can hinder the efficient movement of lithium ions, leading to reduced cumulative capacity.[171] Optimizing the NCM cathode composition involves a delicate balance between maximizing specific capacity, ensuring structural stability, and managing factors such as thermal stability and cost. Researchers work to strike this balance to achieve the optimal performance of NCM batteries.

Thermal stability

Thermal stability is necessary for the development of a risk-free battery. Thus, investigating the thermal stability of cathodes is

equally important.[172–174] Unfortunately, thermal stability decreases with the increase in Ni content (Fig. 5b). The onset temperature of TR for the battery with the NCM811 cathode is 20 °C lower than that with the NCM622 cathode; however, this value is 13 °C lower for single-crystal NCM811.[175] Atomic substitutions to NCM can help suppress the TR behavior.[176] Ca doping to NCM811 increases the onset temperature by almost 30 °C.[177] The addition of a negative-thermal-expansion (NTE) material of Al$_2$(WO$_4$)$_3$ leads to improvement in the thermal stability.[178] The formation of the rock-salt layer on the surface of NCM811 is reported to enhance the thermal stability of an NCM cathode with high Ni contents.[179] The change in the total heat generation with degradation suggests a strong correlation between the heat generation and crystal structure changes during cycling, as indicated by differential scanning calorimetry (DSC) measurements and XAS measurements. Studies focusing on the thermal stability of layered NCM materials envisaged the correlation between the thermal stability and its electrochemical performance.[180,181]

Cost, efficiency, abundance and demand

The optimal use of NCM cathodes in LIBs is not only limited to the optimization of electrochemical performance but the factors affecting their cost also play an important role. Thus, the projected cost of the designed NCM battery,[182] abundance, supply and demand of elements such as Ni, Co, Mn have always been a concern and are being reviewed by the scientific community.[169] Despite the numerous efforts, vehicles based on LIBs are costlier than ICEs (Fig. 4a).[183] Strategies are planned to reduce their cost comparable to the value of ICE-based vehicles in the next 5–6 years. Fig. 4b depicts the cost of various NCM batteries by describing the cost of various components.[184] If the example of LMO is considered, the production cost for a solid-state process is \$7 per kg and requires 6 kW h kg^{-1} of energy. The cost of automotive batteries based on LMO cathode may be reduced by cutting LMO price and plat production volume.[185] Thus, the reduction in cathode price is an effective choice for reducing the cost of LIBs; however, the case of NCM is different. In this case, the use of Co ions is not considered favourable at the industrial level, as Co has issues related to the abundance and cost (Fig. 5a).[169] It is expected that the demand of lithium, cobalt, and nickel will be increased by the factors of 18–20, 17–19, and 28–31, respectively, from 2025 to 2050. In addition to that, a factor of 15–20 of existing cost will be hiked for other auxiliary materials used in LIBs (Fig. 5b).[186] This requires drastic expansion of lithium, cobalt, and nickel supply chains and likely additional resource discovery.[187,188]

Thus, structural degradation,[189] capacity retention,[190] lower thermal stability[191] and production cost[192] are the major challenges towards the development of efficient NCM cathodes. Apart from these challenges specific to the cathode, effects such as release of CO$_2$/O$_2$[193,194] and metal ion dissolution[195,196] are major concerns when the cathode comes into contact with the electrolyte. Thus, the scientific community is working towards overcoming these issues for making global use of LIBs
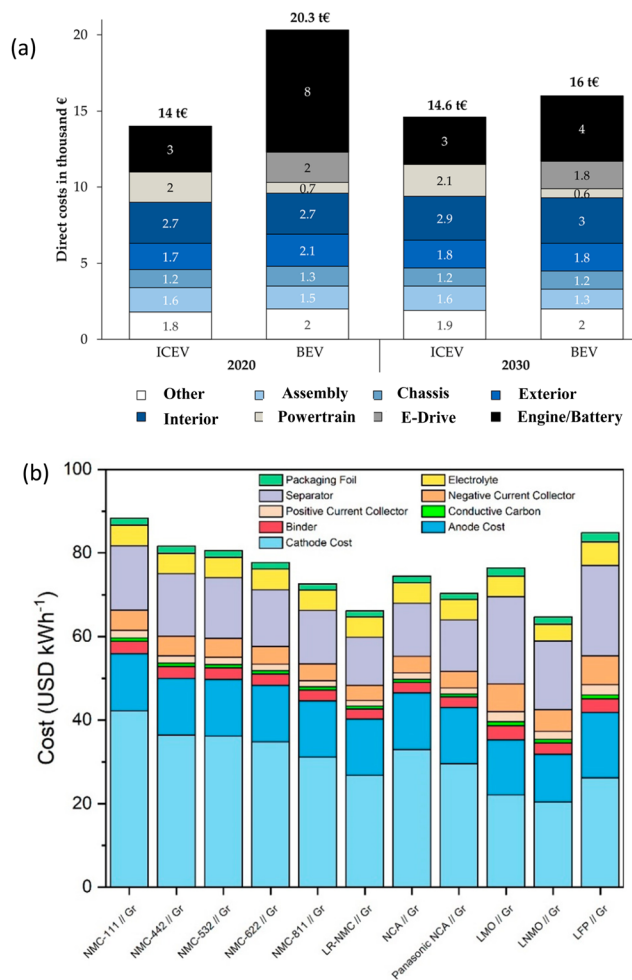
Fig. 4 Cost of li-rechargeable batteries: (a) Comparison of costs in the next 10 years for internal combustion engine battery electrical vehicles (ICEVs) and. Reprinted with permission from A. König, L. Nicoletti, D. Schröder, S. Wolff, A. Waclaw and M. Lienkamp, *World Electr. Veh. J.*, 2021, **12**, 21[183] (b) cost of Li rechargeable batteries for various NCM compositions, Reprinted with permission from M. Wentker, M. Greenwood and J. Leker, A Bottom-Up Approach to Lithium-Ion Battery Cost Modelling with a Focus on Cathode Active Materials, *Energies*, 2019, **12**, 504. open access.[184]

by investigating cathodes,[197,198] cathode/electrolyte interfaces[199,200] and gas evolution phenomena.[201–203] Therefore, this review is focused on exploring the nature of NCM cathodes, and efforts related to this cathode are discussed in the following sections.

Strategies to improve the electrochemical performance

Several strategies including microstructural modifications,[199] doping,[204–206] co-doping[207–209] or coating[210,211] are applied to improve the electrochemical performance[212,213] of parent cathode materials. Studies focusing on air stability,[214] correlating the surface structure with the internal strain, and capacity deterioration[215–217] along with correlation among the structural changes with Li diffusion[218] also provide the opportunities to resolve the electrochemical performance–related issues. Thus,

the present section describes the strategies utilized for the improvement of the electrochemical performance of cathodes.

Coating

Coating is an effective strategy to improve the electrochemical performance of the LIBs based on NCM cathodes.[219–221] Fig. 6a shows the schematic of surface coating processes. As the surface coating of cathode materials may enhance the life and rate capability of LIBs,[222–224] various materials are investigated for the NCM811 cathode as coating materials.[225,226] Carbon seems to be very common to use as a coating material as the presence of carbon on the surface of the cathode is effective to enhance the cycle life by altering the following behaviors.

1. increase in electrode conductivity,

2. improvement in the surface chemistry of the active material and

3. protection of the electrode from direct contact with the electrolyte.

Super-P carbon black (SPB 0.5 wt%)-coated NCM811 delivers excellent cyclability (87.8% after 80 cycles) and rate capability (86.5% at 2C) compared to those of pristine NCM811.[229] The discharge capacity of the 4 nm coating of carbon on NMC811 showed only a 1.26% decrease after 100 cycles at a rate of 0.2C, while pristine NMC811 lost 6.85% of its initial reversible capacity.[230] N-doped carbon-coated NCM maintained good cycling performance (210.2 mA h g^{-1} at 0.1C after 40 cycles and 188.5 mA h g^{-1} at 1C after 100 cycles) and rate ability (131.7 mA h g^{-1} at 5C rate). In comparison, the uncoated (NCM) electrode retained only 56.60% of its capacity (102.5 mA h g^{-1} at 1C after 100 cycles).[231]

Oxides such as Al_2O_3, ZrO_2, Li_2O–$2B_2O_3$ (LBO), and Li_2MnO_3 are also used as coating materials[232–234] apart from utilizing carbon-derived materials such as graphene oxides and polymers. The schematic of the TiO_2 coating procedure is shown in Fig. 6b, which exhibits a significant improvement in the electrochemical performance of LIBs.[227] In Table 6, the capacity retention values of bare and oxide cathodes are collated.[234–252] These observations clearly reflect the improvement in the electrochemical performance of NCM cathodes.

Furthermore, the coating of NMC811 with hydrophobic materials is effective in protecting the cathode surface from environmental moisture or humidity.[253] Fig. 6c shows hydrophobic coating with di hexadecyl phosphate (DHP) on the NCM particle surface. It consists of two layers: (i) an outer-layer hydrophobic alkyl surface, which alleviates the absorption of H_2O/CO_2 on the particle surface in the humid environment and (ii) an inner-layer phosphate-based coating with O=POLi covalent bonds. This layer improves the Li$^+$ transportation coefficient during the charge–discharge process. As a result, profiting from these two synergistic effects, the DHP-coated NCM cathodes have shown excellent rate performance and cycling stability, particularly, after 14 days of exposure to air. The DHP-coated NCM cathodes delivered an initial capacity of 168.7 mA h g^{-1} at 2C rate, but only 134.7 mA h g^{-1} for the pristine NCM.[228] Hydrophobic polydimethylsiloxane-grafted NCM811 suppresses the formation of residual Li$^+$ even in
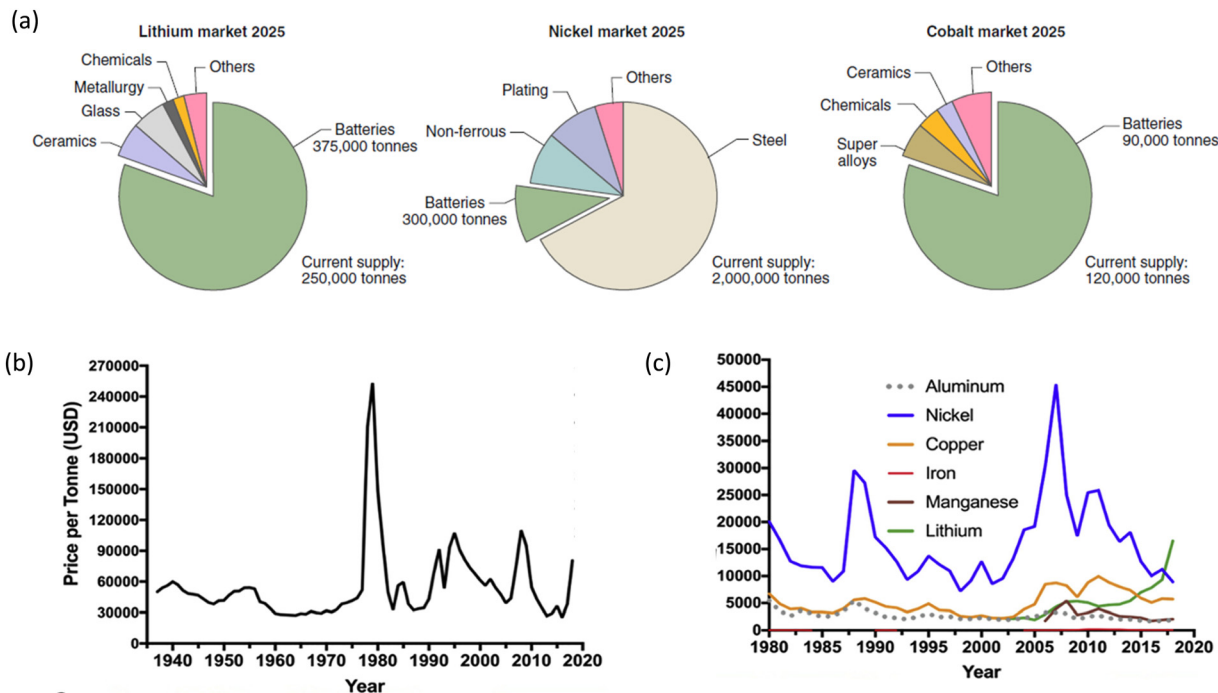
Fig. 5 Market statistics of the NCM cathode: (a) market of various elements by 2025. Reprinted with permission from W. Li, E. M. Erickson and A. Manthiram, *Nat. Energy*, 2020, **5**, 26.[169] (b) Prices per tonne (USD) for Co and (c) other elements related to NCM cathodes. Reprinted with permission from S. W. D. Gourley, Tyler and Z. Chen, *iScience*, 2020, **23**, 101505.[186]

humid air. This leads to the negligible surface degradation of NCM811 and the modified cathode shows excellent electrochemical performance even after storage in humid air for 2 weeks.

Dual coating

Dual coating is considered an effective approach for the improvement of the electrode/electrolyte interface.[254,255] It not only improves the discharge capacity but also increases the cyclic performance.[256] It involves applying two separate layers of protective materials onto the surface of the cathode particles. The first coating layer is typically designed to act as a barrier between the cathode material and the electrolyte. It helps prevent unwanted side reactions that can occur at the electrode–electrolyte interface. It is especially important for high–nickel content NCM cathodes, which are much prone to such reactions. The second coating layer is often chosen to enhance the structural stability of the cathode material. It helps maintain the integrity of the crystal lattice during charge and discharge cycles, reducing structural degradation and extending the lifespan of the cathode.[257] The initial specific discharge capacity of NCA, Y_2O_3-decorated NCA, and graphene/Y_2O_3/NCA was found to be >190 mA h g^{-1} at 0.5C, but the capacity retention of the graphene/Y_2O_3/NCA composite was about 48% higher than that of the bare material during 100 cycles. NCA, Y_2O_3/NCA, and graphene/Y_2O_3/NCA materials deliver specific discharge capacities of 109, 136 and 164 mA h g^{-1}, respectively at 2C.[258] The capacity retention of the polypyrrole $LiAlO_2$-coated NCM (PPy-LA) is 92.8% after 100 loops and a capacity of 128 mA h g^{-1} is obtained at 2 A h g^{-1}.[259] Dimethyl sulfone (DMS) and dimethyl sulfoxide (DMSO)-modified NCM811

cathodes are reported to exhibit improved specific capacity retention (DMS-NCM811: 99.4%; DMSO-NCM811: 88.6%; and NCM811: 78.4%).[260] The capacity retention of Li_3PO_4 and PPy for layered Ni-rich cathodes is 95.1% at 0.1C after 50 cycles, whereas the bare sample exhibits only 86% retention. The coated cathode delivers a cumulative capacity of 159.7 mA h g^{-1} at 10C compared to 125.7 mA h g^{-1} for the bare cathode (Fig. 7a).[261] Heating polyacrylonitrile with NCM811 can simultaneously construct a cyclized polyacrylonitrile outer layer and a rock-salt bridge-like inner layer, forming a compact dual-coating of NCM811.[262] The modified cathode leads to a high reversible capacity of 183 mA h g^{-1} and a high capacity retention of 83% after 300 cycles at 1C rate (Fig. 7b).

Dual coating of polydimethyldiallyl ammonium chloride/graphene oxide (PDDA/GO) on a single-crystalline NCM811 cathode leads to 77% capacity retention after 500 cycles at a current density of 50 mA g^{-1}, against 28% for pristine NCM811 (Fig. 7c).[263] The nano-Al_2O_3 and PPy double-layer coating forms a firm protective shell on the surface of the $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ cathode to alleviate external side reactions (Fig. 7d). This type of double-layer coating was helpful to achieve a discharge capacity retention rate of 90.74% after 100 cycles at 1C rate.[264] Wu *et al.* have investigated the impact of $LiAlO_2$/Al_2O_3 dual coating on the NCM811 cathode. The optimal electrochemical performance is reported to be an appropriate ratio of ion-conducting $LiAlO_2$ and chemical-inert Al_2O_3 phases.[265]

Doping and co-doping

Introducing certain dopants can help stabilize the crystal structure of NCM cathodes.[266–268] This improves the structural
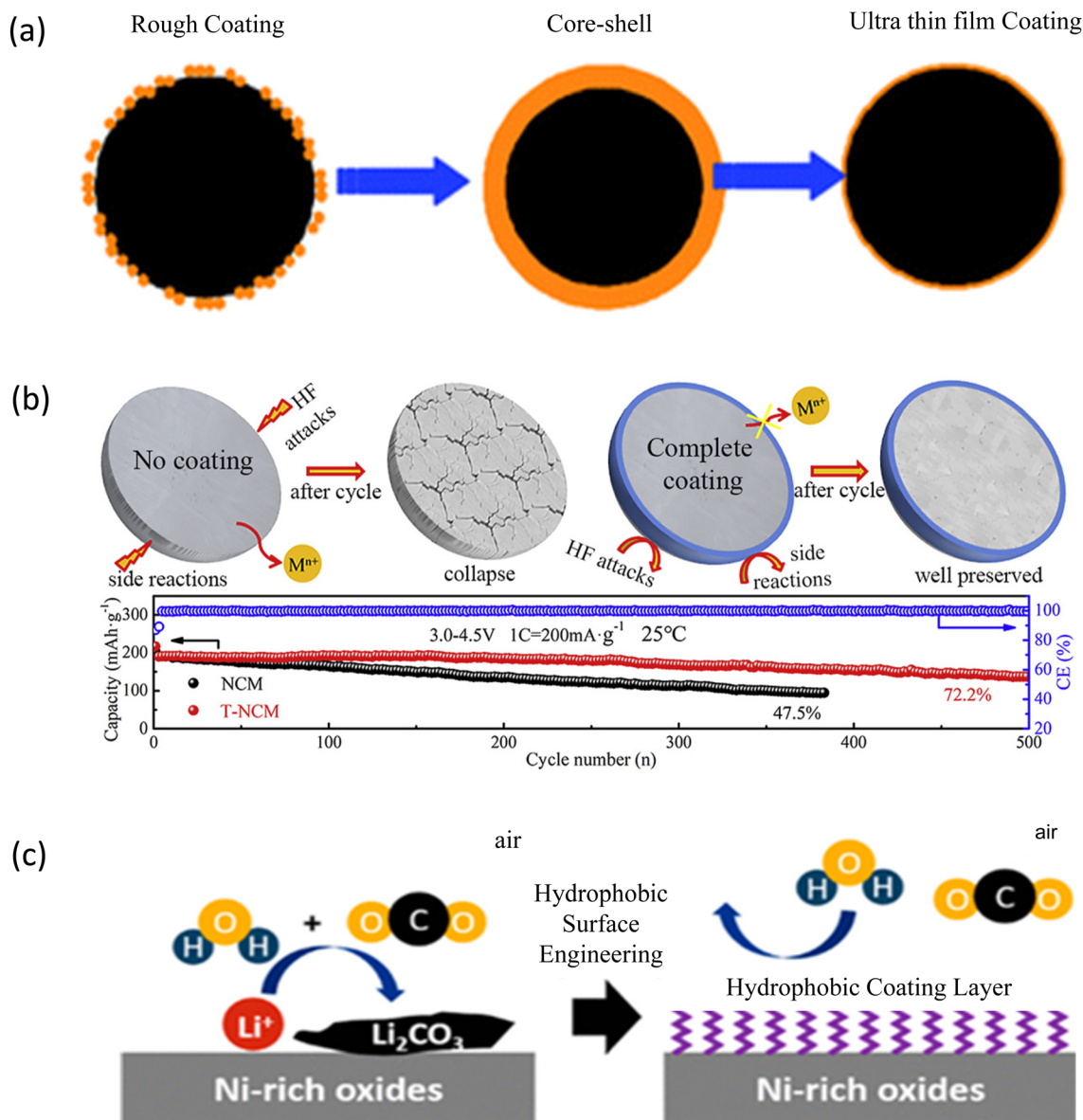
Fig. 6 Coating of the NCM cathodes: (a) surface coating approaches to cathode materials. Reprinted with permission from Z. Chen, Y. Qin, K. Amine and Y.-K. Sun, *J. Mater. Chem.*, 2010, **20**, 7606.[219] (b) Representation of TiO₂ coating on the NCM cathode along with the electrochemical behavior of pure and doped counterparts. Reprinted with permission from Q. Fan, S. Yang, S. Guan. J. Chen, S. Feng, J. Liu, L. Liu, J. Li and Z. Shi, *J. Power Sources*, 2020, **477**, 228745.[227] (c) Hydrophobic Coating Layer for NCM cathode Materials Reprinted with permission from SungWookDooSungWook Doo, More by S. Wook Doo, S. Lee, H. Kim, J. H. Choi and K. Tae Lee, *ACS Appl. Energy Mater.*, 2019, **2**, 6246.[228]

integrity during charge and discharge cycles, reducing degradation. Doping may also enhance the material's ability to withstand high temperatures, reducing the risk of thermal runaway events.[269–271] Dopants can be strategically chosen to influence the distribution of nickel (Ni), manganese (Mn), and cobalt (Co) ions within the crystal lattice. This helps reduce the cation disorder, which can have a negative impact on the electrochemical performance.[272–274] Strategic doping can help stabilize the redox chemistry of NCM cathodes, reducing the phenomenon of voltage fade, where the voltage of the cell decreases over repeated cycles. The doping of NCM811 with cations such as Mg^{2+}, Al^{3+}, Si^{4+}, Ti^{4+}, Zr^{4+}, and Ta^{5+} following "top–down"

approach concludes that Ta^{5+} cations are very promising dopants for Ni-rich NCM cathodes.[275] LIB prototypes, consisting of tungsten-stabilized Ni-rich cathode materials ($x > 0.9$), exhibit specific capacities greater than 220 mA h g⁻¹. This study enables the superiority of doping for enhancing the energy density of LIB without compromising the durability.[276] This is also reflected in the improvement in in the capacity retention of NCM cathodes by various ions such as B,[277,278] V,[279] Mg,[280] F,[281] ZrB₂,[282] Nb,[283] Ti,[284] Dy,[285] Al,[286] Nb⁵⁺,[287] Nb (dual site),[288] Mg,[289] Ga,[290] and Mo.[291] Capacity retention of doped and their pristine counterparts is shown in Fig. 8a. The doping of ions into NCM cathodes, especially rare earth (RE) ions, suppresses

Table 6 Capacity retention (%) of bare and coated cathode materials

Coated materials	Cathode	Bare cathode	Coated cathodes	Cycles	Specification
Metal oxides					
3%Li$_2$MnO$_3$[234]	NCM811	74	93	100	0.1C
		63	81	100	1C
TiO$_2$[227]	NCM811		72.2	500	4.5 V
			63.4	1000	1000 cycles-4.3 V
Li$_3$PO$_4$[235]	NCM811		88.4	100	1C
			84.6	100	1C _exposed to air for 7 days
Li$_3$PO$_4$[236]	NCM811	86	92.6	100	1C
4.53 wt% Li FePO$_4$[237]	NCM811	78	97	100	2.7–4.5 V
		63	86	400	
2% Li$_2$MoO$_4$[238]	NCM811	85.5	93.99	100	1C
LiNbO$_3$[239]	NCM523	73	92	100	1C
2 wt% Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$[240]	LiNi$_{0.83}$Co$_{0.06}$Mn$_{0.06}$Al$_{0.05}$O$_2$	80.9	90.9	300	5C
MoO$_3$[241]	NCM811		84.5	100	0.1C
			79.8		5C
Graphene oxides and nitrides					
r-GO[242]	NCM811		92.8	100	1C
g-C$_3$N$_4$[243]	NCM811	130 mA h g^{-1}	140	225	0.178 mA cm^{-2}
Gr[244]	LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$				
Polymers[245,246]					
Oxy-thiophosphate[247]	NCM811	128 mA h g^{-1}			
Polypyrrole[248]	NCM811		90.7	100	
Poly(thiophene)[249]	NCM811	84.2	91.3		
Polypropylene[250]	NCS*	94.7	96.2		3.0–4.3 V
Polyvinylpyrrolidone (PVP), and polyaniline (PANI)[251]	NCM811		88.7	100	
PMMA[252]	NCM811	181.1 mA h g^{-1}			1C

the Ni/Li cation mixing effect.[292] The functional trace doping of dual-elements has been an effective strategy to address issues such as internal strain accumulation, structural/mechanical degradation, and surface parasitic reaction.[293,294] Titanium and boron co-doped into NMC811 improve the rate performance (183.1 mA h g^{-1} at 1C and 155.5 mA h g^{-1} at 10C) and cycling stability (capacity retention of 94.7% after 100 cycles at 1C). This co-doping also reduces charge transfer impedance and suppresses phase change of NCM811.[295] For La^{3+} and Al^{3+} co-doped NCM811, initial discharge specific capacities of 218.6 mA h g^{-1} (0.05C) and 178.6 mA h g^{-1} (1C) are observed to reduce to 134.6 mA h g^{-1} with 75.4% capacity retention after 100 cycles at 1C (Fig. 8b).[296] In the voltage range of 2.8–4.3 V, the discharge capacity of dual-doped NCM811 with Mg^{2+} and Al^{3+} (NCM-MA) is 138.8 mA h g^{-1} after 200 cycles at 1C, which is 31 mA h g^{-1} higher than that of the pristine NCM (Fig. 8c). NCM-MA also delivers a high discharge capacity of 150.33 mA h g^{-1} at 5C, due to the improvement of Li$^+$ diffusion kinetics.[297]

Doping, co-doping followed by coating or dual modifications of NCM cathodes

Doping followed by coating is used by several researchers to improve the electrochemical performance of LIBs.[189,298] Doping can be used in conjunction with surface coatings to further mitigate unwanted side reactions between the cathode material and the electrolyte. For the NCM950505 cathode, doped with Zr and simultaneously coated with an Li$_2$ZrO$_3$ layer, the capacity-retentions are reported as 86.08%, 92.12%, and 96.85% at the 50th cycle for pristine NCM, S-NCM (synthesized by the solid

method), and L-NCM (synthesized by the liquid/solvent method), respectively. In the 300th cycle, in the voltage range of 2.8–4.35 V, the capacity-retentions for S-NCM and L-NCM are 77.72% and 81.95%, respectively.[299] The 1% Zr-NCM831205 cathode maintains a discharge capacity of 173.9 mA h g^{-1} at 1C after 200 cycles in the 2.5–4.3 V voltage range at 25 °C, corresponding to a capacity retention of 94.6%; however, the unmodified NCM exhibits a capacity retention of 68.6%. The synergistic effect of bulk Zr doping and surface Li$_6$Zr$_2$O$_7$ coating is shown to further improve the cycling stability of this cathode.[300] The La$_2$Li$_{0.5}$Al$_{0.5}$O$_4$-coated and La-and-Al-doped NCM811 exhibits an excellent capacity retention of 97.2% at 1C in the voltage range of 3.0–4.4 V after 100 cycles, which is 18.5% higher than that of the pristine form. With regard to the rate performance, it shows a retention of 95.1% in capacity at 5C after 80 cycles from 3.0 V to 4.4 V, 6.4% higher than that of the pristine form.[301] ZrO$_2$-coated/Zr-doped NCM811 exhibits enhanced cycling stability and lower impedance.[302] The co-doping of cobalt and titanium in NCM811 cathodes is reported to improve the reversible capacity together with the rate capability by obviously alleviating the lattice structure degradation and microscopic inter-granular cracks. Titanium doping effectively reduces the cation mixing and also stabilizes the crystal structure, while the spinel phase formed at the surface by a cobalt oxide coating is more stable than the layered phase at high voltages, which can alleviate the generation of micro-cracks. After 0.5% Co oxide coating and 1% Ti doping (Ti$_1$Co$_{0.5}$-NCM), a superior rate capability of 121.75 mA h g^{-1} at 20C between 2.7 and 4.5 V and a predominant capacity
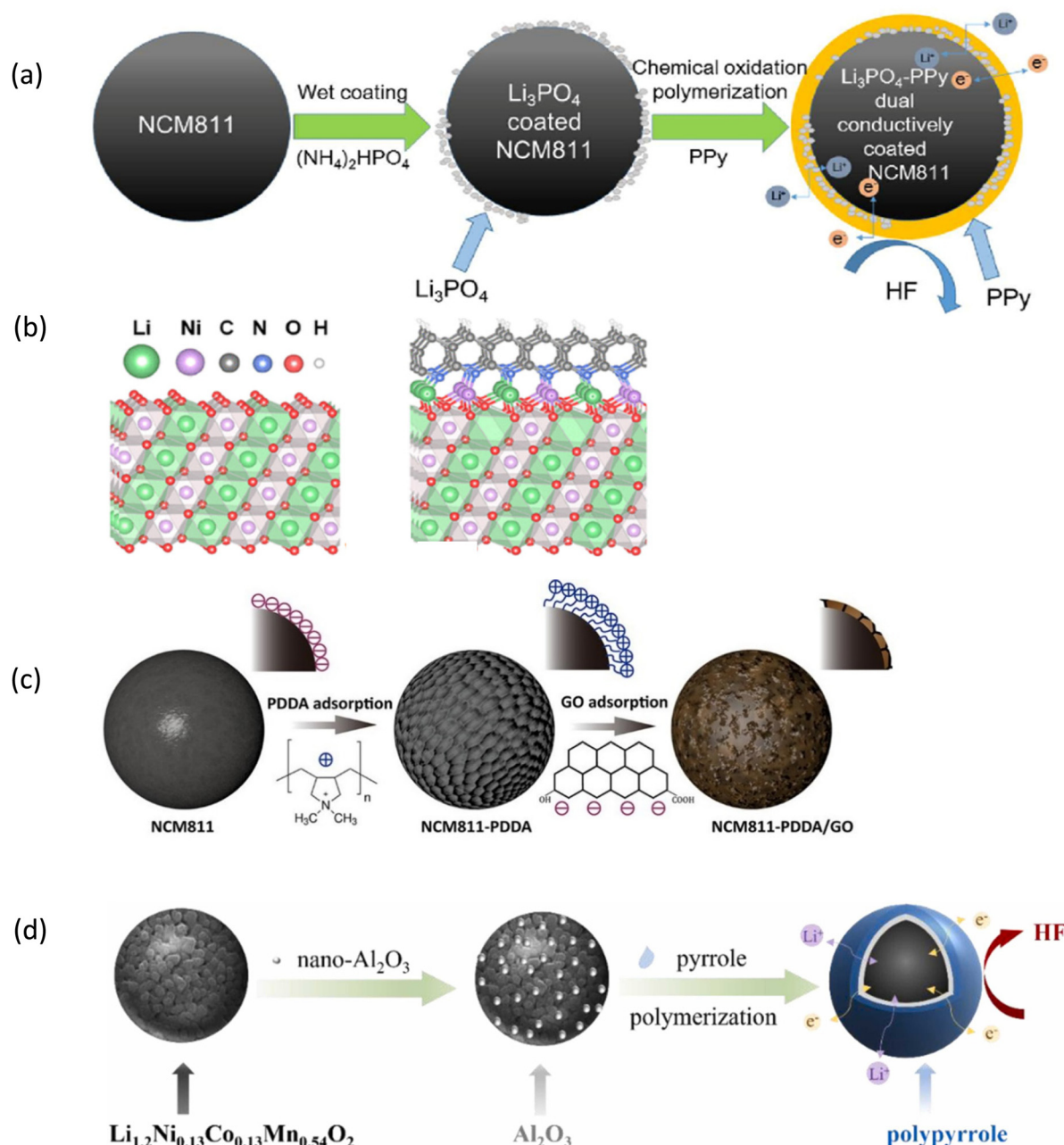
Fig. 7 Dual-coating process: (a) schematic representation of Li_3PO_4–PPy Dual coating on the NCM811 cathode. Reprinted with permission from S. Chen, T. He, Y. Su, Y. Lu, L. Bao, L. Chen, Q. Zhang, J. Wang, R. Chen and F. Wu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 29732–29743.[261] (b) Reprinted with permission from J. Wang, Q. Yuan, Z. Ren, C. Sun, J. Zhang, R. Wang, M. Qian, Q. Shi, R. Shao, D. Mu, Y. Su, J. Xie, F. Wu and G. Tan, *Nano Lett.* 2022, **22**, 5221.[262] (c) Coating of PDDA/Go on NCM811. Reprinted with permission from J. Yu, J. Zhang, Y. Zhang, Z. Wang, Z. Chen, A. Gao, J. Zhang, Y. Wang and R. Zhao, *Appl. Surf. Sci.*, 2022, **577**, 151716.[263] (d) Nano-Al_2O_3 and pyrrole coating on the Li-rich NCM cathode. Reprinted with permission from Y. Beia, Y. Zhang, Y. Li, Y. Song, L. Liu, J. Ma, and J. Liu, *J. Alloys Compds*, 2022, **928**, 167140.[264]

retention of 74.2% are observed compared with the pristine NCM811 with a capacity retention of 59.5% after 400 cycles between 2.7 and 4.7 V.[303] Ti-doped and La_4NiLiO_8-coated NCM811 cathodes show improved electrochemical performance due to the synergetic effect of the conductive La_4NiLiO_8 coating layer and the strong Ti–O bond.[304] Trace Zr-doping and the conductive Li_3BO_3 layer are simultaneously adopted to modify the NCM cathode.[305] The results have indicated that

the Zr^{4+} dopants, diffused to the surface during annealing, are responsible for the improved electrochemical performance compared to the unmodified cathode without additional coatings (Fig. 9a).[306] A maximum discharge capacity of 129.8 mA h g^{-1} at 5C high rate and enhanced cycling performance with a capacity retention of 90.1% after 300 cycles are reported for PPy-coated $LiNi_{0.835}Co_{0.05}Mn_{0.10}B_{0.015}O_2$. The pristine cathode demonstrates a fast decaying capacity and delivers
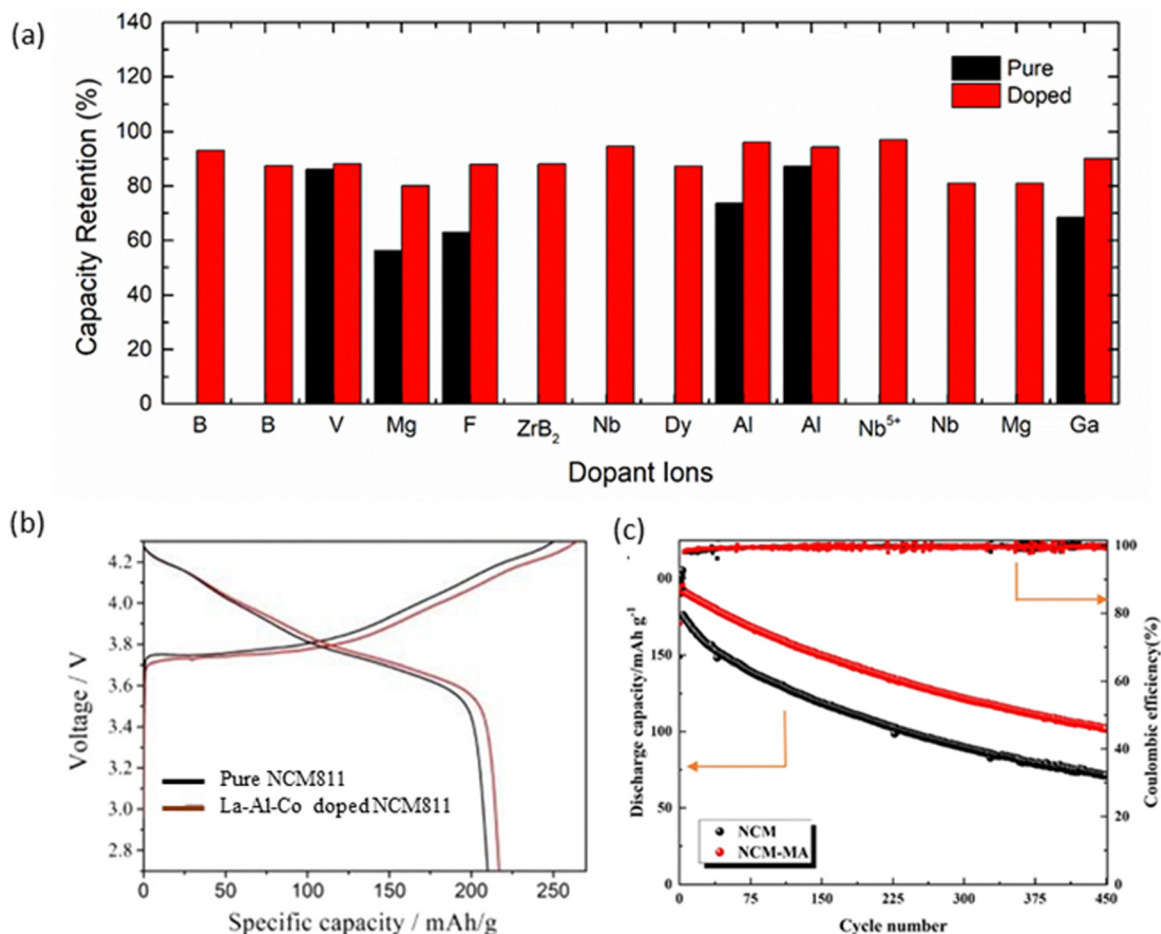
Fig. 8 Doping effect on electrochemical performance: (a) capacity retention in NCM811 cathodes by doping with various ions. Doping improves the retention in these cathodes. The values are taken from previously published work.[277–291] (b) Behaviour of La–Al Co doped NCM811 and pure NCM811. Reprinted with permission from Mi. Zhang, C. Wang, J. Zhang, G. Li and L. Gu, *ACS Omega*, 2021, **6**, 16465[296] (c) discharge capacity of Mg and Al co-doped NCM811. Reprinted with permission from L. Xiao, X. Tang, Z. Ban *et al.*, An Mg–Al dual doping strategy to enhance the structural stability and long cycle life of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode material, *Ionics*, 2022, **28**, 3101.[297]

a capacity retention of only 81.9%.[307] Fig. 9b shows that the sample containing 0.5% Sm has the highest initial discharge specific capacity (1C, 184.2 mA h g^{-1}), capacity retention rate (2.7–4.3 V, 100th cycle, 94.2%), and rate performance (5C, 152.2 mA h g^{-1}).[308] WO_3-coated and Mg^{2+}-doped NCM811 cathodes are synthesized by the co-precipitation and wet coating methods and the electrochemical performance is compared. In Fig. 9c, the WO_3-coated and Mg^{2+}-doped NCM811 cathode exhibits a capacity retention of 73.5% at 1C after 100 cycles, which is considerably higher than that of the raw materials (53.6%).[309] The bulk Zr^{4+}-doped and surface Al_2O_3-coated cathode delivered a high discharge capacity of 120 mA h g^{-1} after 200 cycles at 0.5C.[310]

Composites, morphology/microstructure manipulation and some specialized structures

In the context of NCM batteries, composites can be tailored to optimize the conductivity, stability, and capacity. For example, incorporating conductive additives or coatings within the cathode composite can enhance the electron transport, ultimately

improving the overall battery performance. Furthermore, morphology and microstructure manipulation involve controlling the size, shape, and arrangement of particles within the cathode material. This manipulation enables the optimization of key electrochemical properties. For instance, designing cathode materials with well-defined particle sizes and surface areas can enhance ion diffusion kinetics, leading to improved charge/discharge rates and overall efficiency. Additionally, tailoring the microstructure can help mitigate issues such as particle cracking or phase transformation during cycling, ultimately prolonging the battery's lifespan.[311] Allahyari *et al.* designed an NCM811/LFP/Al composite cathode and reported that the addition of 20 wt% of $LiFePO_4$ to the cathode materials reduces the internal resistance of the electrode and the charge transfer resistance. This is due to the strong P–O bond of PO_4 in $LiFePO_4$ involved in the side reactions between the active electrode and the electrolyte. Al is added to control the ionic conductivity.[312] Carbon nanotube (CNT) and graphene (GN)-based hybrid materials of NCM333 (NCM333/CNT/graphene) form a three-dimensional (3D) spider web-like network
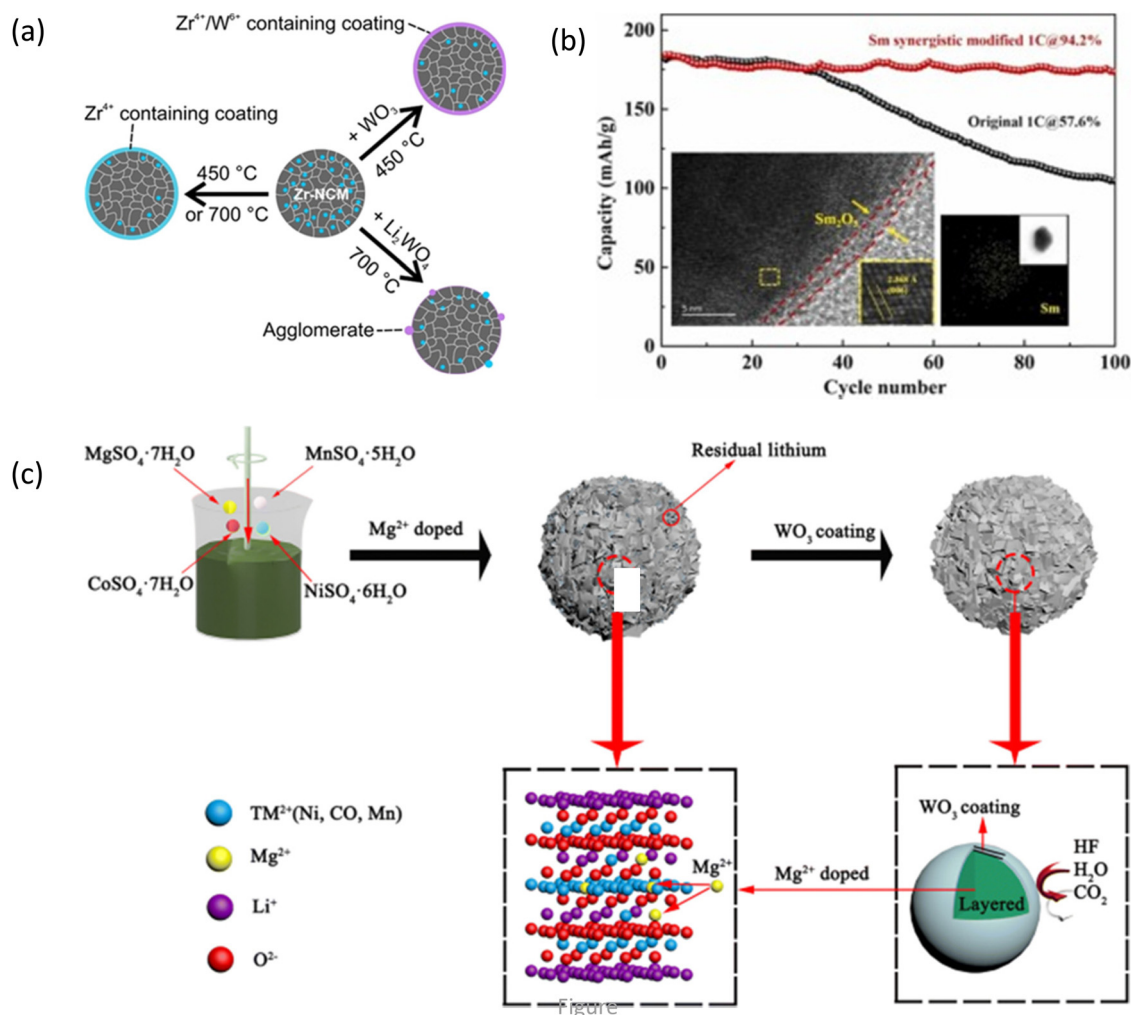
Fig. 9 Dual modification strategy: (a) Zr^{4+}/W^{6+}-coated Zr-doped NCM cathode. Reprinted with permission from F. Reissig, M. A. Lange, L. Haneke, T. Placke, W. G. Zeier, M. Winter, R. Schmuch and A. Gomez-Martin, *ChemSusChem*, 2022, **15**, e202102220[306] (b) electrochemical performance of the Sm-coated and Sm-doped NCM811 cathode. Reprinted with permission from M. Zhang, M. Lv, D. Zhang, Y. Yan, Y. Wang, J. Li, Z. Li, Enhanced electrochemical properties of NCM811 cathode material due to synergistic modification with Sm as doping and coating agent, *J. Alloys Compd.*, 2022, **909**, 164712[308] (c) schematic process of the designing of the WO_3-coated and Mg^{2+}-doped NCM811 cathode. Reprinted with permission from Z. Xiao, C. Zhou, L. Song, Z. Cao and P. Jiang, Dual-modification of WO_3-coating and Mg-doping on $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes for enhanced electrochemical performance at high voltage, *Ionics*, 2021, **27**, 1909.[309]

structure. This material exhibits a high discharge capacity of 134 mA h g^{-1} at 3.0C.[313]

The NCM811 compound, after the addition of ethylene glycol (EG) and surfactant PVP, delivers the highest discharge capacity of 220.18 mA h g^{-1} for the initial cycle, and the capacity retention rate of the spherical-like cathode material is 82.36% at 20 mA g^{-1} after 100 cycles.[314] The hybrid structure of the Li[Ni$_{0.9}$Co$_{0.045}$Mn$_{0.045}$Al$_{0.01}$] cathode compositionally partitioned into inner Li[Ni$_{0.92}$Co$_{0.04}$Mn$_{0.03}$Al$_{0.01}$]O$_2$ and outer Li[Ni$_{0.845}$Co$_{0.067}$Mn$_{0.078}$Al$_{0.01}$]O$_2$ develops radially aligned, size-refined primary particles with a high aspect ratio. This type of microstructure is helpful to improve its cycling stability, which retains 84.7% of its initial capacity after 1500 cycles.[315]

The optimization of cathode active materials in terms of size and morphology is a prerequisite for achieving good rate capability in Ni-rich NCMs.[316,317] The electrode material obtained from microwave-assisted co-precipitation followed by a hydrothermal modification (NCM-WH) method possesses a pure α-NaFeO$_2$ phase and a regular spheroidal morphology with a proper size over 10 μm, which exhibits more excellent discharge capacity of 150 mA h g^{-1} after 200 cycles and a better capacity retention of 88.3% than those obtained by the microwave-assisted co-precipitation method (NCM-W) or the normal co-precipitation method (NCM-N) alone. The improved electrochemical properties are confirmed by their ordered phase structure, regular spheroidal morphology and high tap density, which result in lower Li/Ni cation mixing, faster solid-state ion diffusion, higher electrochemical reversibility and better structure stability during the long-term cycles.[318]

Water washing and surface modification (gases and molecular species)

Washing is a commonly used, easy and cost-effective method to remove the surface impurities of cathode materials for LIBs,[130,319] therefore, it is used to improve the cycling performance and structural stability. In the case of NCM811 cathodes, the untreated sample usually transforms into the spinel phase, whereas the washed sample remains as a layered hexagonal phase. Fig. 10a shows the electrochemical performance of the treated cathode.[320] The crystal and electronic structures are the same in the bulk aspect after the water-washing process for the NCM88 cathode, but there are differences in the surface environment. The amount of Li_2CO_3 decreases while the NiO-like rock-salt phase increases on the surface of the water-washed cathode, and it deteriorates the rate performance by elevating the surface resistances.[321] Heat treatment after washing $LiNi_{0.88}Co_{0.11}Al_{0.01}O_2$ with a stable activation process has a lower increment in the cation disorder and a better local structural retentivity after 300 cycles and, consequently, shows a superior cycle life.[322] A dry cobalt hydroxide coating on high-Ni cathodes, as shown in Fig. 10b, has not only reduced residual lithium contents but also leads to the formation of a Co-rich concentration gradient layer on the surface that suppresses Li leaching when in contact with water (Fig. 10b).[323] The SO_2-treated $LiNi_{0.85}Co_{0.10}Mn_{0.05}O_2$ (NCM85105) material is also found to be significantly thermally stable, demonstrating lower heat evolution upon thermal reactions with standard EC-EMC/LiPF$_6$ solutions by 12–20%, compared to the untreated material (Fig. 10c).[324]
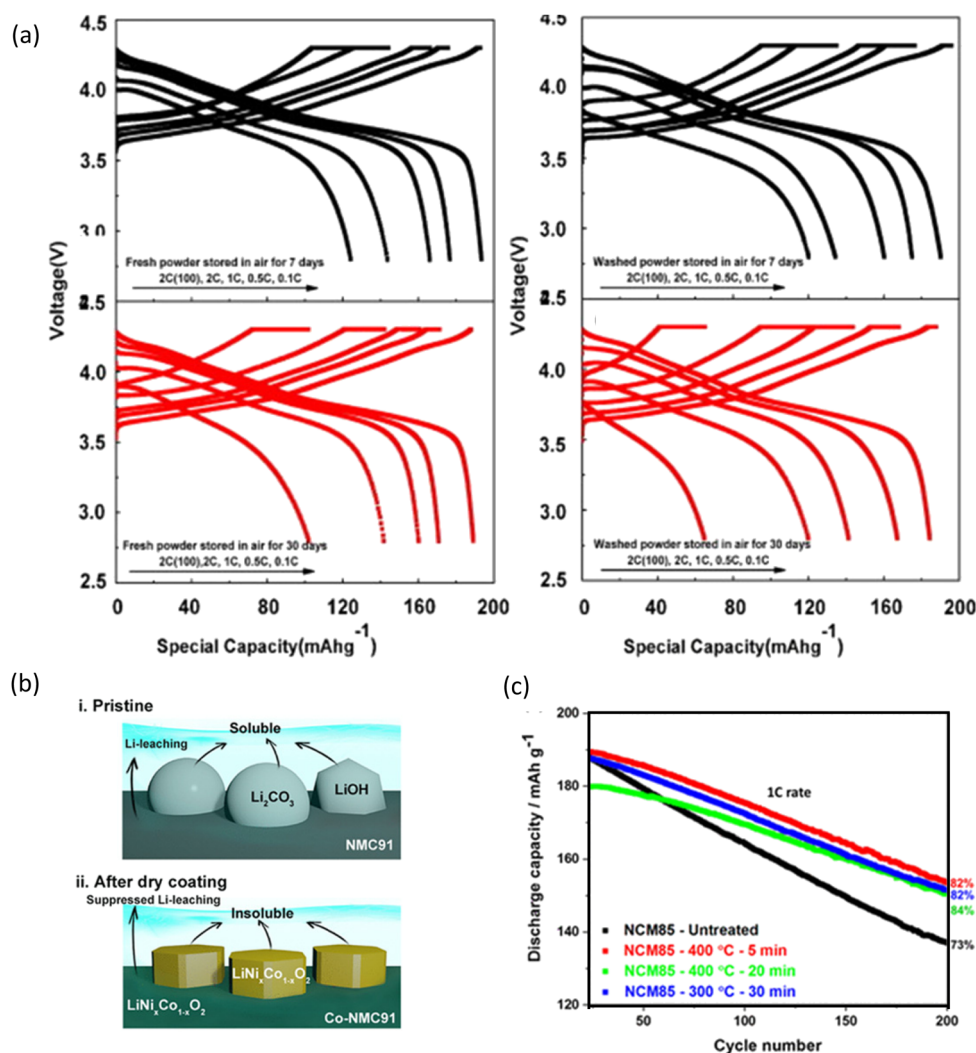
Fig. 10 Washing impact on the electrochemical performance: (a) first charge–discharge curves under different current densities and cycling performance of fresh and washed powders after storage in air for 7 and 30 days. Reprinted with permission from X. Xiong, Z. Wang, P. Yue, H. Guo, F. Wu, J. Wang and X. Li, *J. Power Sources*, 2013, **222**, 318.[320] (b) Approach towards the exaggeration of the LiOH content in residual lithium. Reprinted with permission from Y. Kim, H. Park, J. H. Warner and A. Manthiram, *ACS Energy Lett.*, 2021, **6**(3), 941–948.[276] (c) Electrochemical performance of NMC85 under different SO_2 treatments. Reprinted with permission Required from F. A. Susai, H. Sclar, S. Maiti, L. Burstein, O. Perkal, J. Grinblat, M. Talianker, S. Ruthstein, C. Erk, P. Hartmann, B. Markovsky and D. Aurbach, *ACS Appl. Energy Mater.*, 2020, **3**, 3609.[324]

Crystalline orientation

For industrial applications, single-crystal cathodes (SCCs) have numerous benefits over other forms including good crystallinity, high mechanical strength,[325] high reaction uniformity, small specific surface area, strong structural stability, and high thermal stability.[326,327] The rate performance of the single-crystal NCM333 is 10–15% more than that of polycrystalline NCM333, whereas the capacity retention of single-crystal NCM333 is enhanced by ~12% after 300 cycles at 0.5C.[328] The single-crystal NMC622 exhibits a pronounced improvement in rate performance, especially at high rates (~28.6% better at 5C and ~129% better at 10C) and has a comparable cycle performance to polycrystalline NMC622.[328] Studies carried out on single crystals of NMC811, $LiNi_{0.80}Mn_{0.15}Co_{0.05}O_2$ (NMC80155), and NCM85105 show that while a higher Ni content leads to overall increased reactivity, the presence of Mn provides a stabilizing effect on thermal, structural, and chemical properties.[329] Considering important observations on single crystals, researchers are putting efforts to understand the involved responsible phenomena[330,331] and working towards the use of surface engineering modification methods to further improve the electrochemical performance.[332–334]

Replacement of Mn ions

It is evidenced from the previous experimental research that a complete replacement of Mn ions with B[216] and W,[217] in Ni-rich cathode compositions, has also improved the electrochemical performance. When Mn is replaced with Ta $(Li[Ni_{0.90}Co_{0.09}Ta_{0.01}]O_2)$, a newly designed cathode (NCT) exhibits 90% capacity retention after 2000 cycles at full depth of discharge (DOD) and a cathode energy density $> 850\,W\,h\,kg^{-1}$.[335] $LiNi_{0.90}Co_{0.07}Mg_{0.03}O_2$ microspheres exhibit a high value of capacity (228.3 mA h g^{-1} at 0.1C) and almost 84.3% capacity retention after 300 cycles.[111]

Strategies for cost optimization and recovery

Co-free Ni-rich oxides: an approach towards cost-effectiveness

Considering the low abundance and high cost of Co,[189,336] efforts are made to design Co-free layered oxides by understanding the role of Co ions.[337,338] However, one has to compromise with cumulative capacity and other factors while designing such cathodes.[339,340] Various research groups around the globe are working effortlessly towards designing Co-free Ni-rich layered oxide cathodes by replacing Co ions with suitable ions.[341,342] This is clear from few studies on the development of $LiNi_{0.9}Mn_{0.05}Zn_{0.05}O_2$ (NMZ955) cathodes,[343,344] introduction of Mo Ni-rich oxides[345] and Co-free $LiNi_{0.9}Mn_{0.1}O_2$ with lattice Ge-doping and interface Li_4GeO_4-coating (NMGe).[346] Tan et al., designed a Co-free Ni-rich $LiNi_{0.96}Mn_{0.04}O_2$ cathode material (NM) by doping with Al and Zr.[347] The synthesized material exhibits better thermal and structural stability than that of the NM material. Lv et al. reported that the replacement of Co with Al and In/Sn prolongs the cycle life of the Ni-rich Co-free cathode ($InSn-LiNi_{0.85}Mn_{0.09}Al_{0.06}O_2$, InSn–NMA85) at a high voltage ≥ 4.5 V as well as a high temperature ($\geq 45\,°C$).[348] The search for Co-free cathodes is not limited to the Ni-rich materials but they are also adopted to optimize Li-rich NCM cathodes.[349,350]

Recovery, recycling and reuse of cathodes after cycling

With the rapid development of the EV industry, there is a significant increase in the number of spent power batteries. The recycling of such batteries is profitable and necessary not only to eliminate environment pollution but also to reduce the resource use.[351,352] Thus, many efforts are made by the scientific community in this direction. In this context, a novel green process involving natural L-tartaric acid leaching is reported for the sustainable recovery of Mn, Li, Co, and Ni from spent LIBs. For the first stage, the activation energies (E_{as}) for the leaching of Mn, Li, Co, and Ni were 66.00, 54.03, 58.18, and 73.28 kJ mol^{-1}, respectively. For the second stage, the E_{as} values for the leaching of Mn, Li, Co, and Ni were 55.68, 53.86, 58.94, and 47.78 kJ mol^{-1}, respectively.[353] After single-stage leaching, the spent NCM recovery using $NH_3–(NH_4)_2CO_3–Na_2SO_4$ leaching has exhibited 79.1% of lithium, 86.4% of cobalt, and 85.3% of nickel. For multistage leaching, almost all metals (98.4% of the lithium, 99.4% of the cobalt, 97.3% of the nickel) could be leached and a high-purity ($>99\%$) $MnCO_3$ product was simultaneously obtained.[354] A dual-function electro-oxidation strategy is helpful for highly selective recovery of Li$^+$ from spent NCM batteries. Under the optimal conditions, the selective recovery rate of Li$^+$ exceeded 99%. After electro-oxidation, the electrolyte can be directly heated and concentrated to obtain Li_2CO_3.[355]

Perspectives

Fig. 11 summarises the various strategies that are helpful to optimize the NCM cathode materials. Though these strategies are helpful to design cathodes, complexities affecting the battery performance must be overcome to scale up the manufacture of lithium-ion batteries. The pre-preparation process, extreme environments, defective quality, and the risk of lithium volatilization are obstacles. The development of economic and safe LIBs is the need of the hour. Solid-state electrolytes offer a solid interface that mitigates safety risks associated with nickel-rich cathodes. This could lead to the development of safer, more dependable lithium-ion batteries that have an enhanced energy density. Cobalt-free NCM versions are the subject of research to reduce supply chain difficulties and environmental hazards. The development of nickel-rich, cobalt-free NCM batteries marked a significant advancement in lithium-ion battery technology. Although cobalt increases battery efficiency, its scarcity and the geopolitical issues associated with its extraction provide challenges for the environment, ethics, and supply chain. NCM batteries without cobalt provide a sustainable alternative that alleviates these concerns while maintaining the performance and energy density. In order to overcome
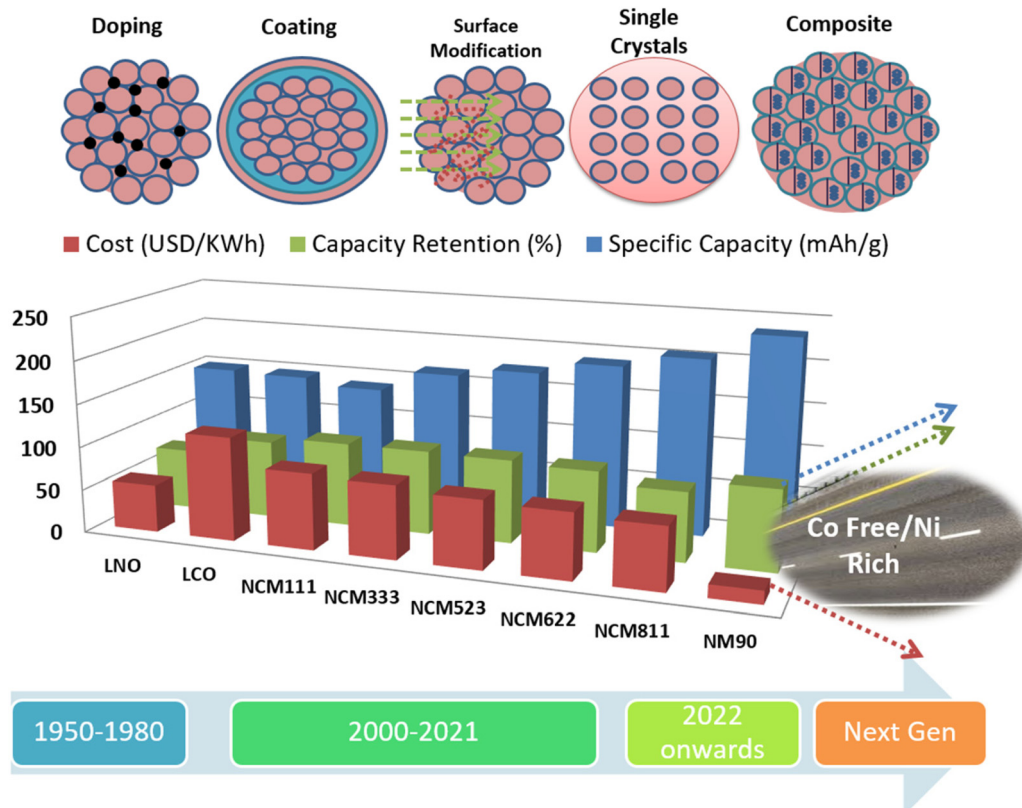
Fig. 11 Strategies for the optimization of NCM cathode materials.

these obstacles, creative mitigation techniques and a thorough understanding of the underlying degradation mechanisms are needed. To ensure compatibility and optimal battery performance, cobalt-free NCM cathodes must be integrated carefully with other battery components, such as electrolytes and anodes. To improve the performance and safety of cobalt-free NCM batteries, research is done to optimize the electrolyte composition, electrode/electrolyte contact, and cell design. To sum up, nickel-rich, cobalt-free NCM batteries show great potential for the development of lithium-ion battery technology. To overcome lingering obstacles and realize the full potential of these high-performance and sustainable energy storage systems, extensive research and innovation in this area are necessary.

Conclusions

This review presents an overview of the opportunities and problems associated with the use of Ni-rich NCM cathodes. Because of the layered structure of these cathodes, intercalation processes result in delithiation and lithiation. High cumulative capacity of the NCM cathode can be achieved by increasing the Ni content, but capacity retention and thermal stability are reduced as a result. This article critically elaborates the effects of doping, coating, morphology, and crystalline orientation on the electrochemical performance of LIBs based on the NCM cathode. These tactics assist in optimizing the Li/Ni disorder

and thermal stability in addition to controlling capacity retention. The design of Co-free, Ni-rich NCM cathodes is in progress in order to address the manufacturing cost and demand of LIBs. Furthermore, these batteries may be more successful if different elements are recovered from spent batteries. In the same way, the creation of a thin-film, Co-free, Ni-rich NCM cathode may continue down the path of environmentally friendly technology and a pollution-free atmosphere at a low cost of transportation.

Author's contribution

JPS & SL – conceptualization & funding; JPS – manuscript preparation; HD, AD, AS & WCL – data acquisition & manuscript view; KHC & SL – supervision; manuscript view.

Data availability

Data will be made available on request.

Conflicts of interest

The authors declare no competing financial interests.

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