Coating – A Potent Method to Enhance Electrochemical Performance of Li(NiₓMnᵧCo₂)O₂ Cathodes for Li-ion Batteries

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Abstract

Layered lithium nickel manganese cobalt oxides, Li(NiₓMnᵧCo₂)O₂ where x + y + z = 1 (NMCs), have been studied extensively due to their higher capacity, less toxicity and lower cost compared to LiCoO₂. However, widespread market penetration of NMCs as cathodes for Li-ion batteries (LIBs) is impeded by their poor capacity retention and low rate capability. Coatings provide an effective solution to these problems. This article focuses on review of the recent advancements in coatings of NMCs from the mechanism viewpoint. This is the first time that coatings on NMCs are reviewed based on their functionalities and mechanisms through which the electrochemical properties and performance of NMCs have been improved. To provide a comprehensive understanding of the functions and mechanisms offered by coatings, the following functions and mechanisms are reviewed individually: (i) scavenging HF in the electrolyte, (ii) scavenging water molecules in the electrolyte and thus suppressing HF propagation during charge/discharge cycles, (iii) serving as a buffer layer to minimize HF attack on NMCs and suppress side reactions between NMCs and the electrolyte, (iv) hindering phase transitions and impeding loss of lattice oxygen, (v) preventing microcracks in NMC particles to keep participation of most NMC material in lithiation/de-lithiation, and (vi) enhancing the rate capability of NMC cathodes. Finally, the personal perspectives on outlook are offered with an aim to stimulate further discussion and ideas on the rational design of coatings for durable and high performance NMC cathodes for the next generation LIBs in the near future.

Keywords: Li-ion batteries, layered lithium nickel manganese cobalt oxides, coating, NMCs.

Introduction

LiCoO₂ is the major cathode material for Li-ion batteries (LIBs) since 1992 because it excels in many electrochemical properties [1]. However, the price and resource of Co have always been a concern since the early stage of using LiCoO₂ [1]. This concern is attested by the fact that the price of Co has nearly tripled over the past few years due to increased demand from LIBs. According to InvestmentMine [2], the Co price has increased from $25/lb to $40/lb in one year (from May 2017 to April 2018). In contrast, the prices of Ni and Mn metals are relatively low in comparison to Co, increasing from $4/lb to $7/lb for Ni and staying at ~$2/lb for Mn during the same period [2]. Because of the cost and resource advantages for Ni and Mn, significant research efforts have been devoted to the development of transition metal oxide (TMO) intercalation materials containing little or no Co in the last 15 years. For example, Li(NiₓMnᵧCo₂)O₂ where x + y + z = 1 (NMC) have been studied extensively since 1999 [3-20], and recently NMCs with very high Ni contents such as Li(Ni₀.₉₅Mn₀.₀₂₅Co₀.₀₂₅)O₂ have been investigated as well [21].

The enormous interest in NMCs as cathode materials for LIBs is also reflected in the inclusion of NMCs in many review articles [22-25]. Furthermore, there are multiple review articles dedicated to layered lithium nickel manganese cobalt oxides [16, 26-28]. The great potential of NMC materials for LIBs is further evidenced by the recent adoption of Li(Ni₀.₉₀Mn₀.₀₅Co₀.₀₅)O₂ (NMC333) for commercial use by Boeing Corporation [29]. There are also several review articles devoted to surface modification strategies to improve electrochemical properties of cathode materials including NMCs [29-32]. It should be pointed out that while Refs. 30 to 32 cover a wide range of cathode materials, Ref. 29 is a review article dedicated to surface coating of NMCs. Furthermore, Ref. 29 has conducted a very nice review in discussing the effects of various coating materials on electrochemical performance of NMCs. The effects of coatings are categorized in terms of the nature of materials (such as electron-conductive materials, ion-conductive materials, polymer materials, amorphous materials, etc.) [29].

The present article focuses on review of the recent advancements in coatings of NMCs for LIBs from the
mechanism viewpoint. This is the first time that coatings on NMCs are reviewed based on their functionalities and mechanisms through which the electrochemical properties and performance of NMCs have been improved. The article will start with a summary of degradation mechanisms of NMC cathodes, followed by coating methods and then functions and mechanisms of various coatings in improving electrochemical properties and performance of NMCs. Finally, the personal perspectives on outlook are offered with an aim to stimulate further discussion and ideas on the rational design of coatings for durable and high performance NMC cathodes for the next generation LIBs in the near future.

Degradation mechanisms of NMCs

In spite of their advantages in low costs and high specific capacities over LiCoO$_2$ cathodes, NMCs suffer from capacity decay over charge/discharge cycles [3-21, 33-46]. Thus, it is important to identify the capacity decay mechanisms and develop effective methods (such as coatings) to solve the capacity decay problem. This is particularly important for electric vehicle applications where over 1,000 cycles with high specific capacities at the cell level (> 350 W h kg$^{-1}$) are required. As such, degradation mechanisms and coating of NMCs have been studied intensively in the last 15 years by many researchers [3-21, 33-46]. Based on the battery operational procedure, the degradation of NMCs can be divided into several stages: (i) when the cathode is immersed in the carbonate electrolyte before charge/discharge cycles, (ii) during the first charge process, (iii) in the subsequent charge and discharge cycles, and (iv) during calendar aging. In what follows, degradation mechanism(s) in each stage are discussed succinctly.

Degradation during soaking

Although majority of research is devoted to capacity decay and voltage fade during charge/discharge cycles [3-21, 33-46], the degradation of NMCs actually starts when the NMC cathode is in contact with the liquid electrolyte during the soaking period. A recent study using total-reflection X-ray absorption spectroscopy (XAS) [47] has unambiguously revealed that when LiCoO$_2$ electrode is in contact with the carbonate electrolyte during soaking, surface Co$^{3+}$ ions are reduced to Co$^{2+}$ ions by the electrolyte with the formation of a Li$_2$Co$_{1-x}$O$_x$ (x < 1) layer of ~3 nm and other reaction products of Li$_2$CO$_3$ and/or lithium alkyl carbonate. The Li$_2$Co$_{1-x}$O$_x$ (x < 1) compound, which contains Co$^{2+}$ ions through the replacement of a Li$^+$ ion by a Co$^{2+}$ ion and another Co$^{3+}$ located at the regular Co$^{3+}$ site, is oxidized to become Co$_2$O$_3$ or other oxides in the first charge process but with insufficient reduction in the subsequent discharge process. As a result, some storage capacity of LiCoO$_2$ has been lost even before charge/discharge cycles begin. Such capacity degradation is not just limited to LiCoO$_2$ which has the same layered crystal structure with space group of $R3\bar{m}$ as NMCs. Indeed, a study utilizing XAS, scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) has revealed that due to the electrode-electrolyte reactivity a surface reduced layer is formed on Li(Ni$_{0.5}$Mn$_{0.5}$Co$_{0.4}$Ti$_{0.2}$)O$_2$ when the Ti-doped NMC is in contact with the electrolyte during soaking [34]. It is known that at the fully discharged condition the Ni, Mn and Co ions in NMCs are present in +2, +4 and +3, respectively [34]. However, Mn and Co ions are present in < +4 and < +3 states in the surface reduced layer [34]. This is similar to LiCoO$_2$ which exhibits reduction of surface Co$^{3+}$ to Co$^{2+}$ during soaking, leading to decreased specific capacity even before the charge/discharge cycle begins [47]. It is also found that the surface reduced layer formed during soaking of the Ti-doped NMC is similar to the one observed during high-voltage cycling although the former is thinner than the latter [34].

Degradation in the first charge process

Most layered TMO intercalation materials are synthesized in the fully lithiated state and thus the first electrochemical operation is charging. However, degradation occurs in the very first charge process, leading to the loss of the first discharge capacity. For example, as shown in Fig. 1, with the aid of transmission electron microscopy (TEM) along with electron energy loss spectroscopy (EELS) Hwang, et al. [33] have revealed that phase transition from the initial layered structure (space group $R3m$) to the disordered spinel structure ($Fd\bar{3}m$) occurs on the surface of LiNi$_{0.5}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles when it is charged to 3.9 V (vs. Li/Li$^+$) at the C/10 rate to form Li$_{0.5}$Ni$_{0.5}$Co$_{0.15}$Al$_{0.05}$O$_2$ in the first charge process after soaking [33]. This study demonstrates that even a mild charge at room temperature can induce structural instability at the surface region of layered TMO intercalation materials. When the layered TMO is overcharged (i.e., extraction of 90% Li), the thickness of surface phase transition zone increases, making the core of the particle a mixed phase of the layered and spinel structures while the outermost surface being transformed to the rock-salt phase (Fig. 1) [33]. A separate study using EELS [48] has obtained similar results, observing the formation of a thin cobalt oxide layer (changing gradually from the surface CoO to the sub-surface Co$_3$O$_4$) on the surface region of LiCoO$_2$ particles when LiCoO$_2$ is only charged to 40% (namely at ~4.1 V vs. Li/Li$^+$). This surface layer of CoO-like phases reaches ~5 nm thick if the first charge reaches 60% [48]. In addition, the surface layer of CoO-like phases is followed by an oxygen-deficient layer with composition of Li$_2$Co$_{2-x}$O$_{3-\delta}$ (0 < x ≤ 0.05, 0 < $\delta$ ≤ 0.67) before reaching the center of stoichiometric LiCoO$_2$ [48]. Thus, not only has surface phase transition occurred at mild charging conditions, but also the loss of lattice oxygen has taken place in the first charge process [48].
Degradation during charge/discharge cycles

Significant studies have been conducted to investigate capacity decay and voltage fade of NMCs during charge/discharge cycles [3-21, 33-46, 49-51], and many degradation mechanisms have been reported. These mechanisms include (i) phase transitions [8, 9, 11, 12, 33, 49], (ii) loss of lattice oxygen [5, 49], (iii) transition metal dissolution [50], (iv) electrolyte decomposition [34, 47, 48], (v) formation of insulating phases at the particle surface [7, 8, 10], (vi) particle cracking [4, 51], and (vii) cation mixing [13, 14]. Several features should be noted for these decay mechanisms. First, many of these decay mechanisms take place simultaneously. For instance, with the aid of time-resolved XRD coupled with mass spectroscopy (MS), Bak, et al. [49] have detected oxygen gas release when the first phase transition from the layered structure to the spinel structure takes place during heating of LiNi0.8Al0.2O2. The two events occur simultaneously even though a change in the oxygen stoichiometry is not required for the phase transition [49]. Second, most of the decay mechanisms start at the particle surface. For example, a detailed TEM analysis has revealed that changes from the layered structure to a spinel-like structure occurs on the surface of Li(Ni0.85Mn0.15)O2 while the particle interior remains intact after 100 charge/discharge cycles [8]. Furthermore, as mentioned before, phase transition from the initial layered structure to the disordered spinel structure also occurs on the surface of LiNi0.8Al0.2O2 particles even in the first charge process [33]. Third, the extent of decay mechanisms is a function of the NMC composition. It has been established that increasing the Ni content in NMCs results in an increase in the specific discharge capacity, but the capacity retention decreases [7, 8]. For example, it has been shown that NMC333 has a low specific capacity (~145 mA h g⁻¹), but good cycle stability. In contrast, Li(Ni0.8Mn0.1Co0.1)O2 (NMC811) has a high specific capacity (~195 mA h g⁻¹), but poor cycle stability [8].

Several factors have contributed to the poor capacity retention of Ni-rich NMCs. These include: (i) Ni-rich NMCs have very active catalytic surfaces due to unstable Ni⁴⁺ when charging these materials, causing the electrolyte oxidation and formation of an insulating NiO phase at the particle surface [7, 8, 10], (ii) Ni-rich NMCs are also prone to have phase transition from hexagonal to monoclinic (H1 → M), monoclinic to hexagonal (M → H2) and hexagonal to hexagonal (H2 → H3) [8, 11, 12], and (iii) Ni-rich NMCs also exhibit significant cation mixing because of the similar sizes of Li⁺ and Ni²⁺ ions (i.e., 0.76 Å for Li⁺ vs. 0.69 Å for Ni²⁺) [13, 14]. Finally, the extent of decay mechanisms is also a strong function of electrochemical operation conditions. It is well known that NMCs exhibit accelerated capacity decay when the upper cutoff voltage is high (e.g., exceeding 4.3 V vs. Li/Li⁺) [5, 41, 43, 50]. This phenomenon is due to the enhanced electrolyte oxidation, surface phase transition, loss of lattice oxygen, fracture of NMC particles, and transition metal dissolution when the upper cutoff voltage is high [5, 41, 43, 50, 51].

Degradation during calendar aging

It is a common practice to distinguish calendar aging and cycle degradation of LIBs [52]. Calendar aging refers to the cell degradation during storage, i.e., without applying a current to a cell. It is found that the degree of cell degradation during storage depends mainly on the state of charge (SOC) and storage temperature [36, 52, 53]. Both increasing SOC and raising storage temperature result in accelerated cell degradation [36, 52, 53]. The loss of the cell capacity during calendar aging is predominately attributed to (i) gradual growth of surface reaction layers at both the anode and cathode which leads to irreversible consumption of cyclable lithium, (ii) transition metal dissolution of NMCs resulting in loss of the active cathode material, (iii) cracking and loosening of NMC particles causing some loss of the active material, and (iv) oxidation of the electrolyte at the cathode leading to an increase in the ohmic resistance of the electrolyte [52, 55]. All of these degradation mechanisms are very similar to those observed during charge/discharge cycles. Further, they all start at the electrode/electrolyte interface and thus can all be mitigated through appropriate coatings.

Methods for forming coatings

Methods to form coatings on NMCs can be broadly classified into two categories: one being in-situ coating formation during synthesis of NMC materials and the other being the formation of coating after synthesis of NMCs (i.e., post-synthesis coating formation). Examples of in-situ coating formation are activated carbon-assisted synthesis of carbon-coated NMCs [56], polymer-
hydrocarbon oil solution-assisted synthesis of carbon-coated NMC [57], and microwave-assisted synthesis of carbon-coated LiCoO$_2$ and LiNiO$_2$ [58]. In the activated carbon-assisted synthesis [56], porous activated carbon is used as an absorbent to absorb the liquid reactants containing species to form NMC333. The activated carbon after the reactant infiltration is subjected to 450 °C holding for 2 h to form NMC333 and then 850 °C holding for 10 h in air to obtain highly crystalline NMC333 and remove part of the carbon. The carbon-coated NMC333 obtained via this approach exhibits high rate capability and improved cycle stability when compared with pristine NMC333 [56]. To form carbon-coated NMC using the polymer-hydrocarbon oil solution-assisted synthesis [57], a NMC-forming solution containing Li, Ni, Mn and Co salts is added dropwise to a polymer-hydrocarbon oil solution at room temperature. The resulting gel is then heated to 850 °C in air or high purity argon to form crystalline NMC and carbon coating simultaneously. The obtained carbon-coated NMC can deliver 190 mA h g$^{-1}$ at 0.2C for 10 cycles [57]. Microwave-assisted synthesis of carbon-coated TMO layered cathodes appears to offer the best capacity retention over charge/discharge cycles among NMCs, with NMC012 and NMC622 coatings [81] among others. Other wet-chemical methods include co-precipitation [20, 21, 82-84], hydrothermal [85], solvothermal [86, 87], spray drying [88], polymer solution coating [89], and chemical reaction in the subsequent heating process [6, 17, 19, 90-92]. These wet-chemical methods normally result in thicker and less uniform coatings when compared with ALD; however, they typically provide more uniform coatings than dry-process coating methods which are generally composed of two processing steps: (i) mechanical mixing and (ii) high-temperature treatment. Examples of dry-process coatings are mixing of NMC333 with graphene to form graphene-coated NMC333 [93], mixing of (Ni$_{0.5}$Mn$_{0.5}$O$_2$)$_2$OH with MoO$_3$ to form Li$_2$MoO$_4$-inlaid NMC352 [94], and mixing of NMC622 with Al-based MOF to form MOF-derived Al$_2$O$_3$-coated NMC622 [95]. Dry-process coatings are normally discrete and non-uniform.

It should be emphasized that the quality and performance of coatings on NMCs depend strongly on coating methods and conditions. Al$_2$O$_3$ is a popular coating used for NMCs and its effect is drastically altered by coating conditions. Fig. 3 shows that sol-gel Al$_2$O$_3$ coating with 0.25 wt. % is better in providing high specific capacity and rate capability for Li-rich NMC than heavy coatings (0.5 wt. % and 1.25 wt. % Al$_2$O$_3$ coatings [75]).

There are a large number of the post-synthesis coating formation methods which can be further divided into several sub-categories, including atomic layer deposition (ALD), chemical vapor deposition (CVD), wet-chemical methods and dry-process methods. ALD, known for its capability to deposit conformal thin films with atomic thickness [4, 59-62], has been successfully used to form various coatings such as Al$_2$O$_3$ [4, 59, 61-66], ZrO$_2$ [67-69], ZnO [70], TiO$_2$ [4, 64, 68, 71], MgO [72] and Al$_2$O$_3$-Ga$_2$O$_3$ [73] on NMCs with significant improvements in electrochemical properties. However, ALD requires expensive equipment and thus less expensive coating methods such as CVD [74], wet-chemical methods [75-90] and dry-process methods [19, 91, 92] have also been actively investigated. Sol-gel coating is one of the widely studied wet-chemical methods and has been successfully used to deposit Al$_2$O$_3$ [75, 76], TiO$_2$ [77], LiAlO$_2$ [78], Li$_2$MnO$_3$ [79], LiVO$_3$ [80], and Li$_{33}$La$_{2/3}$TiO$_3$ coatings [81] among others. Other wet-chemical methods include co-precipitation [20, 21, 82-84], hydrothermal [85], solvothermal [86, 87], spray drying [88], polymer solution coating [89], and chemical reaction in the subsequent heating process [6, 17, 19, 90-92]. These wet-chemical methods normally result in thicker and less uniform coatings when compared with ALD; however, they typically provide more uniform coatings than dry-process coating methods which are generally composed of two processing steps: (i) mechanical mixing and (ii) high-temperature treatment. Examples of dry-process coatings are mixing of NMC333 with graphene to form graphene-coated NMC333 [93], mixing of (Ni$_{0.5}$Mn$_{0.5}$O$_2$)$_2$OH with MoO$_3$ to form Li$_2$MoO$_4$-inlaid NMC352 [94], and mixing of NMC622 with Al-based MOF to form MOF-derived Al$_2$O$_3$-coated NMC622 [95]. Dry-process coatings are normally discrete and non-uniform.

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![Fig. 2. Specific capacity as a function of cycle number at different C rates for: (a) carbon-coated LiCoO$_2$, and (b) carbon-coated LiNiO$_2$. Reproduced with permission [58] @ 2015, Springer Nature.](image1)

![Fig. 3. Rate capability and cyclability of Al$_2$O$_3$-coated Li[Li$_{0.39}$Ni$_{0.39}$Co$_{0.2}$Mn$_{0.2}$]O$_2$ half-cells at 25 °C with varying Al$_2$O$_3$ contents. Reproduced with permission [75] @ 2005, American Chemical Society.](image2)
Fig. 4 depicts how the thickness of AlPO₄ coating alters the cyclability and rate capability of Li[LiₓFe₀.₁₅Ni₀.₅Mn₀.₃]O₂ cathode material as a function of the AlPO₄ coating thickness. AC-3, AC-5 and AC-7 samples stand for Li[LiₓFe₀.₁₅Ni₀.₅Mn₀.₃]O₂ with 3, 5 and 7 wt. % AlPO₄ coating, respectively. Reproduced with permission [96] @ 2015, American Chemical Society.

Carbon coating is another good example illustrating how coating conditions affect the coating quality. Carbon coating is typically formed via pyrolysis of carbon precursors such as table sugar [91], citric acid [92], resorcinol-formaldehyde polymer [97], sucrose [98], and starch [98]. Carbon will be oxidized and become gaseous CO and CO₂ at high temperature in air. However, NMCs can be reduced by carbon at high temperature if coating process is conducted in inert atmosphere. To address these conflicting requirements, coating process is normally carried out in air with low pyrolysis temperature and short holding time, such as 350 °C for 1 h [91] or 600 °C for 0.5 h [92, 98]. However, low pyrolysis temperature typically results in amorphous carbon coatings with low electronic conductivity. As a result, improvement in the electrochemical performance of carbon-coated NMCs is marginal [91, 92, 97, 98]. Alternatively, special coating technique such as microwave-assisted synthesis [58] can be employed which results in carbon-coated LiCoO₂ and LiNiO₂ with remarkable capacity retention over 1,500 charge/discharge cycles (Fig. 2).

In short, coatings on NMCs have been formed via a wide range of methods and their qualities and functionalities depend on coating methods and conditions. Novel coating methods, coating process optimization, and coating composition design are still urgently needed to form high quality, multi-functional coatings so that the cycle stability, specific capacity and rate capability of NMCs can be enhanced simultaneously. The specific directions and challenges for future efforts will be discussed in Section V: Summary and Outlook after the discussion of the functions and mechanisms of coatings below.

**Functions and mechanisms of coatings**

As discussed in Section II, there are many degradation mechanisms taking place in NMCs and many of them occur simultaneously. As such, a coating can often address several decay mechanisms simultaneously and provide multiple functions to improve the electrochemical properties and performance of NMCs. Nevertheless, in what follows the individual function and mechanism offered by coatings will be described first and then coatings with multiple functions will be discussed.

**Scavenging HF in the electrolyte and minimizing HF attack on NMCs**

One of the major functions for amphoteric metal oxide coatings (such as Al₂O₃, TiO₂, ZrO₂, and ZnO) and phosphate coatings (LiPO₄ and AlPO₄) is to work as a HF scavenger and thus reduce the HF attack on NMCs. The mechanism of such a function can be illustrated using Al₂O₃ coating. It is known that LiPF₆-based electrolyte always contains a small amount of water which can cause breakdown of the electrolyte accompanying with HF generation [75]. The breakdown of LiPF₆ is proposed to be as follows [99, 100]:

\[
\text{LiPF}_6 \leftrightarrow \text{LiF} + \text{PF}_3 \quad (1)
\]
\[
\text{PF}_3 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} \quad (2)
\]
\[
\text{POF}_3 + 3\text{Li}_2\text{O} \rightarrow 6\text{LiF} + \text{P}_2\text{O}_5 \quad (3)
\]
The generated HF attacks the NMC leading to dissolution of the NMC surface into the electrolyte, whereas LiF is deposited on the surface of the NMC resulting in an increased impedance of the cell [75]. In the presence of an Al₂O₃ coating, the cycled electrolyte is found to contain less HF than the cell without Al₂O₃ coating, indicating that propagation of HF is suppressed by the Al₂O₃ coating [75]. In other words, Al₂O₃ coating scavenges the acidic HF species from the electrolyte, and the following reactions have been identified to be the mechanism for Al₂O₃ as a HF scavenger [75].

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 2\text{HF} &\rightarrow \text{Al}_2\text{O}_2\text{F}_2 + \text{H}_2\text{O} \\
\text{Al}_2\text{O}_2\text{F}_2 + 2\text{HF} &\rightarrow \text{Al}_2\text{OF}_4 + \text{H}_2\text{O} \\
\text{Al}_2\text{OF}_4 + 2\text{HF} &\rightarrow 2\text{AlF}_3 + \text{H}_2\text{O}
\end{align*}
\]

The insulating Al₂O₃ layer also acts as a protecting layer for the NMC against HF attack [75]. Thus, Al₂O₃ coating has served two major functions: one is to act as a HF scavenger to suppress HF propagation and the other is to serve as a protecting layer against HF attack and thus mitigate dissolution of the NMC surface into the electrolyte.

**Scavenging water in the electrolyte and reducing HF generation**

It has been reported that Li₃PO₄ coating scavenges water molecules in the electrolyte with the following reaction [17].

\[
\text{Li}_3\text{PO}_4 + \text{H}_2\text{O} = \text{Li}_3\text{H}_2\text{PO}_4 \text{ (or PO}_3\text{H}_2\text{)} + \text{Li}_2\text{O}
\]

Removing residual water from the electrolyte is important because it suppresses the reaction between PF₅ and H₂O which creates HF and POF₃, as shown in Reaction (2). As mentioned in Section 4.1, Li₃PO₄ coating also scavenges HF in the electrolyte to suppress HF propagation during charge/discharge cycles. The scavenging mechanism for Li₃PO₄ coating is proposed to be [17]

\[
\text{Li}_3\text{PO}_4 + \text{HF} = \text{Li}_3\text{H}_2\text{PO}_4 \text{ (or PO}_3\text{H}_2\text{)} + \text{LiF}
\]

This reaction is similar to Reaction (7), but directly reduces HF concentration in the electrolyte, thereby minimizing HF attack on NMCs [17].

** Suppressing side reactions between NMCs and the electrolyte**

Almost all coatings (such as Al₂O₃, ZrO₂, MgO, TiO₂, V₂O₅, Li₃PO₄, AlPO₄, LiAlO₂, LiVO₃, AlF₃, etc.) that are chemically and electrochemically stable with the carbonate electrolytes have this function. As discussed in Sections 2.1 and 2.2, the surface of NMCs is reduced by the electrolyte during soaking and in the first charge process [34, 47, 48]. Coatings can form a physical barrier to prevent the direct contact between the electrolyte and the reactive transition metal (TM) ions in high oxidation states (such as Co⁶⁺ and Ni⁴⁺), thereby suppressing side reactions between NMCs and the electrolyte [101, 102]. Coatings can also function as a “buffer” layer to decrease the reactivity of evolved oxygen species during high voltage charge, thereby minimize electrolyte oxidation [101, 102].

Our recent study [103] has clearly revealed that LiAlO₂/Al₂O₃ coating can impede side reactions between nano-LiCoO₂ particles and the carbonate electrolyte during soaking and in the first charge process, leading to significant enhancement in the first discharge capacity. As shown in Fig. 5a, the first discharge capacity of nano-LiCoO₂ has been improved by 15% with 21 wt. % LiAlO₂/Al₂O₃ coating. Furthermore, this enhanced first discharge capacity is retained in the subsequent charge/discharge cycles, reflecting the potent effect of LiAlO₂/Al₂O₃ coating on capacity retention over cycles. In fact, after 45 cycles the specific capacity of 21 wt. % LiAlO₂/Al₂O₃-coated nano-LiCoO₂ is 100% higher than that of pristine nano-LiCoO₂ (Fig. 5a). In addition, if the weight of the inactive LiAlO₂/Al₂O₃ coating is included in the calculation of the specific capacity (Fig. 5b), pristine nano-LiCoO₂ exhibits the highest specific capacity for the first two cycles, but 21 wt. % LiAlO₂/Al₂O₃-coated nano-LiCoO₂ has the highest specific capacity for all of the remaining cycles. This result unequivocally tells us that the improvement in the specific capacity of nano-LiCoO₂ provided by LiAlO₂/Al₂O₃ coating is so large that it outweighs the penalty of the weight of the inactive coating [103].

![Fig. 5.](image-url)

**Fig. 5.** The cyclability of various LiAlO₂/Al₂O₃-coated nano-LiCoO₂ cathode materials with 12 wt. % LiAlO₂/Al₂O₃, 17 wt. % LiAlO₂/Al₂O₃, and 21 wt. % LiAlO₂/Al₂O₃ coating in comparison with that of the pristine material: (a) the specific capacity is calculated based on the weight of LiCoO₂ only, and (b) the specific capacity is computed based on the weight of both LiCoO₂ nano-particles and LiAlO₂/Al₂O₃ coating.
As mentioned before, reducing side reactions also means minimization of electrolyte oxidation, which is very important for long-term cell performance. A recent study [104] reveals that AlPO3-coated LMR material (Li1.2Mn0.54Ni0.13Co0.13O2) has the highest specific capacity and the best capacity retention, followed by AlPO4-coated counterpart and finally pristine Li1.2Mn0.54Ni0.13Co0.13O2. The cycled half cells are examined and it is found that cell failure is correlated to “cell drying”, in which the electrolyte appears to have completely degraded [104]. Interestingly, when the cathodes from these cycled cells are harvested and placed into fresh cells, the cells resume their normal capacity, suggesting that the degraded electrolyte is the cause for failure [104]. AlBO3- and AlPO3-coated Li1.2Mn0.54Ni0.13Co0.13O2 exhibit better capacity retention and longer cycle life than pristine counterpart because these coatings have minimized electrolyte oxidation during charge/discharge cycles.

**Hindering phase transitions and loss of lattice oxygen**

It is known that layered TM oxide cathodes like NMCs and LMR cathodes are prone to phase transitions, particularly during high voltage charge and for layered TM oxides with high Ni contents [4, 8, 49, 101]. At high states of delithiation, metal redox potentials overlap with oxygen 2p energies leading to oxygen anion oxidation and molecular oxygen release [49]. The resulting oxygen vacancies could accelerate phase transition because they provide low-energy pathways for TM ions to migrate from TM layer to Li layer, leading to phase transitions from the layered structure to defect spinel and rock salt structures [4, 101]. Ni-rich NMCs are particularly prone to phase transitions because unstable and reactive Ni^{4+} ions tend to transform to more stable Ni^{2+} by moving from the octahedral sites to tetrahedral sites, concurrently accompanied by oxygen release [8]. Phase transition originates from the particle surface because the oxygen atoms in the surface structure lattice are extracted first during charge. Furthermore, surfaces are vulnerable to the attack by acidic species and the reduction by the electrolyte.

Since phase transitions start at the particle surface, many coatings have been found to be capable of suppressing or delaying phase transitions. For example, Li13La2/3TiO3-coated NMC622 particles exhibit prominent structural stability with phase transition only at the surface region while the inner region remains at the layered structure [81]. In contrast, pristine NMC622 particles have transformed from the layered structure to the spinel structure and finally to the rock-salt structure after the same charge/discharge cycles as Li13La2/3TiO3-coated counterpart [81]. Al2O3 coating has prevented NMC811 from phase transitions, whereas pristine NMC811 exhibits spinel structure transition at the surface of NMC811 particles [4]. Al2O3 coating has also been shown to suppress phase transitions for NMC333 particles [65]. Both Al2O3 [105] and Li3PO4 [106] coatings have prevented phase transitions of LMR cathodes, while AlF3 coating has delayed phase transition of LMR cathodes from the layered structure to the spinel-like structure [101].

Improvements in the structural stability of NMCs and LMR cathodes by coatings are likely accomplished via several mechanisms. First, surface coatings may restrict oxygen release at high voltages, thereby stabilizing the surface structure of NMCs and LMR cathodes [4]. Second, coatings suppress the attack by acidic species and significantly reduce the formation of host lattice vacancies and oxygen-deficient surfaces, leading to stabilization of the layered structure and delay of phase transitions to the defect spinel structure and eventually rock salt structure [101]. Third, even after the formation of the spinel-like phase at the surface of LMR cathode materials, coatings can still protect the spinel-like phase from the attack by the acidic species in the electrolyte, which allows reversible lithium
intercalation/de-intercalation in the spinel-like phase and thus mitigate capacity decay [101]. Finally, coatings can impede the reduction of reactive Ni\textsuperscript{3+} ions at the surface by the electrolyte and the concurrent oxygen release for Ni-rich NMCs, thereby suppressing phase transitions.

**Preventing microcracks in NMC particles**

Microcracks or particle disintegration have been observed in cycled NMCs and LMR cathodes [4, 51, 80]. Microcracking is associated with the large lattice strain due to volume expansion of phase transitions and the erosion from acidic species in the electrolyte [4, 80]. Volume expansion is particularly serious for Ni-rich NMCs because the unit cell volume expansion of NMCs increases with increasing Ni content at the same number of charge/discharge cycles [8]. Since coatings can hinder surface phase transitions and prevent the attack by the acidic species in the electrolyte, it is expected that coatings can avoid microcracking and particle disintegration of NMCs. This expectation is indeed confirmed by several studies [4, 51, 80]. Al\textsubscript{2}O\textsubscript{3} coating has been shown to prevent microcracking of NMC811 [4], while Li\textsubscript{3}PO\textsubscript{4} coating is effective in avoiding particle disintegration of Ni-rich NMCs [51]. LiVO\textsubscript{3} coating can preserve the clear grain edge at the surface of a LMR material (Li\textsubscript{12}Mn\textsubscript{0.5}Ni\textsubscript{0.13}Co\textsubscript{0.15}O\textsubscript{2}) [80].

Another possible mechanism for coatings to prevent microcracking of NMCs is mechanical constraint derived from the surface coating. Cho, et al. [107] applied a series of oxide coatings to LiCoO\textsubscript{2} particles and proved that the cycle stability of LiCoO\textsubscript{2} is correlated to the expansion of the lattice constant c of LiCoO\textsubscript{2} during delithiation. The latter in turn decreases as the fracture toughness of the coating increases [107]. Fig. 7 shows that ZrO\textsubscript{2}-coated LiCoO\textsubscript{2} has the best capacity retention, followed by Al\textsubscript{2}O\textsubscript{3} coating, then TiO\textsubscript{2} and finally B\textsubscript{2}O\textsubscript{3} coating. This order of capacity retention is in good agreement with the order of fracture toughness of the coatings, i.e. ZrO\textsubscript{2} > Al\textsubscript{2}O\textsubscript{3} > TiO\textsubscript{2} > B\textsubscript{2}O\textsubscript{3} [107]. As microcracking of NMCs is induced by volume expansion of phase transitions, mechanical constraint from coatings leading to zero-strain intercalation is likely to play a role in hindering microcracks of NMCs during cycles.

**Enhancing the rate capability of NMC cathodes**

The rate capability of NMCs have been improved by many coatings, which may not be a surprise for electronically conducting coatings (like carbon) [56, 74] or for ionically conducting coatings such as Li\textsubscript{3}PO\textsubscript{4} [17, 18], LiVO\textsubscript{3} [80], Li\textsubscript{2}La\textsubscript{0.1}TiO\textsubscript{3} [81], and conductive polymers [89]. However, the rate capability of NMCs has also been enhanced by non-conductive coatings like Al\textsubscript{2}O\textsubscript{3} [65, 75], TiO\textsubscript{2} [77], and MgO [72]. These results suggest that the surface reaction layer between the electrolyte and NMCs has very high resistance to ionic or electronic conduction. As a result, even a non-conductive coating like Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and MgO that retards side reactions between the electrolyte and NMC surface can offer better transport properties or lower charge transfer resistance. Indeed, if the thickness of a non-conductive coating is too large, the rate capability of the coated NMC will be lower than that of the uncoated counterpart [77], 1 wt. % TiO\textsubscript{2}-coated NMC622 has the highest rate capability, whereas 3 wt. % TiO\textsubscript{2}-coated NMC622 has the lowest rate capability and the uncoated counterpart has the intermediate rate capability [77]. Interestingly, if the thickness of a conductive coating is too large, the rate capability of the coated NMC or LMR material could become lower than that of the uncoated counterpart. This is demonstrated lately by Liu, et al. [80] who show that 5 wt. % LiVO\textsubscript{3} coating offers the best rate capability for Li\textsubscript{12}Mn\textsubscript{0.5}Ni\textsubscript{0.13}Co\textsubscript{0.15}O\textsubscript{2}, whereas 10 wt. % LiVO\textsubscript{3} coating has the worse rate capability than the pristine Li\textsubscript{12}Mn\textsubscript{0.5}Ni\textsubscript{0.13}Co\textsubscript{0.15}O\textsubscript{2}. This result suggests that long diffusion distance induced by a thick coating, even if it is an ionic conductor, could hurt the rate capability of NMCs.

**Multi-functional coatings**

The review above has revealed that most coatings have multiple functions in improving the electrochemical properties of NMCs. For example, as discussed previously, Al\textsubscript{2}O\textsubscript{3} coating has been demonstrated to be capable of scavenging HF in the electrolyte, serving as a buffer layer to minimize HF attack on NMCs and suppress side reactions between NMCs and the electrolyte, hindering phase transitions and impeding loss of lattice oxygen, preventing microcracks in NMC particles, and enhancing the rate capability of NMC cathodes. Li\textsubscript{3}PO\textsubscript{4} coating has one more function than Al\textsubscript{2}O\textsubscript{3}, i.e., it also scavenges water molecules in the electrolyte and thus suppresses HF propagation during charge/discharge cycles. However, not every coating is so versatile. A recent study [4] discovers that Al\textsubscript{2}O\textsubscript{3} ALD coating on NMC811 can prevent phase transitions at the NMC811 surface, whereas TiO\textsubscript{2} ALD coating cannot. As a result, Al\textsubscript{2}O\textsubscript{3}-coated NMC811 exhibit significant improvement in cycle stability, while TiO\textsubscript{2}-coated NMC811 displays poor cycle stability [4]. High resolution TEM analysis reveals that TiO\textsubscript{2} coating loses its distinct coating phase from the surface after cycling, indicating that TiO\textsubscript{2} coating is not stable with NMC811.

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**Fig. 7.** The cycle-life performance of ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, and B\textsubscript{2}O\textsubscript{3}-coated and uncoated LiCoO\textsubscript{2}. The cells were initially cycled at the rate of 0.1C, followed by 0.5C rate between 2.75 and 4.4 V (vs. Li/Li\textsuperscript{+}) at 21 °C (n: cycle number, x: discharge capacity). Reproduced with permission [107] @ 2001, Wiley.
during cycling and thus loses its function to suppress phase transitions at the NMC surface [4]. Therefore, the functionality of a specific coating on NMCs depends on the coating properties as well as its compatibility with NMCs.

A recent study [72] compares the electrochemical performance of MgO-, ZrO2- and Al2O3-coated NMC532 and finds that all ALD coatings exhibit multi-functionalities, i.e., improving capacity retention and rate capability simultaneously over uncoated NMC532. However, Al2O3 coating provides the best capacity retention, whereas MgO coating offers the highest rate capability. Thus, even though most coatings have multi-functionalities, some are more suitable for capacity retention and the others are more appropriate for high-rate applications.

Summary and outlook

Significant and rapid progress were made in understanding of the degradation mechanisms of NMCs in the last 15 years. Coatings have been investigated extensively as an effective approach to address degradation of NMCs during soaking and in the subsequent charge/discharge cycles. It is established that proper coatings can provide the following functionalities: (i) scavenging HF in the electrolyte, (ii) scavenging water molecules in the electrolyte and thus suppressing HF propagation during charge/discharge cycles, (iii) serving as a buffer layer to minimize HF attack on NMCs and suppress side reactions between NMCs and the electrolyte, (iv) hindering phase transitions and impeding loss of lattice oxygen, (v) preventing microcracks in NMC particles to keep participation of most NMC material in lithiation/de-lithiation, and (vi) enhancing the rate capability of NMC cathodes.

In spite of the aforementioned progresses, some major challenges still need to be overcome for widespread adoption of electric vehicles which demand additional improvements in the following areas. First, the specific capacity of NMCs needs to be enhanced to above 200 mA h g⁻¹. This is possible with Ni-rich NMCs because the initial specific capacity of NMCs increases with increasing Ni content [8, 9]. However, Ni-rich NMCs have poor cycle stability [8] and this problem needs to be solved before they can be embraced by the society. Second, the cost of batteries should be reduced drastically. A large portion of the battery cost is from Co element [1] and thus Ni-rich NMCs with little or no Co, if successful, can provide a solution to this problem. Third, the charge time of LIBs needs to be reduced because short charge time can enable long distance travel and remove a critical barrier to consumer acceptance of electric vehicles [108]. Coatings are expected to play a critical role in addressing these three challenges in the near future. Specifically, we anticipate the following coating research will attract significant attention in the next several years to address the challenges listed above.

Novel coating methods

Facile coating methods that can provide coatings with multi-functionalities will improve the performance of NMCs significantly. Recently, Jo, et al. [17] have proposed an interesting wet-chemical method to form Li3PO4 coatings on NMC622 by subjecting NMC622 powder to a H3PO4 solution treatment, followed by a heating treatment during which H3PO4 reacts with residual LiOH, Li2O and Li2CO3 on the surface of NMC622, as shown by Eqs. (9), (10) and (11) below. This coating method addresses two issues at the same time: (i) formation of a Li3PO4 coating and (ii) elimination or minimization of Li residuals on the surface of NMC622 [17].

\[3\text{LiOH} + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{Li}_3\text{PO}_4 + 3\text{H}_2\text{O} \quad (9)\]
\[3\text{LiOH} + \text{H}_3\text{PO}_4 \rightarrow \text{Li}_3\text{PO}_4 + 3\text{H}_2\text{O} \quad (10)\]
\[3\text{Li}_2\text{CO}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{Li}_3\text{PO}_4 + 3\text{CO}_2 + 3\text{H}_2\text{O} \quad (11)\]

It should be pointed out that removing residual LiOH, Li2O and Li2CO3 on the surface of NMCs is important because these Li residuals can cause gelation of the slurry in electrode preparation. Even when the electrode is successfully fabricated, they experience oxidative decomposition at high voltage, generating gases [16]. Therefore, it is essential to reduce the Li residuals to an acceptable level (< 3000 ppm) [16]. The Li3PO4-coated NMC622 exhibits much better capacity retention and higher rate capability than pristine NMC622 [17]. Furthermore, the Li3PO4-coated NMC622 is able to deliver 1,000 cycles at 1 C for charge and 2 C for discharge with only ~5% capacity loss, unequivocally demonstrating that the Li3PO4 coating formed through the H3PO4 treatment is very effective in mitigating the capacity decay of NMC622 over charge/discharge cycles [17].

Microwave-assisted synthesis [58] also deserves further investigation as this method has offered remarkable improvements for LiCoO2 and LiNiO2 (Fig. 2). However, to our knowledge this effective coating method has not been reported for NMCs yet. The advantage of this method is that it can form a carbon coating and limit particle growth at the same time during synthesis. However, the mechanism(s) for forming a high performance carbon coating through microwave-assisted synthesis remain to be studied if reproducible results and large scale production are desired.

Design of coating functionalities

Coatings with multi-functionalities by design are highly desirable and can be tailored to offer superior properties for specific applications. Efforts along this line have been made lately. Laskar, et al. [73] have used ALD to deposit an (Al2O3)1-x(Ga2O3)x coating on NMC532 and investigated the functions of coatings as a function of the Ga2O3 concentration in the coating (i.e., 25, 50 and 75 at. % Ga2O3). Ga2O3 is an electronic conductor and adjusting its concentration can tune the electrical conductivity of the coating [73]. Interestingly, pure
Al₂O₃ coating offers the best capacity retention in the cycle tests, while all mixed oxide-coated NMC532 have better capacity retention than pristine NMC532. For the rate tests, (Al₂O₃)₀.₃(Ga₂O₃)₀.₅-coated NMC532 has the best performance for 1C, 2C, 5C, 8C and 10C tests [73]. This study proves that coating composition can be tuned to enhance certain properties with little compromise in other properties for specific applications.

With a similar goal to tune the coating properties but using a very different approach, Liu, et al. [19] have deposited a Li₃PO₄-C composite coating on a LMR layered oxide (Li₁₂Mn₀.₅Ni₀.₅Co₁.₅O₄). In this composite coating Li₃PO₄ offers ionic conductivity, whereas carbon provides electronic conductivity [19]. The coating is deposited by first forming Li₃PO₄ coating via a wet-chemical method, followed by heating at 450 °C for 5 h in air. After the formation of Li₃PO₄ coating, the coated LMR layered oxide is dispersed in a N-methy pyrrolidone (NMP) suspension which contains well dispersed Super P particles. The mixture is then sonicated for 2 h and dried in vacuum at 110 °C. The dried powder is fired at 350 °C for 2 h to obtain Li₃PO₄-C coated LMR layered oxide particles [19]. It is found that Li₃PO₄-C coated LMR layered oxide has the best rate capability as well as the best capacity retention, followed by Li₃PO₄-coated counterpart with the uncoated counterpart being the worst performer [19]. This study demonstrates that it is possible to enhance multiple properties simultaneously if the coating composition is properly designed.

**Integration of coating and doping**

Ni-rich NMCs have the potential to offer high specific capacity cathodes at low cost. However, they have poor capacity retention over charge/discharge cycles [8]. Coatings can address decay mechanisms associated with surface-related degradation, as discussed in this article, but cannot solve the intrinsic structural instability issue of Ni-rich NMCs. It is known that Ni-rich NMCs exhibit phase transition from hexagonal to monoclinic (H₁ → M), monoclinic to hexagonal (M → H₂) and hexagonal to hexagonal (H₂ → H₃) when charged to 4.3 V vs. Li⁺/Li [8, 11, 12]. The phase transition from H₂ to H₃ occurs at near 4.3 V and induces rapid volume change, leading to capacity decay [8, 12]. Such phase transition is the intrinsic property of the material and difficult to be solved by coatings. However, doping can be an effective approach to address such an issue. For example, addition of 2 at. % Ga can improve the cycle stability of LiNiO₂ drastically because the well-known phase transition of LiNiO₂ from hexagonal to hexagonal (H₂ → H₃) when charged to 4.3 V vs. Li⁺/Li has been eliminated [109]. Therefore, by integrating coating and doping strategies it is possible to tackle all the challenges faced by NMCs. Studies along this direction are rare, but can attract significant attention in the near future.

In conclusion, we expect that coatings will remain to be a very active research area in the future and is indispensable for successful use of NMCs for high performance LIBs. In particular, novel coating methods, design and development of coatings with multifunctionalities, studies of synergistic effects of integration of coating with doping, and further development of fundamental understanding of the mechanisms of multi-functional coatings are expected to attract significant research efforts in the next several years. We are optimistic that through integration of coating and doping strategies, the best NMC material with high specific capacity, superior cycle life and excellent rate capability at low costs will be ready for revolution of LIBs. With the advancement in coatings, we will witness breakthroughs in NMC cathodes and the future blooming of LIBs as the energy storage solution for the future.

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