

Review

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# Research progress on the surface/interface modification of high-voltage lithium oxide cathode materials

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## Abstract

Lithium oxides are the most promising cathode candidates for high-performance lithium-ion batteries (LIBs), owing to their high theoretical capacity and average working voltage, which are conducive to achieving the ultimate goal of upgrading energy density. By raising the upper limit of the cutoff voltage, we may be able to further improve both the practical capacity and average voltage of lithium oxide cathodes. Unfortunately, the high-voltage operation of these cathodes results in significant challenges, namely, reduced surface structural stability and interfacial stability with electrolytes, thus degrading the electrochemical performance. Accordingly, surface/interface modification strategies, including surface coating, electrolyte regulation, binder design, and special surface treatments, are systematically summarized and comprehensively analyzed for high-voltage lithium oxide cathode materials in this review. Furthermore, the corresponding modification mechanisms are discussed in detail to better grasp the internal mechanisms for the enhanced electrochemical performance. Based on recent progress, we further propose predictable development directions for high-performance LIBs in future practical applications. This review provides new insights into various high-voltage lithium oxide cathodes and their universal surface/interface modification strategies towards advanced next-generation LIBs with high energy and power density and long cycle life.



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**Keywords:** Lithium-ion batteries, oxide cathodes, high-voltage operation, stability, surface/interface modification strategies

## INTRODUCTION

Lithium-ion batteries (LIBs) have attracted ever-increasing attention since they were first successfully commercialized by SONY in 1991. After decades of relentless exploration, LIBs are now considered the most promising energy storage systems for portable electronics (e.g., mobile phones) and electric vehicles (e.g., electric buses), owing to their excellent characteristics of high energy and power density, working voltage, and safety and long cycle life<sup>[1-3]</sup>. Persistent efforts are still needed to further develop next-generation advanced LIBs and fulfill the growing practical application requirements. Energy density is well known as an important parameter to evaluate battery performance and satisfies the relationship of energy density = specific capacity × average working potential. Among the components of LIBs, including the cathode, anode, electrolyte, and separator, cathode materials greatly limit the energy density of LIBs<sup>[4,5]</sup>. Therefore, the design and optimization of cathode materials with high capacity and working potential are urgently required to achieve advanced LIBs with higher energy density.

Current cathode materials mainly include transition metal oxides and polyanion compounds<sup>[6]</sup>. Transition metal oxides play a particularly dominant role on account of their advantages of high theoretical specific capacity and working voltage and mature preparation processes<sup>[7-9]</sup>. Transition metal oxides can generally be divided into four categories in accordance with their crystal structure and composition: (1) layered lithium cobalt oxides,  $\text{LiCoO}_2$  (LCO); (2) layered lithium ternary oxides, like  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  (NCM) and  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  (NCA); (3) spinel lithium manganese oxides,  $\text{LiMn}_2\text{O}_4$  and deuterogenic  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNMO); (4) layered Li-rich oxides, typically, Mn-rich  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  and  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ . Specifically, although LCO was discovered to be the first commercial cathode material for LIBs with a theoretical specific capacity of  $274 \text{ mAh g}^{-1}$ , it only delivers half of this capacity with  $\sim 0.5 \text{ Li}^+$  (de)intercalation under  $4.2 \text{ V}$  (vs.  $\text{Li}^+/\text{Li}$ )<sup>[10]</sup>. With a widening voltage window, it is possible to increase the specific capacity along with more  $\text{Li}^+$  (de)intercalation. Furthermore, LCO suffers from structural degradation and fast capacity decay.

In order to solve these issues associated with LCO, layered ternary oxide materials have also been widely investigated as prospective candidates by replacing part of the expensive and toxic Co element with more abundant Ni, Mn, or Al elements. Ternary oxide materials are therefore lower in cost compared with LCO<sup>[11-13]</sup>. Additionally, Ni-rich ternary oxide cathodes usually deliver a higher discharge specific capacity that increases with increasing Ni content<sup>[14]</sup>. However, in contrast, high Ni contents inevitably result in poor structural and cyclic stability. Different from layered oxides, spinel LNMO can exhibit a high working voltage and stable crystal structure<sup>[15]</sup> and therefore is a good cathode material for high-voltage LIBs. Nevertheless, LNMO usually simultaneously delivers a low discharge capacity, and novel electrolytes with wide electrochemical windows are urgently required. Compared to these cathode materials, Li-rich cathodes show an extremely high specific capacity of  $250\text{-}300 \text{ mAh g}^{-1}$  based on the combination of transition metal cation and oxygen anion redox. However, these materials also feature a series of issues, including insufficient initial coulombic efficiency (CE), fast capacity and voltage loss, oxygen release, and insufficient rate capability<sup>[16]</sup>.

Although these transition metal oxide cathode materials have been extensively studied regarding their structural and electrochemical performance, several problems remain, including structural and cycling instability and complicated decay mechanisms, especially under elevated cutoff voltages, which must be

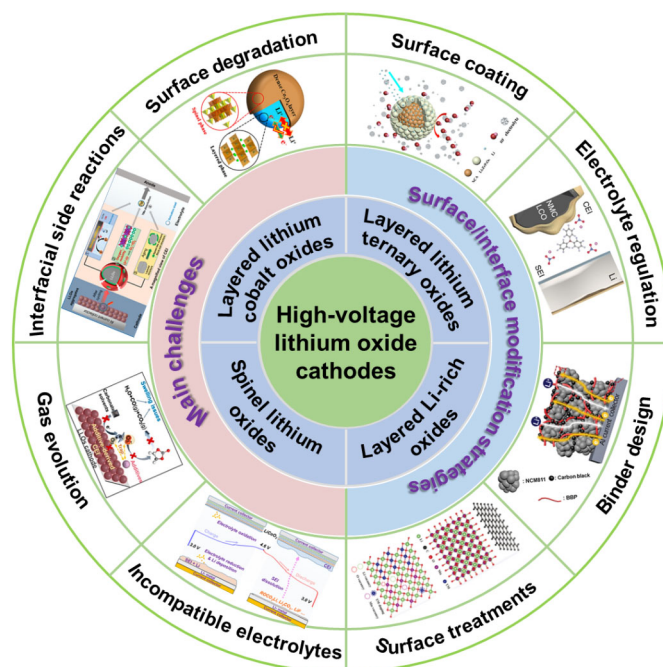
solved for next-generation LIBs with distinguished electrochemical performance. The instability of layered crystal structures mainly originates from aggravating irreversible phase transformations, lattice oxygen loss, and interfacial side reactions between oxide cathodes and electrolytes under high-voltage operation, thus hindering their electrochemical performance for further commercial applications.

Specifically, high-voltage operation causes transition metal oxide cathode materials to suffer from the following challenges. The first issue is surface degradation, which can result from transition metal migration and dissolution, phase transformations, and the generation of microcracks<sup>[17-19]</sup>. For instance, as more Li<sup>+</sup> ions are extracted from the crystal structure of LCO under high voltage, the LCO surface may suffer from an irreversible phase transformation from the layered to spinel and even rock salt phase, thereby deteriorating the electrochemical performance<sup>[20]</sup>. In particular, Ni-rich oxides usually go through severe Li/Ni mixing because of the similar ionic radii of Li<sup>+</sup> and Ni<sup>2+</sup>, which causes slow ion diffusion and increased internal resistance<sup>[21]</sup>.

The second challenge is interfacial side reactions, which become more dramatic when the upper cutoff voltage increases<sup>[22,23]</sup>. These harmful side reactions will consume the electrolyte and Li<sup>+</sup> from the active materials. Furthermore, the formation of an unstable and thick cathode electrolyte interface (CEI) or solid electrolyte interface (SEI) can lead to increased internal resistance. As discussed in the literature, interfacial side reactions, especially the parasitic reactions between electrolytes and charged electrodes, tend to take place under high-voltage operation<sup>[24,25]</sup>. Pham *et al.* investigated cathode-electrolyte interfacial processes with increasing charge cutoff voltages of 4.5, 4.8, 5.0, 5.2, and 5.5 V based on a Li-rich layered oxide cathode and a model electrolyte of 0.1 M LiPF<sub>6</sub> in di-(2,2,2 trifluoroethyl) carbonate<sup>[26]</sup>. It was found that the oxidative decomposition of the carbonate begins at 4.7 V, forming a protective film on the cathode surface, thereby inhibiting or reducing the further structural degradation of active materials. Nonetheless, cathode-electrolyte interfacial stabilization can be compromised with persistent surface deterioration and the accumulation of byproducts from electrolyte decomposition when the voltage reaches 5.2-5.5 V. For conventional electrolytes, the tolerable limit of the charge cutoff voltage will be lower.

The third issue is gas evolution<sup>[19,27,28]</sup>, mainly including O<sub>2</sub> and CO<sub>2</sub>. O<sub>2</sub> release causes damage to the lattice oxygen and the migration of transition metal ions. CO<sub>2</sub> release is attributed to the oxidative decomposition of carbonate solvents, which have adverse effects on the electrochemical performance and safety of LIBs. The final challenge is incompatible electrolytes. High-voltage operation is also a significant challenge to the stability of electrolytes<sup>[29-32]</sup>. Generally, conventional carbonate-based electrolytes will undergo oxidative decomposition above 4.5 V. The resulting HF can attack cathode materials and thus contribute to the dissolution of transition metal ions. So far, it remains highly challenging to pursue advanced LIBs with improved structural stability and electrochemical performance by alleviating these unfavorable factors at high voltages.

Accordingly, based on the above considerations, this review concentrates on recent progress regarding surface/interface modification strategies for high-voltage lithium oxide cathode materials in advanced LIBs with prominently meliorative electrochemical performance, as shown in [Figure 1](#)<sup>[20,23,32-36]</sup>. Herein, we comprehensively summarize several commonly used surface/interface modification strategies and further elaborate on their underlying working mechanisms. First, surface coating with metal oxides, fluorides, phosphates, fast ionic conductors, and polymers has been regarded as the most simple and effective modification strategy, which generally functions by constructing a protective thin layer on the active material surface to avoid electrolyte corrosion and transition metal ion dissolution. In addition, reasonable electrolyte regulation with novel functional additives can also effectively enhance the cycling stability under



**Figure 1.** Schematic of main challenges and surface/interface modification strategies for high-performance LIBs with high-voltage lithium oxide cathode materials. Reproduced from Refs. <sup>[20,23,32-36]</sup>. LIBs: Lithium-ion batteries.

high-voltage operation, where the additive can be preferentially decomposed to construct a uniform and stable interface layer *in situ*. Furthermore, binder design has also proved to be a novel strategy. Some binders with superior binding ability and electrochemical windows can help to create robust CEIs, which contribute to improved electrochemical stability under high voltages. Binders with polar functional groups can also coordinate with transition metal ions to reduce their dissolution. Finally, special surface treatments with chemical substances are considered. These simple treatments can make artificial surface reconstructions to protect active materials and improve their electrochemical performance. Based on the above discussions, several possible development directions can be proposed for high-performance LIBs in the future. This review provides new insights into advanced LIBs for practical applications.

## CHALLENGES FACING HIGH-VOLTAGE LITHIUM OXIDE CATHODE MATERIALS

At present, high-voltage oxide cathode materials for LIBs mainly include four types: layered high-voltage LCO; layered lithium ternary oxides (e.g., NCM and NCA); spinel lithium manganese oxides and derivatives (e.g., LNMO); Li-rich layered oxides  $x\text{LiMnO}_2 \cdot (1-x)\text{Li}_2\text{MnO}_3$ . In recent years, substantial developments have been made regarding crystal structures, degradation mechanisms, and modification strategies for next-generation advanced LIBs. The detailed structural features, challenges, mechanisms, and modification strategies for these oxide cathode materials are discussed in the following section to further our understanding of their different electrochemical characteristics. In particular, a series of similar challenges regarding electrochemical degradation are presented, from the instability of the active material surface to interfacial instability between the electrode and electrolyte under high-voltage operation. As a result, the corresponding surface/interface modification strategies are extensively discussed.

### High-voltage layered lithium cobalt oxide cathodes

LCO is widely regarded as one of the most popular layered oxide cathode materials for high-performance LIBs. LCO is composed of edge-sharing  $\text{LiO}_6$  and  $\text{CoO}_6$  octahedra. Its crystal structure is similar to that of

layered  $\alpha$ -NaFeO<sub>2</sub>, belonging to a hexagonal crystal system with the R-3m space group, in which O<sup>2-</sup> ions arrange in cubic close packing (6c site) and Li<sup>+</sup> and Co<sup>3+</sup> occupy alternate octahedral 3a and 3b sites in the oxygen layer, respectively<sup>[37]</sup>. Encouragingly, LCO delivers a high theoretical capacity and density (~4.2 g cm<sup>-3</sup>). However, it only shows an initial discharge specific capacity of ~140 mAh g<sup>-1</sup> with an average voltage of 3.9 V from 3.0 to 4.2 V. Many studies have reported a remarkable increase in reversible capacity from 155 to 170 and 185 mAh g<sup>-1</sup>, along with a slightly increasing average voltage that can be easily implemented by raising the upper cutoff voltage from 4.3 to 4.4 and 4.5 V, thereby leading to a considerable improvement in energy density<sup>[38]</sup>. In particular, the reversible capacity can reach 220 mAh g<sup>-1</sup> when the upper cutoff voltage is increased to 4.6 V<sup>[39]</sup>.

In spite of these substantial improvements in capacity and energy density, there are still some inherent issues caused by the high-voltage operation. For example, the layered crystal structure of LCO becomes unstable with more Li<sup>+</sup> (de) intercalation from the lattice when charging to a higher voltage. Simultaneously, traditional organic electrolytes are also subjected to oxidative decomposition, which further results in a series of issues, mainly including deteriorative cyclic stability and safety, increased interfacial impedance, aggravated irreversible phase transformation and transition metal dissolution, and obstructed Li<sup>+</sup> diffusion<sup>[10]</sup>. Moreover, significant research has been carried out to better understand the specific decay mechanisms of high-voltage LCO cathodes. The structural instability of LCO at high working voltages is well known as the major obstacle to achieving a high capacity with prominent capacity retention. Li *et al.* investigated the origin of high-voltage instability for the LCO crystal structure through an advanced three-dimensional (3D) continuous rotation electron diffraction technique in combination with high-resolution transmission electron microscopy, with an atomistic understanding proposed<sup>[40]</sup>. Curved cobalt oxide layers, especially at the near surface, are identified as the fundamental reason for poor structural stability and unsatisfactory electrochemical performance. Furthermore, the experimental result was proved to be in good agreement with theoretical calculations.

In order to effectively enhance the surface stability of LCO and interfacial stability between a cathode and electrolyte, modification strategies, like surface coating and electrolyte regulation, have been widely developed. Guo and co-workers<sup>[41]</sup> designed a surface multilayer, including Zn-rich surface coating, rock-salt buffer, and surface gradient Al doping layers, to modify LCO, which synergistically improved the electrochemical performance when operating at 4.6 V. As a consequence, severe side reactions between the electrode and electrolyte, interfacial impedance and irreversible collapse of the crystal structure all can be vigorously mitigated, so that 65.7% of the initial capacity can be well maintained, even after 500 cycles. Unremitting efforts are still being devoted to the development of advanced LCO cathodes with higher energy density and longer cycle life.

### Layered lithium ternary oxide cathodes

Considering the limitations of LCO regarding limited discharge capacity, cost, and toxic Co, layered lithium ternary oxide materials derived from LCO have been extensively developed and researched by means of partially replacing Co with Ni, Mn, or Al. In ternary oxide materials, Ni<sup>2+/4+</sup> with a redox reaction of two electrons contributes to the high specific capacity, Co<sup>3+</sup> is beneficial to the electronic conductivity and rate capacity, while Mn<sup>4+</sup> and Al<sup>3+</sup> are electrochemically inactive but stabilize the crystal structure<sup>[5]</sup>. Generally, these materials have a similar crystal structure and theoretical capacity to LCO, and their chemical compositions, discharge specific capacity, and electrochemical behaviors can be easily adjusted. Ternary oxides, especially Ni-rich ternary oxides, like LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) and LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> (NCM622), have been identified as highly attractive cathode materials, owing to their high reversible capacity and operating potential. Increasing the Ni content while reducing the content of Co has been a tendency that can improve the capacity of oxide cathodes and simultaneously reduce the cost<sup>[14]</sup>. However,



this also results in several problems, including reduced thermal stability and increased sensitivity to air and moisture<sup>[42]</sup>. In addition, due to the similar ionic radii of Ni<sup>2+</sup> (0.69 Å) and Li<sup>+</sup> (0.76 Å), cation mixing usually occurs in Ni-rich oxides. Consequently, Ni-rich ternary oxide cathode materials inevitably suffer from fast capacity loss during cycling at a high voltage or temperature<sup>[43,44]</sup>.

The degradation mechanisms of these cathode materials can be divided into four main categories, namely, detrimental phase transformations, irreversible electrolyte breakdown and gas release, transition metal dissolution, and microcrack generation. There have been a number of modification strategies to ameliorate these issues of structural instability and deficiencies in electrochemical performance. In addition to conventional surface coating and bulk doping strategies, the rational design of novel functional electrolytes has also been proved to be a facile and feasible method to effectively promote the electrochemical performance. Recently, Huang and his team<sup>[45]</sup> successfully introduced dual additives, namely, lithium bis(oxalate)borate and dopamine, into a traditional carbonate electrolyte, where the additives with elevated highest occupied molecular orbital energy levels tend to be preferentially oxidized. They also subsequently generated a uniform and robust N, B, and O-rich inorganic/polymer interphase on the surface of a Ni-rich NCM811 cathode. More significantly, the formed CEI can contribute significantly to strengthening the interfacial stability and reducing the detrimental side reactions. Thus, the electrochemical performance can be remarkably promoted, including an enhanced capacity retention of over 90% after 200 cycles and an outstanding rate capability with 118 mAh g<sup>-1</sup> at 20 C. Although reasonable progress has been made regarding layered Ni-rich ternary oxide cathode materials, they still have significant development prospects.

### **Spinel lithium manganese oxides and substituted cathodes**

In comparison to the above layered oxides, the spinel framework with a robust 3D network is capable of providing fast Li<sup>+</sup> diffusion channels and thus endowing spinel active materials with superior thermal stability and excellent rate and power capability. Typically, spinel LiMn<sub>2</sub>O<sub>4</sub>, one of the most attractive commercial cathode materials for LIBs, belongs to the Fd-3m space group<sup>[46]</sup>. Its electrochemical behavior is studied with a Mn<sup>3+/4+</sup> redox couple operating at ~4.0 V and a discharge capacity of ~140 mAh g<sup>-1</sup> (approaching its theoretical capacity of 148 mAh g<sup>-1</sup>). Moreover, it has the advantages of abundant resources, low cost, and easy synthesis, and is thus widely used in the field of electric vehicles. However, in addition to a low discharge specific capacity, its structural and cycling stability under high temperatures still need to be enhanced for further applications.

The attenuation mechanism of LiMn<sub>2</sub>O<sub>4</sub> has been extensively studied, and the overwhelming majority of studies attribute its fast capacity loss to the malignant dissolution of Mn<sup>2+</sup> and the Jahn-Teller distortion of Mn<sup>3+</sup><sup>[47]</sup>. Another representative spinel cathode material is LNMO, in which partial Mn ions are replaced with Ni<sup>2+</sup>, leading to a more ordered crystal structure with an increased average valence state of Mn ions and a mitigated Jahn-Teller effect. LNMO delivers an extremely high working voltage (4.7 V vs. Li<sup>+</sup>/Li) and moderate discharge capacity (~148 mAh g<sup>-1</sup>) based on the Ni<sup>2+/4+</sup> redox couple and has been considered as the most prospective 5 V cathode material for high energy density LIBs<sup>[48]</sup>. Nevertheless, the high-voltage operation will inevitably lead to severe interfacial instability between the electrode and electrolyte, as well as electrolyte decomposition. Therefore, its practical application is still limited by the development of compatible high-voltage electrolytes. At present, commonly used modification strategies, including surface coating, bulk doping, particle morphology control, and electrolyte and binder optimization, are also applied to spinel cathode systems. More detailed developments on modification strategies for spinel lithium oxide cathode materials are discussed later.

### Layered Li-rich oxide cathodes

Since Li-rich layered oxides were discovered, the discussions regarding their crystal structure have remained controversial. On the one hand, it is well recognized that Li-rich layered oxides are composed of  $\text{LiMO}_2$  ( $M = \text{Ni, Co or Mn}$ ) with the R-3m space group and  $\text{Li}_2\text{MnO}_3$  with the C2/m space group in a certain ratio<sup>[17]</sup>. On the other hand, it has also been reported that Li-rich layered oxides exist as solid solutions for these two phases<sup>[49]</sup>. The electrochemical behavior was characterized via galvanostatic charge/discharge tests to uncover the specific working mechanism. It is believed that Li-rich cathodes generally display a redox reaction of transition metal ions coinciding with  $\text{Li}^+$  deintercalation from the  $\text{LiMO}_2$  lattice when charging below 4.5 V. As the charging voltage reaches more than 4.5 V, the  $\text{Li}_2\text{O}$  extraction from the  $\text{Li}_2\text{MnO}_3$  lattice occurs to generate  $\text{MnO}_2$  irreversibly or  $\text{Li}_2\text{MnO}_3$  undergoes the oxygen anion redox reaction<sup>[50]</sup>. Therefore, from the perspective of energy density, Li-rich layered oxide cathodes can display better electrochemical properties in comparison with the aforementioned oxide cathode materials, owing to their higher specific capacity of over 250 mAh  $\text{g}^{-1}$  and average working voltage of  $\sim 3.6$  V. However, failures in the structural and electrochemical stability result from a number of severe problems, such as irreversible oxygen release, phase transformations, transition metal ion dissolution and migration and interfacial side reactions<sup>[8]</sup>. Their unfavorable effects on electrochemical performance mainly include a low initial CE, rapid capacity and voltage decays, and deteriorative rate capability, which inhibit their further commercial applications.

In order to ameliorate the issue of irreversible oxygen evolution, Kim and his colleagues<sup>[51]</sup> recently reported a layered Li-rich Mn-rich cathode material with a polydopamine (PDA) surface coating that demonstrated an enhanced rate capability and suppressed capacity fading during cycling. It is noteworthy that the PDA layer can function as an oxygen radical scavenger, which can effectively protect cathode materials and thus diminish surface transformation and oxygen release. In addition, numerous modification strategies, including conventional coating, doping, and some novel surface treatments, have been investigated to overcome these difficulties.

## SURFACE/INTERFACE MODIFICATION OF HIGH-VOLTAGE LITHIUM OXIDE CATHODE MATERIALS

There are several modification strategies to improve the surface stability of oxide cathode materials and the interfacial stability between the electrode and electrolyte under high voltages<sup>[52-58]</sup>, such as coatings, electrolyte regulation, binder design, and special surface treatments. Bulk doping<sup>[59-61]</sup> is also a well-known effective approach that focuses on enhancing the intrinsic crystal structural stability of a cathode material and is therefore not discussed in detail in this review.

### Surface coating

Surface coating is the most widely used modification strategy, which has a significant effect on surface structural stability, interfacial stability between a cathode and electrolyte, and comprehensive electrochemical performance for lithium oxide cathode materials under high voltages. In contrast to bulk doping, the surface coating does not change the crystal structure of the bulk material but plays a pivotal role in the surface structure. Generally, the role of surface coating can be summarized as follows: (1) an effective projective layer to improve the surface stability, which avoids the detrimental side reaction between the cathode and electrolyte, such as metal fluorides; (2) HF scavengers to remove the byproducts from electrolyte decomposition and reduce attack on the material surface. A series of surface modifications in terms of coating material and method and electrochemical performance enhancement for various oxide cathode materials are systematically summarized in Tables 1-5<sup>[34,51,62-138]</sup> and discussed in detail in the following sections.

**Table 1. Summary of recent surface modifications using metal oxides and fluorides**

Coating material	Coating method	Cathode material	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
Al <sub>2</sub> O <sub>3</sub>	Wet-chemical	LCO	3.0-4.5	82.6%, 500th at 1C	130 at 10C	[62]
Al <sub>2</sub> O <sub>3</sub>	Solid-state	NCM811	2.8-4.3	95.42%, 200th at 1C	-	[63]
Al <sub>2</sub> O <sub>3</sub>	ALD	LNMO	3.5-5.0	-	-	[64]
Al <sub>2</sub> O <sub>3</sub>	Solid-state	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	2.0-4.8	86.3%, 200th at 2C	105.6 at 10C	[65]
SiO <sub>2</sub>	Solid-state	NCM811	3.0-4.3	87.3%, 100th at 0.5C	165 at 2C	[66]
SiO <sub>2</sub>	Ball milling	LNMO	3.5-4.9	82.4%, 400th at 80C	106 at 80C	[67]
SiO <sub>2</sub>	Sol-gel	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	89.7%, 200th at 1C	150.4 at 5C	[68]
TiO <sub>2</sub>	Magnetron sputtering	LCO	3.0-4.5	86.5%, 100th at 1C	109 at 10C	[69]
TiO <sub>2</sub>	Hydrolyzation	NCM811	-	104.9%, 100th at 0.1C	-	[70]
TiO <sub>2</sub>	Modified sol-gel	LiMn <sub>2</sub> O <sub>4</sub>	3.0-4.5	90.1%, 250th at 0.5C	-	[71]
Li <sub>2</sub> TiO <sub>3</sub>	Molten salt	Li <sub>1.08</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> Ni <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	99.7%, 125th at 0.2C	225 at 1C	[72]
ZnO	ALD	NCM523	2.5-4.5	91.5%, 60th at 2C	148.2 at 5C	[73]
ZnO	Sol-gel	LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	2.8-4.3	91.3%, 100th at 0.2C	135 at 10C	[74]
AZO	Wet-mixing	LCO	3.0-4.5	80%, 650th at 0.2C	96 at 8C	[75]
SnO <sub>2</sub>	CVD	LCO	3.0-4.5	> 60%, 500th at 1C	112 at 10C	[76]
SnO <sub>2</sub>	Coprecipitation	LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	2.8-4.3	70.1%, 400th at 1C	115.2 at 2C	[77]
SnO <sub>2</sub>	Solid-state	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	2.0-4.8	89.9%, 200th at 1C	189.7 at 1C	[78]
Fe <sub>2</sub> O <sub>3</sub>	Ball milling	LCO	3.0-4.5	92.6%, 50th at 1C	126 at 5C	[79]
Co <sub>3</sub> O <sub>4</sub>	Wet-chemical	LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	2.8-4.3	91.6%, 100th at 1C	145 at 10C	[80]
CeO <sub>2</sub>	Wet-chemical	NCM523	2.8-4.6	57.7%, 100th at 10C	97.4 at 10C	[81]
MoO <sub>3</sub>	Precipitation	LNMO	3.5-5.0	80.1%, 500th at 10C	124 at 10C	[82]
MoO <sub>3</sub> /Li <sub>2</sub> MoO <sub>4</sub>	Drying coating	NCM811	2.8-4.3	94.8%, 100th at 1C	-	[83]
Nd <sub>2</sub> O <sub>3</sub>	Liquid phase coating	NCM811	3.0-4.4	88%, 100th at 1C	164 at 8C	[84]
RuO <sub>2</sub>	Wet-chemical	LNMO	3.0-5.0	101.9%, 150th at 0.5C	100 at 1C	[85]
La <sub>2</sub> O <sub>3</sub>	Wet-chemical	LiNi <sub>0.91</sub> Co <sub>0.06</sub> Mn <sub>0.03</sub> O <sub>2</sub>	3.0-4.3	87.2%, 100 <sup>th</sup> at 0.5C	80.3 at 5C	[86]
Y <sub>2</sub> O <sub>3</sub>	Sol-gel	NCM523	2.8-4.6	76.3%, 100th at 10C	145.9 at 20C	[87]
ZrO <sub>2</sub>	Ball-milling	NCM622	2.8-4.5	82.5%, 100th at 0.5C	112.7 at 10C	[88]
AlF <sub>3</sub>	ALD	LNMO	3.5-4.9	-	-68 at 0.8C	[89]
AlF <sub>3</sub>	Wet-chemical	Li <sub>1.2</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> Mn <sub>0.54</sub> O <sub>2</sub>	2.0-4.8	-100%, 50th at 0.1C	208.8 at 1C	[90]
CaF <sub>2</sub>	Coprecipitation	NCM811	2.7-4.3	85.36%, 200th at 1C	181.7 at 5C	[91]
LiF	Coprecipitation	LCO	3.0-4.5	71.4%, 300th at 0.1C	141 at 4C	[92]
LiF	ALD	LNMO	3.5-4.9	-64%, 100th at 0.1C	43 at 1.6C	[93]
LiF/FeF <sub>3</sub>	Aqueous solution	Li <sub>1.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> O <sub>2</sub>	2.0-4.8	89.14%, 60th at 0.1C	129.9 at 20C	[94]
LaF <sub>3</sub>	Coprecipitation	LNMO	3.5-4.9	92%, 150th at 0.1C	-102 at 1C	[95]

AZO: Al-doped ZnO; NCM523: LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub>; ALD: atomic layer deposition; CVD: chemical vapor deposition.



### *Metal oxides, fluorides and phosphates*

Considering the simple preparation and high chemical stability of metal oxides, a series of metal oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ , and  $\text{ZrO}_2$ , have been widely studied as surface coatings of oxide cathode materials. They can effectively protect oxide cathode materials from liquid electrolytes and hence reduce the side reactions between them, eventually resulting in prominently improved electrochemical performance, including superior cycling stability and rate capability under high-voltage operation. There are several coating methods used, including wet-chemical, ALD, magnetron sputtering, and so on. Although the wet-chemical coating method is easy to operate, it is difficult to control the uniformity and thickness of the coating layer. In contrast, control is simple with ALD, but it has a higher cost and is impractical for large-scale applications. The magnetron sputtering approach combines the advantages and disadvantages of these two methods.

Zhou *et al.* proposed a low-cost and environmentally-friendly wet-chemical method to coat  $\text{Al}_2\text{O}_3$  on LCO using only an  $\text{Al}_2(\text{SO}_4)_3$  aqueous solution via a hydrolysis reaction and strong adsorption of intermediate  $\text{Al}(\text{OH})_3$  on the LCO surface<sup>[62]</sup>. In sharp contrast to bare LCO, the modified LCO electrode exhibited outstanding high-voltage performance under 4.5 V, including excellent cycling stability (82.6% of capacity retention after 500 cycles at 1C) and preeminent rate capability ( $130 \text{ mAh g}^{-1}$  at 10C). This can be explained by the fact that the  $\text{Al}_2\text{O}_3$  coating can not only suppress electrolyte decomposition under high voltages but also decreases the irreversible CEI/SEI formation. Additionally, Nie *et al.* reported a simple wet-mixing method to obtain a uniform AZO coating for LCO to achieve superior long-term cycling stability and rate capability simultaneously, even under 4.5 V<sup>[75]</sup>. Furthermore, due to the establishment of a stable surface and SEI layer, the phenomenon of surface degradation and Co dissolution can be significantly inhibited for AZO-coated LCO, as shown in Figure 2A. Excellent ionic and electronic conductivity were found for the AZO-coated LCO.

Similar to the surface coating of LCO, other oxide cathode materials can also benefit from these coating materials, methods and mechanisms. As shown in Figure 2B, Yao *et al.* recently reported a thin amorphous  $\text{ZrO}_2$  layer that was generated *in situ* on a Ni-rich cathode (NCM622) surface using a Zr-based metal-organic framework (UiO-66) as a coating precursor (u-NCM622)<sup>[88]</sup>. This could provide a significant amount of active sites for fast  $\text{Li}^+$  diffusion and effectively inhibit severe side reactions and microcrack generation to maintain the structural integrity upon cycling. As a result, significant improvements in electrochemical performance for u-NCM622 cathode materials can be achieved for large-scale practical applications in high-performance LIBs.

For spinel  $\text{LiMn}_2\text{O}_4$ , a uniform, continuous and porous nanosized  $\text{TiO}_2$  coating material was successfully developed by Zhang *et al.* via a modified sol-gel method based on a kinetically-controlled coating process<sup>[71]</sup>. The prepared  $\text{TiO}_2$  layer covering the  $\text{LiMn}_2\text{O}_4$  cathode surface is so robust that it is able to greatly inhibit Mn dissolution and capacity deterioration during long-term cycling, even at elevated temperatures and voltage windows. Otherwise, for the traditional chemical coating method, it usually fails to completely coat the surface of active materials, inevitably leading to continuous degradation of the materials during the repeated charging and discharging process [Figure 2C].

Likewise, metal oxides also have been successfully introduced into Li-rich cathode material systems to mitigate their intrinsic issues, e.g., fast capacity and voltage decay. Recently, Zhai *et al.* reported a Li-rich layered oxide ( $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ ) decorated with a thin  $\text{SiO}_2$  layer to enhance its structural and

**Table 2. Summary of recent surface modifications using phosphates**

Coating material	Coating Technology	Cathode material	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
Li <sub>3</sub> PO <sub>4</sub>	Magnetron sputtering	LCO	3.0-4.5	79.3%, 100th at 1C	127 at 12C	[96]
Li <sub>3</sub> PO <sub>4</sub>	Sol-gel	NCM622	2.8-4.7	79.7%, 100th at 1C	86.6 at 10C	[97]
Li <sub>3</sub> PO <sub>4</sub>	Coprecipitation	Li <sub>1.18</sub> Co <sub>0.15</sub> Ni <sub>0.15</sub> Mn <sub>0.52</sub> O <sub>2</sub>	2.0-4.8	94.5%, 70th at 0.2C	121.1 at 10C	[98]
AlPO <sub>4</sub>	Sol-gel	LiNi <sub>0.7</sub> Co <sub>0.15</sub> Mn <sub>0.15</sub> O <sub>2</sub>	3.0-4.5	81.5%, 100th at 1C	-	[99]
AlPO <sub>4</sub>	Sol-gel	LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>	3.0-4.3	92%, 60th at 100 mA g <sup>-1</sup>	-	[100]
AlPO <sub>4</sub>	Solid-state	NCM111	3.0-4.6	95.6%, 100th at 0.5C	-	[101]
AlPO <sub>4</sub>	Sol-gel	Li <sub>1.2</sub> Fe <sub>0.1</sub> Ni <sub>0.15</sub> Mn <sub>0.55</sub> O <sub>2</sub>	2.0-5.0	74.4%, 50th at 0.1C	136.1 at 10C	[102]
MnPO <sub>4</sub>	Sol-gel	LiNi <sub>0.4</sub> Co <sub>0.2</sub> Mn <sub>0.4</sub> O <sub>2</sub>	3.0-4.5	92.2%, 100th at 10C	129.2 at 10C	[103]
FePO <sub>4</sub>	Hydrothermal method	LCO	3.0-4.7	92%, 50th at 1C	-	[104]
FePO <sub>4</sub>	Coprecipitation	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	95%, 100th at C/2	166 at 2C	[105]
NiPO <sub>4</sub>	Solid-state	LiNi <sub>0.8</sub> Co <sub>0.15</sub> Al <sub>0.05</sub> O <sub>2</sub>	2.7-4.3	75%, 100th at 0.5C	149 at 10C	[106]
YPO <sub>4</sub>	Wet-chemical	LNMO	3.5-4.9	77.5%, 240th at 0.1C	-77 at 5C	[107]

NCM111: LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

electrochemical stability<sup>[68]</sup>. In addition, the surface modification mechanism of the SiO<sub>2</sub> coating layer was also explained in detail, as shown in Figure 2D. After chemically grafting SiO<sub>2</sub> on the active material through the hydrogen bond interaction between -Si-OH from the hydrolysis of tetraethyl orthosilicate and -OH from the natural surface of the Li-rich layered oxide, the detrimental lattice oxygen loss, transition metal dissolution, and HF erosion can be remarkably restrained because of the synergistic shielding and scavenging effects of the SiO<sub>2</sub> coating layer.

Considering the general reaction between metal oxides and HF from electrolyte decomposition (e.g., Al<sub>2</sub>O<sub>3</sub> + HF → AlF<sub>3</sub> + H<sub>2</sub>O), the corresponding metal fluorides are generated to maintain the stability of the surface while H<sub>2</sub>O molecules are unfavorable, which can accelerate the decomposition of electrolytes. Therefore, metal fluorides, including LiF, AlF<sub>3</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, LaF<sub>3</sub>, and so on, are regarded as prospective coating materials to modify various oxide cathodes for high-performance LIBs under high voltage. Recently, Wei *et al.* demonstrated a uniform and anticorrosive nanosized LiF thin film-coated LCO cathode material in order to achieve an electrochemical performance enhancement under high voltage<sup>[92]</sup>. In particular, the LiF-modified LCO exhibited superior long cycle performance with 72% capacity retention compared with 20% for bare LCO after 300 cycles at 0.5C between 3.0 and 4.5 V, as shown in Figure 2E<sup>[92]</sup>. The specific mechanism of LiF-coated LCO was also investigated. The LiF thin film on the surface of the LCO cathode can be regarded as a stable artificial CEI, which is capable of effectively resisting the corrosion of the electrolyte and mitigating the irreversible phase transitions, oxygen loss, and metal ion dissolution, thus leading to suppressed capacity decay under high voltage [Figure 2F]. On this basis, surface modification strategies based on metal fluorides have been proved to be feasible for NCM, LNMO, and Li-rich cathode materials to boost their electrochemical performance. Dai *et al.* successfully designed a CaF<sub>2</sub> coating layer with excellent thermal stability to modify a NCM811 cathode via a traditional wet-chemical method and achieved reformative electrochemical performance, even at high temperatures<sup>[91]</sup>.

Like the metal oxides and fluorides mentioned above, a variety of metal phosphates<sup>[96,99,103]</sup>, including Li<sub>3</sub>PO<sub>4</sub>, AlPO<sub>4</sub>, MnPO<sub>4</sub>, FePO<sub>4</sub>, and Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, with inferior electronic conductivity but superior ionic conductivity and chemical stability have been extensively exploited as typical surface coating layers for improving the

**Table 3. Summary of recent surface modifications using Li-ion conductors**

Coating material	Coating method	Cathode material	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
Li <sub>1.5</sub> Al <sub>0.5</sub> Ti <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	Solid-state	LCO	3.0-4.6	88.5%, 100th 0.5C	118.6 at 5C	[108]
Li <sub>1.4</sub> Al <sub>0.4</sub> Ti <sub>1.6</sub> (PO <sub>4</sub> ) <sub>3</sub>	Sol-gel	LCO	3.0-4.5	93.1%, 50th at 0.2C	120 at 5C	[109]
Li <sub>1.5</sub> Al <sub>0.5</sub> Ge <sub>1.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	Solid-state	LCO	3.0-4.5	88.3%, 400th at 0.1C	163 at 6C	[110]
Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	Solution method	Li <sub>1.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> O <sub>2</sub>	2.0-4.8	94.3%, 80th at 0.2C	68.9 at 10C	[111]
LiZr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	Sol-gel	LiNi <sub>0.82</sub> Co <sub>0.15</sub> Al <sub>0.03</sub> O <sub>2</sub>	2.7-4.5	49%, 500th at 1C	204 at 1C	[34]
Li <sub>2</sub> O-BPO <sub>4</sub>	Wet-chemical	LiNi <sub>0.87</sub> Co <sub>0.1</sub> Al <sub>0.03</sub> O <sub>2</sub>	2.7-4.3	86.83%, 100th at 1C	140 at 10C	[112]
LiAlSiO <sub>4</sub>	Sol-gel	LNMO	3.5-4.9	97.1%, 150th at 1C	-	[113]
Li <sub>1.3</sub> Ti <sub>1.7</sub> Al <sub>0.3</sub> (PO <sub>4</sub> ) <sub>3</sub>	Sol-gel	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	-, 500th at 1C	169.7 at 5C	[114]
Li <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> -P <sub>2</sub> O <sub>5</sub>	Coprecipitation	LNMO	3.5-5.0	83%, 100th at 2C (55 °C)	92.1 at 10C (55 °C)	[115]
LiTaO <sub>3</sub>	Solid-state	LiNi <sub>0.9</sub> Co <sub>0.06</sub> Mn <sub>0.04</sub> O <sub>2</sub>	2.8-4.3	-, 100th at 0.2C	140 at 10C	[116]
LiTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	Charge attraction	NCM622	2.7-4.3	94%, 100th at 1C	152.1 at 5C	[117]

**Table 4. Summary of recent surface modifications using conductive polymers**

Coating material	Coating method	Cathode material	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
PI	Thermal imidization	LCO	3.0-4.4	85%, 50th at 0.5C	-119 at 2C	[118]
PI/PVP	Thermal imidization	LCO	3.0-4.4	85%, 80th at 0.5C	-	[119]
Polysiloxane	<i>In situ</i> hydrolysis-condensation	NCM811	3.0-4.3	91.5%, 120th at 1C	171.4 at 5C	[120]
PPC	<i>In situ</i> photopolymerization	NCM811	3.0-4.5	102.66%, 200th at 1C	123.1 at 10C	[121]
half-cyclized polyacrylonitrile	Wet-chemical	NCM811	2.8-4.3	94.24%, 100th at 1C	133.9 at 10C	[122]
PANI-PEG	Wet-chemical	NCM811	2.8-4.3	92.4%, 100th at 1C	156.7 at 10C	[123]
PANI-PVP	Wet-chemical	NCM811	2.8-4.3	88.7%, 100th at 1C	152 at 5C	[124]
PPy	Wet-chemical	LNMO	3.5-4.9	91%, 300th at 1C	85 at 5C	[125]
PI	Thermal imidization	Li <sub>1.2</sub> Ni <sub>0.13</sub> Mn <sub>0.54</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	90.65%, 50th at 0.1C	191.5 at 2C	[126]
PDA	Wet-chemical	LRLO	2.0-4.7	-82%, 200th at 1C	-	[51]

PI: polyimide; PVP: polyvinyl pyrrolidone; PPC: poly(pyrrole-co-citral nitrile); PANI: polyaniline; PEG: polyethylene glycol; PPy: polypyrrole; PDA: polydopamine; LRLO: Li-rich layered oxide.

stability of lithium oxide cathode materials under extended operating voltage windows and temperatures. The underlying mechanisms of the electrochemical performance enhancement for various lithium oxide cathode materials with phosphate coatings have been explored in detail. Typically, Li<sub>3</sub>PO<sub>4</sub> is proved to act as an ideal coating layer on the surface of LCO, which not only induces a spinel phase by ALD to accelerate Li<sup>+</sup> transport but also protects the surface by effectively hindering the interfacial side reactions and suppressing the irreversible oxygen release. Similarly, AlPO<sub>4</sub> coating films have also been introduced to modify LCO, and their features are responsible for the significant enhancement in electrochemical performance.

**Table 5. Summary of recent surface modifications using electrode and other materials**

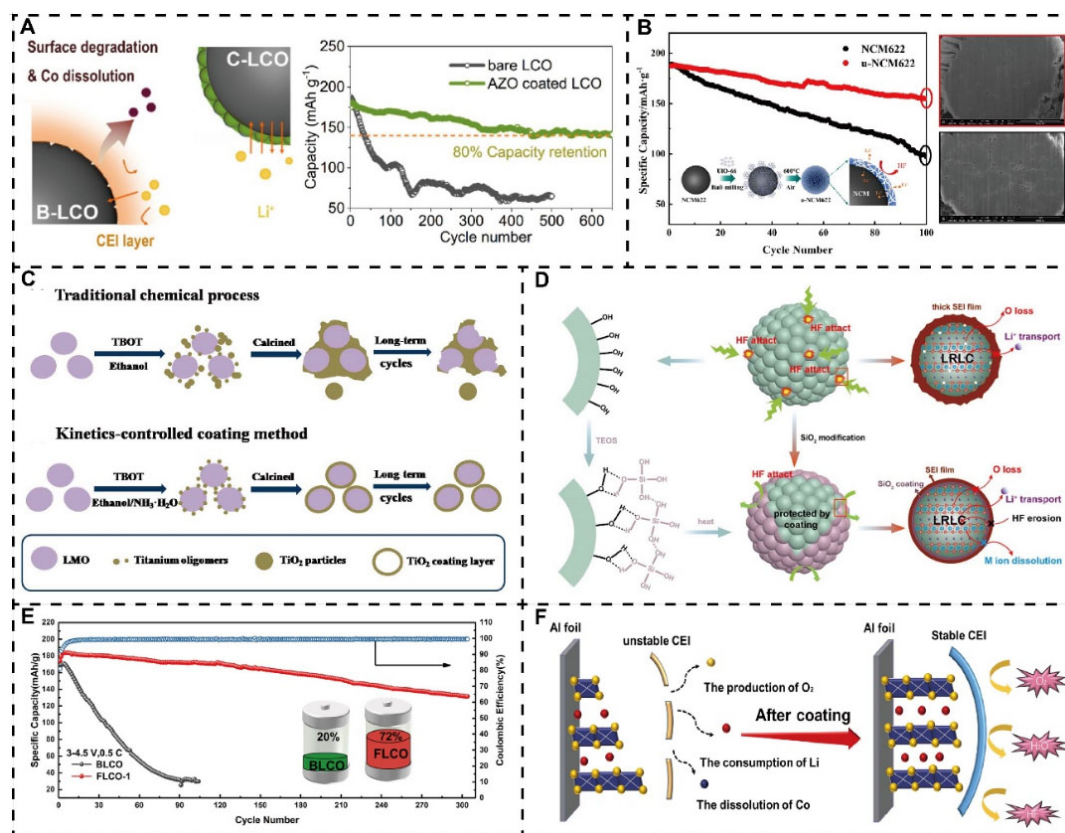
Coating material	Coating method	Cathode material	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
LiCoPO <sub>4</sub>	Solid-state	LCO	3.0-4.6	87%, 300th at 1C	178 at 10C	[127]
Li <sub>1.2</sub> Mn <sub>0.6</sub> Ni <sub>0.2</sub> O <sub>2</sub>	Sol-gel	LCO	3.0-4.5	96.4%, 100th at 0.2C	-167 at 2C	[128]
Li <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	Chemical deposition	Li <sub>1.17</sub> Ni <sub>0.2</sub> Co <sub>0.05</sub> Mn <sub>0.58</sub> O <sub>2</sub>	2.0-4.8	90.1%, 50th at 0.2C	153.4 at 5C	[129]
Li <sub>4</sub> V <sub>2</sub> Mn(PO <sub>4</sub> ) <sub>4</sub>	Solid-state	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	78.1%, 200th at 1C	157.5 at 2C	[130]
LiFePO <sub>4</sub> @C	Physical mixing	NCM622	2.7-4.6	84.6%, 100th at 0.5C	-	[131]
pyrazine-linked 2D sheet	Wet-chemical	NCM811	2.8-4.5	88.8%, 100th at 1C	161.2 at 2C	[132]
PVDF	Wet-chemical	LNMO	3.5-4.9	97.8%, 300th at 1C	119.2 at 10C	[133]
CNT	Wet-chemical	Li <sub>1.15</sub> Mn <sub>0.55</sub> Ni <sub>0.2</sub> Co <sub>0.1</sub> O <sub>2</sub>	2.0-4.8	92.3%, 200th at 1C	146 at 10C	[134]
Nd <sub>0.6</sub> Sr <sub>0.4</sub> CoO <sub>3</sub>	Sol-gel	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	2.0-4.8	91%, 300th at 1C	53 at 50C	[135]
LiBH <sub>4</sub>	Wet-chemical	LCO	3.0-4.6	95.1%, 100th at 1C	173 at 5C	[136]
LiAlH <sub>4</sub>	Wet-chemical	LCO	3.0-4.6	70.4%, 1000th at 1C	168.9 at 10C	[137]
WSe <sub>2</sub>	CVD	LNMO	3.5-4.9	99%, -400th at 1C	-	[138]

LiFePO<sub>4</sub>@C: carbon-coated LiFePO<sub>4</sub>; PVDF: polyvinylidene fluoride; CNT: carbon nanotube.

### Inorganic fast Li-ion conductors

Even though advanced progress has been made through extensive surface modification strategies, most surface coating materials exhibit poor Li<sup>+</sup> and electron transport and limited structural stability simultaneously. Therefore, significant efforts are still required to develop novel surface coating materials that have both fast ion transport paths and good chemical stability. Inorganic fast Li-ion conductors mainly include solid electrolytes, such as Li<sub>1.4</sub>Al<sub>0.4</sub>Ti<sub>1.6</sub>(PO<sub>4</sub>)<sub>3</sub> and LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, and have also been intensively researched as coating materials to endow oxide cathodes with improved structural stability and electrochemical performance.

For example, as displayed in [Figure 3A](#), a facile solid-state method was developed to modify a commercial bare LCO sample with Li<sub>1.5</sub>Al<sub>0.5</sub>Ti<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) (LATP@LCO) nanoparticles<sup>[108]</sup>. Further studies explored the effects of different annealing temperatures on the electrochemical performance and demonstrated that the LATP@LCO sample with an annealing temperature of 700 °C (LATP@LCO-700) exhibited the best cycling stability, which may originate from the surface structure under different annealing temperatures. It was found that a series of continuous reactions between LCO and LATP occur as the temperature increases, and there are only the olivine Li<sub>3</sub>PO<sub>4</sub> phase and spinel species (Co<sub>3</sub>O<sub>4</sub>, CoAl<sub>2</sub>O<sub>4</sub>, and Co<sub>2</sub>TiO<sub>4</sub>) on the LATP@LCO-700 surface, as depicted in [Figure 3B](#). Schematic diagrams of an *in situ* formed thin and uniform surface layer with the detailed composition and structure are presented in [Figure 3C](#). On the one hand, the spinel phase and layered LCO are able to combine closely because of the coherent lattice structure between them. The spinel structure is well known to be more stable than the layered structure at high voltages, which is advantageous to the structural and electrochemical stability enhancement. On the other hand, the outer Li<sub>3</sub>PO<sub>4</sub> species is not only a good Li<sup>+</sup> conductor but also has superior chemical and thermal stability, even at high temperatures and voltages. Consequently, the modified LCO with LATP through the method developed above can deliver visibly improved cycling stability with 88.3% and 72.9% capacity retentions at 0.5C after 100 cycles at 25 and 45 °C, respectively, while only 50.3% and 32.5% were achieved

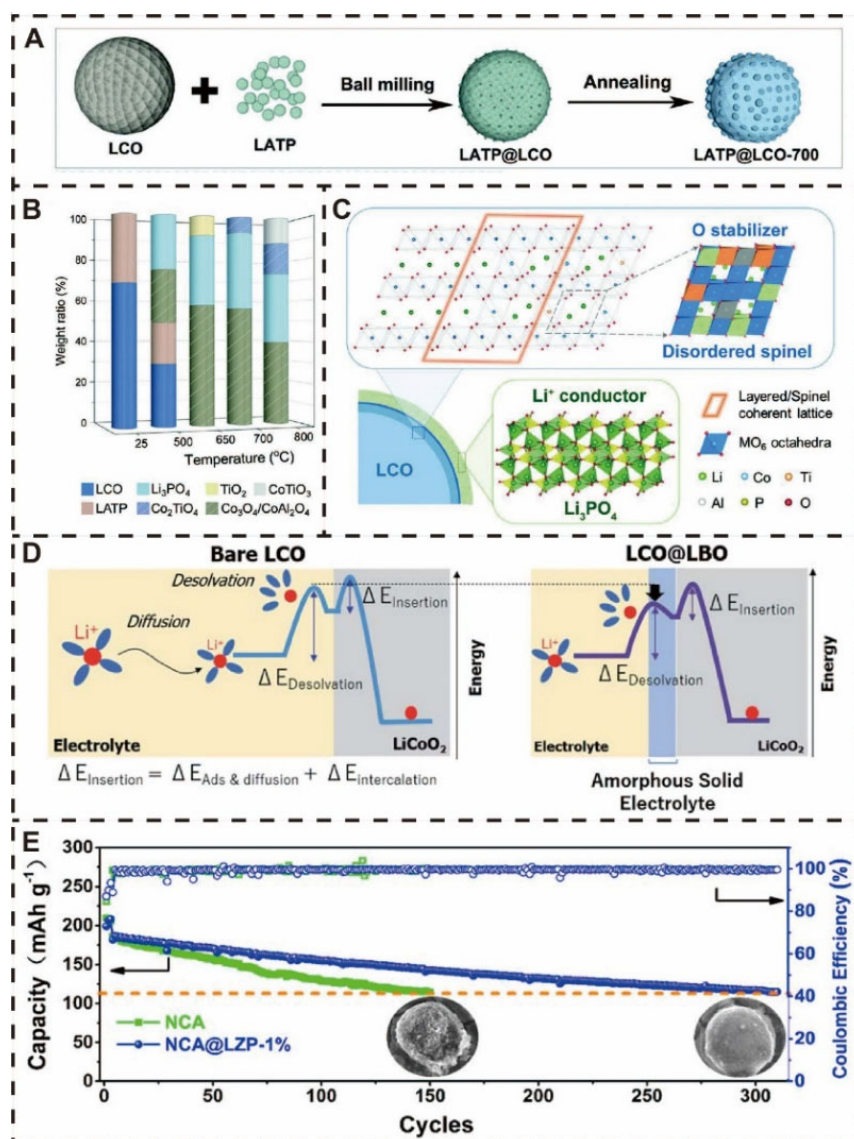


**Figure 2.** Metal oxide and fluoride surface modification for lithium oxide cathode materials. (A) Schematic of the working mechanism of AZO coating layer and improved cycling stability. Reproduced from Ref. [75] with permission from Elsevier. (B) Cyclic performance enhancement of *in situ* ZrO<sub>2</sub>-coated NCM622 cathode and scanning electron microscopy (SEM) images after 100 cycles for NCM622 with and without the coating. Reproduced from Ref. [88] with permission from Elsevier. (C) Schematic of TiO<sub>2</sub> coating process for LiMn<sub>2</sub>O<sub>4</sub> particles. Reproduced from Ref. [71] with permission from the American Chemical Society. (D) Schematic of SiO<sub>2</sub> grafted on LRLC and its protective effects. Reproduced from Ref. [68] with permission from the Electrochemical Society. (E) Long cycle performance of LCO with and without a LiF coating. (F) Schematic of mechanism of LiF-coated LCO. Reproduced from Ref. [92] with permission from Elsevier. B-LCO: Bare LiCoO<sub>2</sub>; C-LCO: coated LiCoO<sub>2</sub>; TBOT: tetrabutyl titanate; LMO: LiMn<sub>2</sub>O<sub>4</sub>; LRLC: Li-rich layered cathode; FLCO-1: LiCoO<sub>2</sub> with 1 mol.% LiF.

for bare LCO. Furthermore, a higher discharge capacity of 118.6 mAh g<sup>-1</sup> was exhibited for the LATP@LCO-700 electrode at 5C, with only 68.5 mAh g<sup>-1</sup> achieved for bare LCO, thereby confirming a remarkably modified rate capability.

In addition, the solid electrolyte Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> [139] (LBO) has also been applied as a Li<sup>+</sup>-conductive coating layer for LCO to enhance its kinetic properties, and the working mechanism was investigated by electrochemical impedance spectroscopy. The calculated activation energies at different temperatures were used to explain the influence of the LBO coating on the discharge reaction [Figure 3D]. It was found that the amorphous LBO coating enables LCO to exhibit significantly lower activation energy for the desolvation process than bare LCO. In another study, a self-assembled fast ionic conducting LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LZP) nanolayer was introduced for the surface modification of Ni-rich LiNi<sub>0.82</sub>Co<sub>0.15</sub>Al<sub>0.03</sub>O<sub>2</sub> (NCA) via an electrostatic charge attraction [34]. It was noted that the NCA and LZP precursor particles have opposite charges according to zeta potential measurements, which allowed the LZP precursor particles to adhere homogeneously to the NCA surface and successfully construct a representative core-shell microstructure. As expected, NCA with 1 wt.% LZP (NCA@LZP-1%) could maintain the highest capacity of 120 mAh g<sup>-1</sup> at 1C after 300 cycles with a





**Figure 3.** Inorganic fast Li-ion conductor surface modification for lithium oxide cathode materials. (A) Schematic of LAMP surface engineering for LCO. (B) Phase compositions of LCO and LAMP at variable temperatures. (C) Schematic of surface layer growth mechanisms. Reproduced from Ref. [108] with permission from Wiley-VCH. (D) Influence of LBO coating on  $\text{Li}^+$  insertion reaction based on activation energies. Reproduced from Ref. [139] with permission from the Royal Society of Chemistry. (E) Cycling properties for NCA and NCA@LZP-1%. Reproduced from Ref. [34] with permission from the American Chemical Society. LCO@LBO:  $\text{Li}_2\text{B}_4\text{O}_7$ -coated  $\text{LiCoO}_2$ .

voltage window of 2.7–4.3 V, while only after 150 cycles could the same capacity be reached for the pristine NCA [Figure 3E]. These findings clearly demonstrate the effectiveness of this fast ionic conductor with the charge attraction method.

### Conductive polymers

Despite a large number of studies having proved that inorganic modification layers, such as metal oxides, fluorides, phosphates, and fast ionic conductors, play an important role in improving electrochemical performance, there are still some issues to be further solved, including uneven coverage, limited ion and electron transport, complex and expensive coating methods and coatings that can easily be removed under extreme conditions. In order to overcome the difficulties faced by the abovementioned inorganic surface

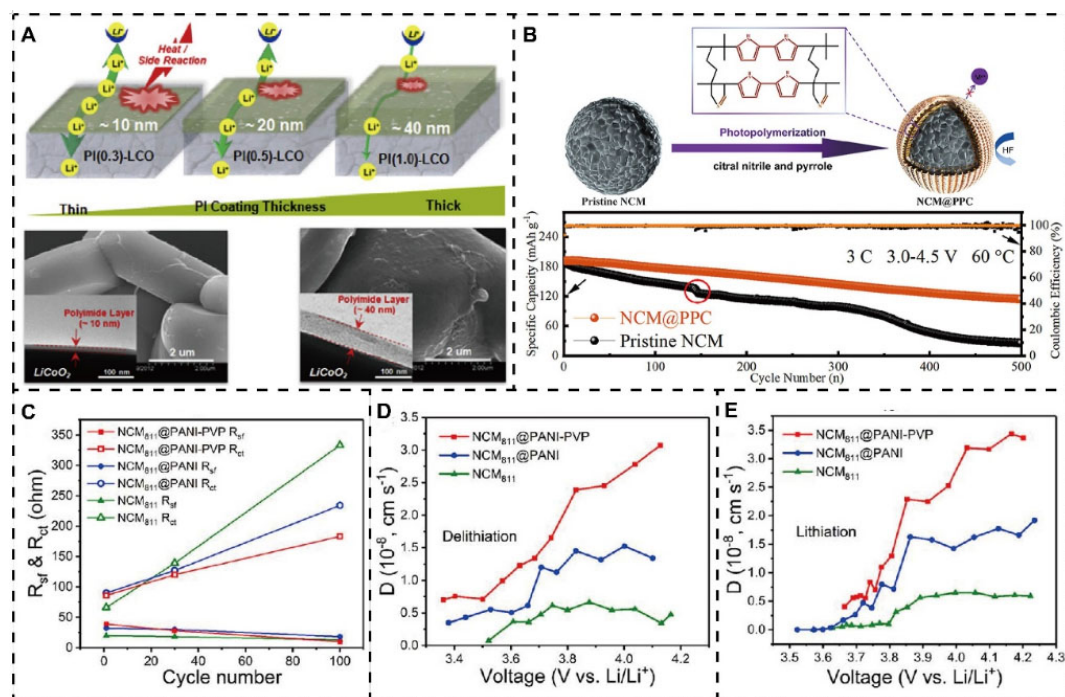
coatings, conductive polymers, like PI, have attracted significant interest and have also been introduced as prominent coating materials to modify lithium oxide cathodes for advanced next-generation LIBs. PI has been employed as a novel surface coating material for high-voltage LCO and the effects of the PI encapsulating layer thickness on the electrochemical performance under high voltage, and interfacial exothermic reactions between the LCO cathode and liquid electrolyte were investigated<sup>[118]</sup>. As depicted in [Figure 4A](#), with increasing PI layer thickness from 10 to 40 nm, although the interfacial side reactions can be effectively suppressed, Li<sup>+</sup> transport is reduced, which results in poor rate and cycling performance. Therefore, LCO with a ~10 nm PI thin film can attain a well-balanced result between electrochemical performance and thermal stability.

In addition, due to its functions of HF scavenging and polarity tuning, PVP is well designed to be combined with PI to form a multifunctional PI/PVP semi-interpenetrating polymer network on the LCO surface<sup>[119]</sup>. As expected, PI/PVP-modified LCO exhibits enhanced electrochemical performance and thermal stability under a high working voltage compared to single PI- or PVP-coated LCO and pristine LCO. Similarly, a PPC coating layer was *in situ* constructed on a Ni-rich NCM811 cathode material to form a sweater-like cross-linked network skeleton via a UV-induced photopolymerization self-assembly process<sup>[121]</sup>, as shown in [Figure 4B](#). The PPC-modified NCM (NCM@PPC) electrode exhibited a remarkable electrochemical stability enhancement in a hostile environment with a high cutoff voltage of 4.5 V and operating temperature of 60 °C, even after long-term cycling of 500 cycles. This performance may be attributed to the enhanced electronic and ionic conductivity provided by the PPC co-polymer, particularly the cyano groups of citral nitrile, which can effectively ameliorate the problem of transition metal dissolution by coordination and ensure the formation of a continuous and uniform coating layer. Gan *et al.* reported a PVP surfactant-induced uniform PANI conductive coating layer for NCM811 surface modification, which can relieve the issues of particle rupture and irreversible side reactions due to the strong hydrogen bond and coordination interactions, thereby accelerating the interfacial dynamics, as shown in [Figure 4C-E](#)<sup>[124]</sup>.

#### *Other special surface coating materials*

Some representative electrode materials, such as Li<sub>4</sub>V<sub>2</sub>Mn(PO<sub>4</sub>)<sub>4</sub> and LiFePO<sub>4</sub>, can be adopted to modify lithium oxide cathodes with the aim of improving the electrochemical performance, particularly for long cycling stability under difficult conditions. Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is a well-known cathode material for LIBs due to its high average operating voltage (> 4.0 V) and specific capacity (197 mAh g<sup>-1</sup>), superior Li<sup>+</sup> kinetics, and excellent structural and cyclic stability. Consequently, it is reasonable to conclude that a Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>-modified spinel LNMO cathode is capable of delivering the accelerated Li<sup>+</sup> diffusion process, suppressed surface structural deterioration and interfacial side reactions, and depressed interfacial resistance<sup>[140]</sup>, as depicted in [Figure 5A](#). These are responsible for the satisfactory improvement in electrochemical performance; for example, the ever-increasing R<sub>sf</sub> and R<sub>ct</sub> can be suppressed very well [[Figure 5B](#)], the capacity retention is as high as 87.8%, even after 500 cycles [[Figure 5C](#)], and the reversible specific capacity maintained at 90.4 mAh g<sup>-1</sup>, even at an extremely high rate of 20C. Moreover, the reduced dissolution of transition metal ions in the LNMO active material is clearly shown in [Figure 5D](#). Likewise, Li<sub>4</sub>V<sub>2</sub>Mn(PO<sub>4</sub>)<sub>4</sub> was introduced successfully to act as a coating layer on the surface of a Li-rich Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> cathode<sup>[130]</sup>. Through a series of experimental characterizations combined with theoretical calculations, it has been demonstrated that this surface modification not only reduces residual Li species, like LiOH and Li<sub>2</sub>CO<sub>3</sub>, on the material surface but also relieves the dissolution of transition metal ions, thereby bringing about enhanced electrochemical performance.

Very recently, a simple and targeted masking modification strategy via LiFePO<sub>4</sub>@C nanoplates was proposed to function with the reduced active sites by means of the preferential adsorption of PO<sub>4</sub><sup>3-</sup> at



**Figure 4.** Conductive polymer surface modification for lithium oxide cathode materials. (A) PI coating layers with different thicknesses and their effect on interfacial side reactions and ion transport. Reproduced from Ref. [118] with permission from Elsevier. (B) Schematic of specific synthesis of NCM@PPC and improved cycling stability. Reproduced from Ref. [121] with permission from Elsevier. (C) Comparison of surface film and charge-transfer resistance evolution during cycling. Diffusion coefficients calculated from GITT curves during (D) delithiation and (E) lithiation process. Reproduced from Ref. [124] with permission from the American Chemical Society. PI(0.3)-LCO, PI(0.5)-LCO and PI(1.0)-LCO: LCO with 0.3, 0.5 and 1.0 wt.% coating solutions, respectively; NCM<sub>811</sub>@PANI: PANI-modified NCM811; NCM<sub>811</sub>@PANI-PVP: PANI and PVP-modified NCM811;  $R_{sf}$ : surface film resistance;  $R_{ct}$ : charge-transfer resistance; GITT: galvanostatic intermittent titration technique.

transition metal sites, resulting in significant improvements in both electrochemical and thermal stability<sup>[131]</sup>. In addition to the representative electrode materials discussed above as coating layers, many carbon-based materials can also be utilized as surface modification layers on lithium oxide cathodes. It has been demonstrated that oxidized carbon nanotubes work as a coating layer on the spinel LNMO surface<sup>[141]</sup> and can suppress adverse side reactions and thus improve the rate and cycling capability.

In addition, the synergetic effects of multiple coating materials on lithium oxide cathode materials are also significant. For instance, a combination of both ionic and electronic conductive modification with  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$  and PANI has been introduced to modify a Li-rich  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  cathode, leading to a remarkable electrochemical enhancement<sup>[142]</sup>.

### Electrolyte regulation

Surface modification by decorating the surface of active materials with various coating layers has significantly alleviated surface degradation for high-voltage oxide cathodes. Considering the existing significant interface issues, the design of novel electrolyte systems compatible with high-voltage cathode materials remains essential. It is well known that electrolytes are generally composed of lithium salts, like  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiTFSI}$ , and  $\text{LiFSI}$ , organic solvents, such as ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC), and additives, like fluoroethylene carbonate (FEC) and vinylene carbonate (VC)<sup>[143,144]</sup>. On the one hand, introducing novel functional additives into conventional carbonate-based electrolyte systems is popular. Table 6<sup>[33,145-163]</sup> summarizes a number of recently reported additives for

**Table 6. Summary of electrolyte additives for high-voltage lithium oxide cathode materials**

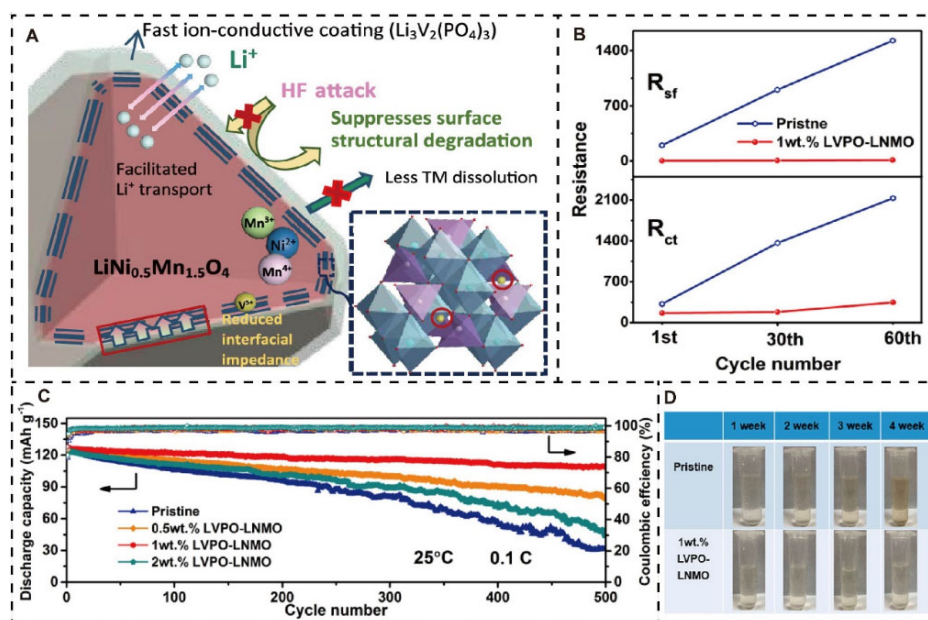
Electrolyte additive	Cathode material	Modification mechanism	Voltage range (V vs. Li <sup>+</sup> /Li)	Capacity retention	Ref.
TFPN	LCO	Form a protective layer to suppress the decomposition of electrolyte solvent and salt	3.0-4.4	90.6%, 100th at 0.5C	[145]
ATCN	LCO	<i>In situ</i> construct a stable CEI film	3.0-4.5	91%, 200th at 1C	[146]
TCEB	LCO	Form a CEI protective film	2.8-4.5	78.2%, 200th at 1C	[147]
BA	NCM811	Construct a robust CEI film and capture HF/H <sub>2</sub> O effectively	3.0-4.5	84%, 200th at 1C	[148]
LiPO <sub>2</sub> F <sub>2</sub>	NCM111	Generate a steady low impedance CEI film	3.0-4.5	48%, 1000th at 10C	[149]
DPDMS	NCM622	Modify CEI layer through scavenging HF and PF <sub>5</sub> ; promote thermal stability	2.8-4.3	93.3%, 200th at 2C (55 °C)	[150]
IPTS	NCM622	Form a uniform and dense CEI film; react with water	2.5-4.5	73.1%, 150th at 0.3C	[151]
TPB	NCM721	Remove residual lithium species from Ni-rich cathode surface and create effective CEI layer	3.0-4.3	88.6%, 100th at 1C	[152]
TAPi	NCM622	Form an interfacial film to protect the electrode surface	2.8-4.2	91.7%, 50th at 1C	[153]
TIB	NCM622	Form a CEI to inhibit the electrolyte decomposition and dissolution of transition metal ions	3.0-4.5	82.7%, 300th at 1C	[154]
AIP	NCM811	Induce <i>in situ</i> polymerization of EC to fabricate a robust CEI	2.7-4.3	97.8%, 200th at 1C	[155]
ETFB	LiNi <sub>0.7</sub> Co <sub>0.15</sub> Mn <sub>0.15</sub> O <sub>2</sub>	Construct protective layers on both electrodes	3.0-4.4	84.8%, 300th at 0.5C (45 °C)	[156]
SA	NCM811	Form a uniform and robust CEI layer	2.8-4.3	93.8%, 400th at 1C	[157]
EGBE	Li <sub>1.2</sub> Mn <sub>0.54</sub> Ni <sub>0.13</sub> Co <sub>0.13</sub> O <sub>2</sub>	Form a stable and robust CEI layer	2.0-4.8	89%, 150th at 0.5C	[158]
BTMSC	Li <sub>1.2</sub> Mn <sub>0.55</sub> Ni <sub>0.15</sub> Co <sub>0.1</sub> O <sub>2</sub>	Build a protective film on the cathode and eliminate HF	2.0-4.8	72%, 200th at 0.5C	[159]
PFPDPP	LNMO	Stabilize LiPF <sub>6</sub> salt; form a good CEI film	3.0-5.0	71%, 300th at 2C	[160]
TMSOMs	Li <sub>1.2</sub> Ni <sub>0.16</sub> Co <sub>0.08</sub> Mn <sub>0.56</sub> O <sub>2</sub>	Form an effective protection layer to remove fluoride species in electrolyte	2.0-4.6	Over 77%, 100th at 0.5C	[161]
SN	Li <sub>1.2</sub> Ni <sub>0.2</sub> Mn <sub>0.6</sub> O <sub>2</sub>	Have good thermal stability and wide electrochemical oxidation window and form a CEI layer	2.0-5.0	-89.5%, 50th at 0.1C	[162]
MA-C60	Li <sub>1.17</sub> Ni <sub>0.17</sub> Mn <sub>0.5</sub> Co <sub>0.17</sub> O <sub>2</sub>	Eliminate undesirable reactive substances and tune interfacial structures	2.0-4.5	86%, 100th at 0.5C	[163]
LiNO <sub>3</sub> and TFPFB/TFPFP	NCM811	Form a robust SEI and amorphous CEI	2.8-4.3	78.5%, 100th at 0.3C	[35]

TFPN: 2-(trifluoroacetyl)thiophene; TCEB: tris(2-cyanoethyl) borate; BA: benzoic anhydride; DPDMS: diphenyldimethoxysilane; IPTS: 3-isocyanatopropyltriethoxysilane; TPB: triphenyl borate; TAPi: triallyl phosphite; TIB: triisopropyl borate; AIP: aluminum isopropoxide; SA: succinic anhydride; EGBE: ethylene glycol bis (propionitrile) ether; BTMSC: bis(trimethylsilyl)carbodiimide; PFPDPP: (pentafluorophenyl)diphenylphosphine; TMSOMs: (trimethylsilyl)methanesulfonate; SN: succinonitrile; MA-C60: malonic acid-decorated fullerene; TFPFB: tris(pentafluorophenyl) borane; TFPFP: tris(pentafluorophenyl)-phosphine.

high-voltage lithium oxide cathode materials. On the other hand, an alternative approach is to optimize conventional carbonate-based low concentration electrolytes (LCEs) by increasing the salt concentration to generate high concentration electrolytes (HCEs) or localized high-concentration electrolytes (LHCEs). In addition, other high-voltage electrolyte systems, such as ionic liquids and sulfone-, nitrile- and fluorinated carbonate-based electrolytes, have also been proposed and widely studied.

Overall, electrolyte additives have been intensively studied and draw considerable attention due to their unique effect on interfacial stability, even with very small concentrations. In particular, most additives can be preferentially oxidized to generate stable CEI/SEI layers to restrain the continuous electrolyte decomposition and further mitigate the dissolution of transition metal ions from active materials, thus leading to improved electrochemical performance. In contrast, some additives can also coordinate with transition metal ions and mitigate side reactions between the electrode and electrolyte. As demonstrated in





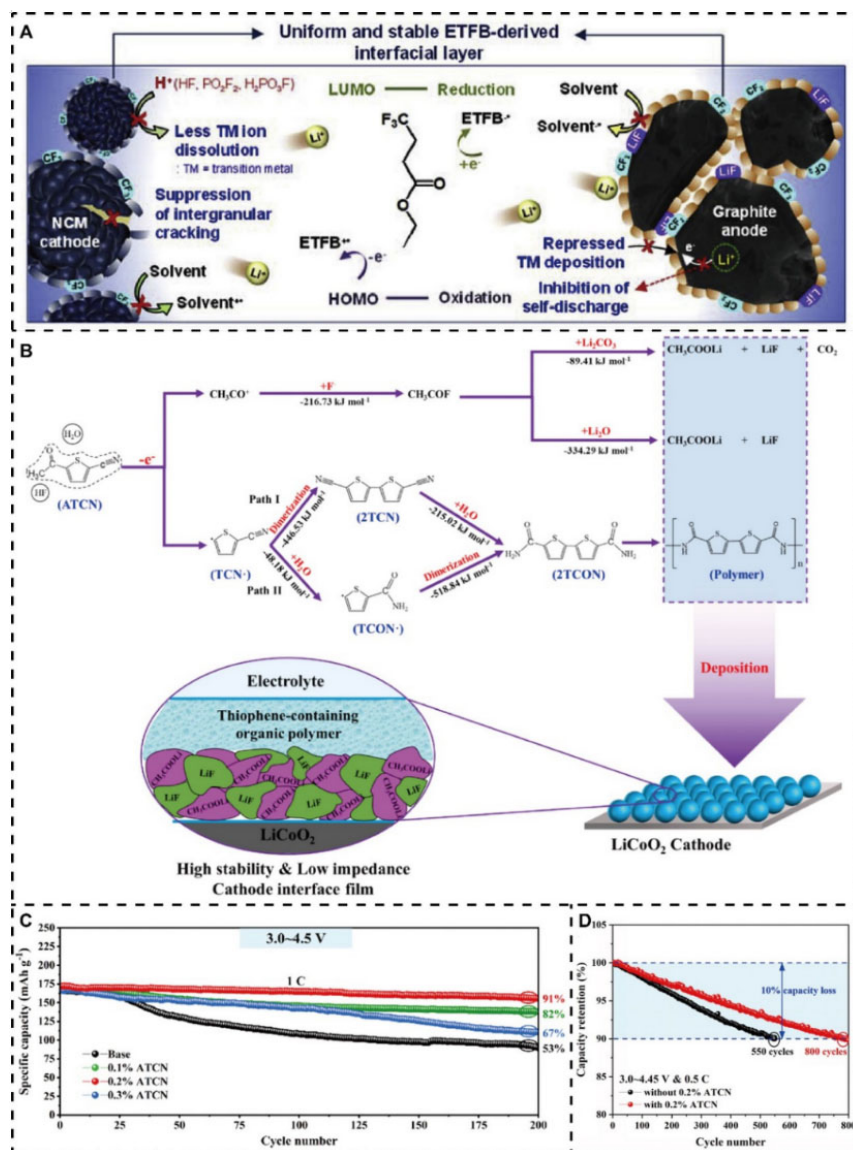
**Figure 5.** Phosphate-based electrode surface modification for lithium oxide cathode materials. (A) Schematic of the underlying mechanism for a LVPO-modified LNMO particle. (B) Evolution of  $R_{sf}$  and  $R_{ct}$  for pristine and modified LNMO during charge-discharge cycling. (C) Cycling performance for LNMO with or without LVPO. (D) Color changes of electrolytes with increasing soakage times for pristine and 1 wt.% LVPO-modified LNMO. Reproduced from Ref. [140] with permission from the American Chemical Society. LVPO:  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ; LVPO-LNMO:  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with different LVPO concentrations.

**Figure 6A**, Kim *et al.* introduced ethyl 4,4,4-trifluorobutyrate (ETFB) into the baseline electrolyte 1.15 M  $\text{LiPF}_6$  in EC/EMC/DEC (2:5:3 in volume) as a bifunctional additive to stabilize the interfacial structure by establishing uniform and stable protective layers on the surface of a Ni-rich  $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$  cathode and graphite anode in full cells [156]. Specifically, ETFB delivers a higher highest occupied molecular orbital energy and can undergo oxidative decomposition to form the corresponding radical species and then react with EC molecules to induce the formation of a CEI layer with fluorine ( $-\text{CF}_3-$ )-containing compounds on the surface of the NCM cathode. The ETFB-derived CEI is so robust that it can effectively ameliorate the intractable issues of continuous electrolyte decomposition, severe rupture of secondary particles, and significant dissolution of transition metal ions during repeated charge-discharge cycling.

Furthermore, ETFB can function as an electron acceptor to undergo reductive decomposition at the graphite anode due to its lower energy of lowest unoccupied molecular orbital than EC, EMC, and DEC. Its reactive intermediate species can induce the decomposition of EC molecules and further decomposition to generate fluorine ( $-\text{CF}_2-$ )-containing compounds and LiF, which constitute a SEI layer. Therefore, the unwanted self-discharge of the charged graphite anode and the deposition of transition metal ions can be decreased by the ETFB-derived SEI on the surface of the anode. Consequently, the full cell based on the 1% ETFB-modified electrolyte is capable of exhibiting a remarkably enhanced capacity retention of 84.8% with a high CE of above 99.8%, even after 300 cycles at  $45^\circ\text{C}$ .

Recently, using a similar method, Ruan *et al.* used 5-acetylthiophene-2-carbonitrile (ATCN) to serve as a novel electrolyte additive, which can construct a CEI thin film with high stability and low impedance on LCO *in situ* [146]. **Figure 6B** shows the detailed mechanism of the *in situ* formed CEI on the LCO cathode by the ATCN additive. ATCN is oxidized to generate an acetyl cation ( $\text{CH}_3\text{CO}^+$ ) and thiophenecarbonitrile radical ( $\text{TCN}\cdot$ ). The former can react with HF,  $\text{Li}_2\text{O}$ , and  $\text{Li}_2\text{CO}_3$  to ultimately form stable  $\text{CH}_3\text{COOLi}$  and





**Figure 6.** Representative electrolyte additives for high-voltage lithium oxide cathode materials. (A) Schematic of ETFB-derived interfacial layers with favorable effects on both NCM cathode and graphite anode. Reproduced from Ref. [156] with permission from Elsevier. (B) Schematic of *in situ* constructed CEI on LCO cathode by ATCN additive. (C) Cycling performance of LCO/Li coin half-cells with and without ATCN in the base electrolyte for 200 cycles at 1C and 3.0–4.5 V. (D) Cycling stability of commercial LCO/graphite pouch cells with and without 0.2% ATCN at 0.5C and 3.0–4.45 V. Reproduced from Ref. [146] with permission from Elsevier.

LiF species as the inner layer of the CEI film. In contrast, the latter reacts to generate thiophene-containing organic polymers, which constitute the outer layer of the CEI film with excellent ionic and electronic conductivity. As a result, distinguished cycling stability and rate capability could be achieved for LCO under high voltage due to the unique *in situ* constructed artificial CEI film with both inorganic and organic components. In particular, the cycling performance of LCO/Li coin half cells with and without ATCN in the base electrolyte is displayed in Figure 6C, indicating that LCO with a 0.2% ATCN-containing electrolyte exhibited the highest capacity retention of 91% after 200 cycles at 1C and 3.0–4.5 V. Moreover, the excellent cycling stability of commercial LCO/graphite pouch cells with 0.2% ATCN was also shown at 0.5C and 3.0–4.45 V [Figure 6D]. These results prove that this novel electrolyte additive strategy has excellent application prospects.

In addition to the application of individual additives, there have been several studies featuring the simultaneous introducing of several additives into conventional electrolytes. For example, nitrile (suberonitrile or 1,3,6-hexanetricarbonitrile) and FEC co-additives have been reported to synergistically modify an electrolyte to achieve a high-voltage LCO cathode with high energy density<sup>[164]</sup>. It is well known that nitrile additives can be widely applied to widen the electrochemical window of electrolytes. It was proved that the cyano groups of nitriles can coordinate strongly with transition metal ions to suppress the side reactions between the cathode and electrolyte. Simultaneously, a FEC additive is considered to be helpful for the generation of a uniform CEI thin film. If only nitriles or FEC are introduced alone, there is still no significant improvement in the electrochemical performance.

In addition to introducing novel additives, some other electrolytes, including HCEs, LHCEs, ionic liquid electrolytes, and sulfone-, nitrile- and fluorinated carbonate-based electrolytes, have also been developed to improve the structural and interfacial stability for high-voltage lithium oxide cathodes in LIBs. Generally, HCEs and ionic liquids show high viscosity and cost. Sulfone- and nitrile-based electrolytes show superior oxidation stability but inferior compatibility with lithium metal or graphite anodes. Although fluorinated carbonate-based electrolytes display high thermal and electrochemical stability, they are high in cost. Typically, in recent years, an innovative concept of LHCEs has been proposed and widely developed. This is mainly due to the fact that LHCEs have the advantages of both HCEs and LCEs with an optimized Li<sup>+</sup> solvation structure and low viscosity and cost. Accordingly, LHCEs are able to endow LIBs with lithium oxide cathodes that exhibit superior structural and electrochemical stability under high cutoff voltage. Generally, LHCEs can be obtained by adding a dilute solvent [like 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE)] into HCEs. For example, Zhang *et al.* designed an advanced LHCE made up of a LiFSI salt, 1,2-dimethoxyethane (DME) solvent, and TTE dilute solvent (1:1.2:3 in molar ratio) for a Ni-rich LiNi<sub>0.94</sub>Co<sub>0.06</sub>O<sub>2</sub> cathode<sup>[165]</sup>. It was noted that the unique LHCE not only created a uniform LiF-rich CEI to significantly alleviate the structural degradation of the cathode, but also formed a robust SEI to protect the anode from corrosion from the electrolyte. Consequently, the LHCE endowed the Ni-rich cathode material with a remarkably improved electrochemical stability (81.4% capacity retention after 500 cycles) and excellent fast charging ability (209 mAh g<sup>-1</sup> at 3C), thereby achieving high energy and power density for next-generation LIBs with wide working voltage and temperature windows.

### Binder design

Electrolyte regulation has been proved to play a crucial role in optimizing structural and interfacial stability and electrochemical performance under high working voltages and wide operating temperature ranges for the practical applications of high energy density LIBs. Furthermore, other battery components, like binders, can also be optimized for high-voltage operation. Although binders make up a very small part of the overall battery components (less than 5%), they are still indispensable due to their prominent role in maintaining good connections between the active materials, current collector, and conductive agents. Significant progress has been made in novel functional binder design for next-generation high-performance LIBs. Table 7<sup>[33,166-178]</sup> lists a number of representative binders for high-voltage lithium oxide cathode materials, including their advantages or working mechanisms and electrochemical performance in LIBs. According to the literature, an ideal functional binder design should meet several principles: (1) high adhesion and cohesion through chemical or physical interactions, which can make electrode components combine closely, even during long-term cycling; (2) excellent chemical and electrochemical stability, which make the electrode work with wide electrochemical windows; (3) outstanding dispersive capability, which allows the electrode components homogeneous distribution; (4) superior electronic or ionic conductance, which is helpful to improve diffusion kinetics. In addition, some binders with polar groups are able to coordinate with transition metal ions to mitigate their dissolution and further enhance the electrochemical performance. Some binders with special groups, like phenol, are capable of scavenging free radicals. The

**Table 7. Summary of selected novel binder designs for high-voltage lithium oxide cathode materials**

Binder	Cathode material	Voltage range V (vs. Li <sup>+</sup> /Li)	Advantages	Capacity retention	Rate capacity (mAh g <sup>-1</sup> ) at C-rate	Ref.
DSL	LCO	2.8-4.6	Generate an artificial CEI and enhance the stability of Co-O bonds	93.4%, 100th at 0.5C	-	[166]
SBR	LCO	3.0-4.5	High adhesion strength and flexibility	93.9%, 50th at 1/8C	150 at 4C	[167]
PAA	NCM811	3.0-4.3	Decrease pH of the slurry and improve the electrode adhesion	84.2%, 100th at 0.2C	160 at 2C	[168]
BBP	NCM811	3.0-4.2	Well-balanced amphiphilicity and bottlebrush-based structural uniqueness	80.6%, 240th at 0.2C	150 at 3C	[33]
PEO	NCM622	2.8-4.2	High ionic conductance and flexibility, improve the adhesion and electrode integrity	96.1%, 100th at 1C	147.3 at 2C	[169]
PI-FTD	NCM811	2.7-4.4	<i>in situ</i> build surface protective PI layer; non-flammable	79%, 100th at 0.2C	-82 at 10C	[170]
P(MVE-LMA)	LNMO	3.5-5.0	Superior adhesion and cohesion capabilities; interact with transition metal cations	92%, 400th at 1C	111.8 at 10C	[171]
γ-PGFO	LNMO	3.5-5.0	High-voltage resistant and favorable cathode interfacial stability property, superior coordination capability	88.2%, 500th at 1C	108.1 at 5C	[172]
CCTS/PEO	LNMO	3.5-4.9	Show a high electrochemical oxidation potential of above 5.0 V, improved mechanical properties	81.4%, 200th at 0.5C	-70 at 2C	[173]
LiPAA and Na-Alg	LNMO	3.5-5.0	Enhance cathode adhesion and cohesion; create an effective passivating CEI layer	97.4%, 100th at 0.5C	-	[174]
Lignin	LNMO	3.5-5.0	Have numerous phenol groups; scavenge free radicals and generate compatible interfaces	94.1%, 1000th at 1C	-	[175]
FPI	LMNC	2.5-4.7	Superior binding ability and form a robust surface structure	89%, 100th at 0.2C (55 °C)	-	[176]
XG	Li <sub>1.144</sub> Ni <sub>0.136</sub> Co <sub>0.136</sub> Mn <sub>0.544</sub> O <sub>2</sub>	2.0-4.8	Have a unique double-helix superstructure with abundant charged functional groups	98.4%, 200th at 0.1C	-	[177]
Al <sup>3+</sup> -doped Na-Alg	Li <sub>1.116</sub> Mn <sub>0.6</sub> Co <sub>0.12</sub> Ni <sub>0.12</sub> O <sub>2</sub>	2.0-4.8	Form a coating layer on the surface of the primary particles	99.9%, 150th at 0.5C	-150 at 5C	[178]

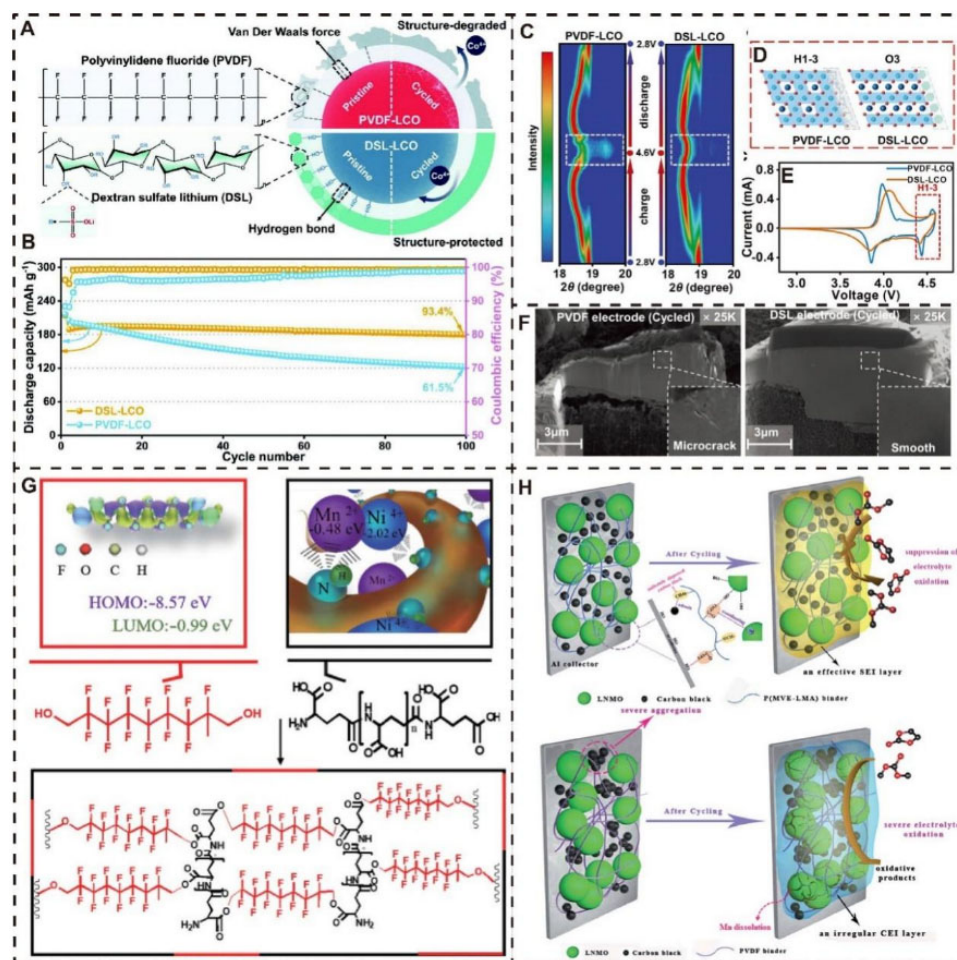
DSL: dextran sulfate lithium; SBR: styrene-butadiene rubber; PAA: poly(acrylic acid); BBP: bottlebrush polymers; PEO: polyethylene oxide; PI-FTD: fluorinated polyimide; P(MVE-LMA): poly(methyl vinyl ether-alt-lithium maleic acid); γ-PGFO: poly(γ-glutamic acid)-c-1H, 1H, 9H, 9H-perfluoro-1,9-nonanediol; CCTS/PEO: carboxymethyl chitosan/poly(ethylene oxide); LiPAA and Na-Alg: lithium polyacrylate and sodium alginate; FPI: fluorinated polyimide; XG: xanthan gum.

following section reviews a number of aqueous and non-aqueous binders for high-voltage lithium oxide cathodes in LIBs.

### Aqueous binders

Aqueous binders, primarily carboxymethyl cellulose, have been widely applied in battery systems. However, when used in high-voltage lithium oxide electrode material systems, there are usually some issues, e.g., the surface structure of layered lithium oxide materials may be damaged in the water slurry because of the irreversible reaction with H<sub>2</sub>O molecules. Therefore, it is essential to reasonably design novel functional binders with a unique structure to withstand high voltages.

Recently, an innovative modification strategy has been developed to enhance the cycling stability of LCO under high cutoff voltages using a DSL binder instead of the traditional PVDF binder<sup>[166]</sup>. Figure 7A characterizes the different interactions between a LCO cathode and two binders and the effects on surface



**Figure 7.** Representative aqueous binders for high-voltage lithium oxide cathode materials. (A) Schematic of different interactions between LCO and PVDF/DSL binders and their effects on surface stability. (B) Cycling performance of LCO electrodes with PVDF and DSL binders at 0.5C and 2.8-4.6 V. (C) *In situ* X-ray diffraction measurements with (003) diffraction peak during the first charge-discharge cycle at 0.1 C. (D) Crystal structure under high voltage. (E) CV curves. (F) SEM images (cross-sectional view) after 50 cycles for two LCO electrodes. Reproduced from Ref. [166] with permission from Wiley-VCH. (G) Schematic of generation of the  $\gamma$ -PGFO binder with chemical structure. Reproduced from Ref. [172] with permission from Springer Nature. (H) Schematic of effects of P(MVE-LMA) and PVDF binders on LNM0 electrode during cycling. Reproduced from Ref. [171] with permission from the Royal Society of Chemistry.

stability during repeated cycling. Due to strong hydrogen bonds, the DSL binder contributes to generating a uniform coating layer *in situ*, which can provide important protection against damage from electrolyte decomposition. In addition, the sulfate acid groups can be used to enhance the stability of Co-O bonds, which is beneficial in suppressing the phase transition under high voltage. As a result, LCO electrodes with PVDF and DSL binders (PVDF-LCO and DSL-LCO) can exhibit capacity retentions of 61.5% and 93.4% after 100 cycles at 0.5C, respectively, demonstrating a conspicuous improvement in cycling stability [Figure 7B].

Furthermore, *in situ* X-ray diffraction measurements of PVDF-LCO and DSL-LCO electrodes were performed to reveal the crystal structural evolution of LCO with different binders. The distinctive (003) peak shifts above 4.55 V are marked by dashed squares in Figure 7C, and the DSL-LCO electrode delivers a smaller peak movement, confirming that the irreversible phase transformation of LCO from O3 to H1-3 under high voltage can be greatly suppressed in comparison with the PVDF-LCO electrode [Figure 7D].



These results are also consistent with the cyclic voltammetry curves in [Figure 7E](#). Both of these electrodes demonstrate two couples of anodic and cathodic peaks at 3.9 and 4.5 V, which represent the benign phase transition between two O<sub>3</sub> phases and the malignant phase transition from O<sub>3</sub> to H1-3, respectively. Moreover, it can be observed that the peaks under a higher voltage are well suppressed for the DSL-LCO electrode. In addition, according to the cross-section SEM images of both the cycled PVDF-LCO and DSL-LCO electrodes in [Figure 7F](#), the former shows apparent microcracks while the latter can maintain an intact morphology with a flat and smooth surface.

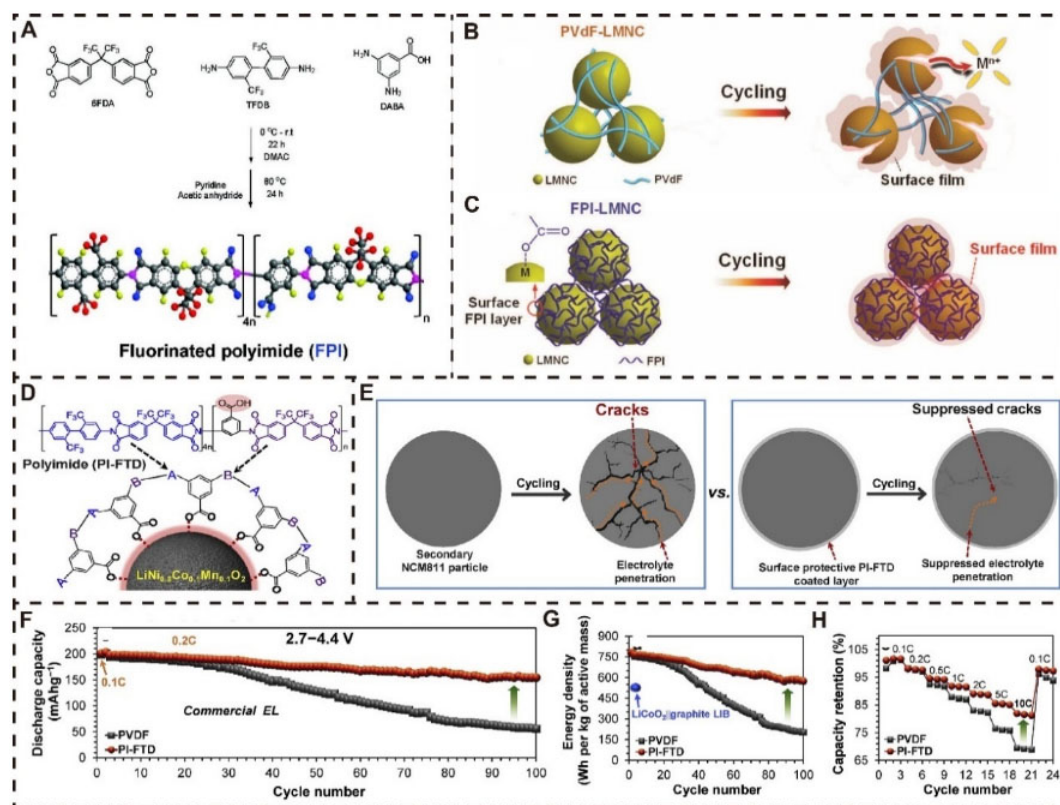
A unique binder design was also considered as a feasible strategy to improve the instability of electrode materials under high-voltage operation. A well-designed amino acid-based binder ( $\gamma$ -PGFO) was applied to achieve superior high-voltage performance for a spinel LNMO cathode<sup>[172]</sup>. As shown in [Figure 7G](#), IH,1H,9H,9H-perfluoro-1,9-nonanediol functioning as a high-voltage resistant block with a well-matched energy level was introduced and grafted to a poly( $\gamma$ -glutamic acid) backbone with a powerful coordination interaction with transition metal ions. Therefore, the synergistic effect from the unique binder can endow the LNMO cathode with outstanding electrochemical properties, including an enhanced capacity retention of 88.2% after 500 cycles at 1C and 3.5-5.0 V. In addition, similarly, the group of Cui<sup>[171]</sup> also reported a novel water-soluble binder [P(MVE-LMA)], which can deliver excellent adhesion properties with both active materials and an Al current collector. Furthermore, a stable CEI layer can be formed to effectively suppress the electrolyte decomposition and transition metal dissolution [[Figure 7H](#)]. However, in comparison, the LNMO cathode with a conventional PVDF binder goes through severe aggregation of electrode components, generation of an irregular CEI layer, severe electrolyte oxidative decomposition, and Mn dissolution from cathode materials.

#### *Not-aqueous binders*

According to recent reports and the above discussions, aqueous binders have made significant progress regarding the structural design and working mechanisms for high-performance lithium oxide cathodes in LIBs. In addition to aqueous binders, non-aqueous binders have also been widely investigated to obtain high-performance lithium oxide cathode materials under high working voltage. For example, FPI<sup>[176]</sup> was synthesized as an innovative high-voltage binder via the approach shown in [Figure 8A](#). According to the chemical structure of FPI, PI with heterocyclic imide rings is well known to provide superior thermal stability, while the oxidation resisting -F or -CF<sub>3</sub> groups are introduced to further improve the stability under high-voltage operation. The specific surface structure changes for Li<sub>1.13</sub>Mn<sub>0.463</sub>Ni<sub>0.203</sub>Co<sub>0.203</sub>O<sub>2</sub> (LMNC) combined with PVDF and FPI binders (PVDF-LMNC and FPI-LMNC) are demonstrated in [Figure 8B](#) and [C](#), respectively. Obviously, the PVDF-LMNC electrode inevitably suffers from a series of issues, including transition metal dissolution, oxygen loss, electrolyte decomposition, and particle microcracking during repeated cycling. In sharp contrast, for FPI-LMNC, there is a uniform thin film on the surface of the electrode active materials via -COO...metal (M) bonds, which help to restrain these harmful side reactions mentioned above, thus contributing to the electrochemical performance enhancement, even in harsh conditions.

This research team also introduced a novel functional binder (PI-FTD) into layered lithium ternary oxides system to improve their electrochemical performance for practical applications<sup>[170]</sup>. As illustrated in [Figure 8D](#), the carboxylic acid group (-COOH) from the PI-FTD binder can be chemically grafted onto the surface of a NCM811 active material by covalently binding/combining with transition metal ions to build a PI-FTD coating layer *in situ*. The PI-FTD coating can function as a surface protective layer to ensure the integrity of active particles and avoid serious crack generation and electrolyte decomposition. However, for the NCM811 cathode combined with a traditional PVDF binder, a large number of cracks are created due to





**Figure 8.** Representative non-aqueous binders for high-voltage lithium oxide cathode materials. (A) Synthesis of FPI. Schematic of changes in surface structure for (B) PVDF-LMNC and (C) FPI-LMNC electrodes. Reproduced from Ref. [176] with permission from Wiley-VCH. (D) Chemical structure of PI-FTD binder and its interaction with NCM811 cathode surface. (E) Mechanism of crack formation for NCM811 electrodes with PVDF and PI-FTD during cycling. Comparison of electrochemical performance: (F) cycling performance; (G) energy density; (H) rate capability. Reproduced from Ref. [170] with permission from Elsevier.

the stress caused by anisotropic lattice expansion and contraction and thus aggravate electrolyte penetration and decomposition during the repeated charge-discharge process with a high cutoff voltage, as exhibited in Figure 8E. Unsurprisingly, the NCM811 electrode with the PI-FTD binder delivered better electrochemical performance than that of the conventional NCM811 electrode with the PVDF binder. In particular, the NCM811 electrode with PI-FTD exhibited superior cycling stability with a dramatically increased capacity retention of 79% after 100 cycles with a voltage window of 2.7–4.4 V at 0.2 C, while only 30% of the initial capacity could be maintained for the NCM811 electrode with PVDF [Figure 8F]. The conspicuously improved energy density and rate capability are also displayed in Figure 8G and H.

### Other modification strategies via special surface treatments

In addition to the aforementioned conventional surface modification strategies, including surface coating, electrolyte regulation, and binder design, emerging modification strategies based on specific surface treatments have also been proved to be facile and efficient for substantial electrochemical improvements in LIBs. Recently, Xiao and co-workers reported the introduction of  $\text{LiBH}_4$  and  $\text{LiAlH}_4$  to modify the LCO surface by means of simple chemical treatments [136,137]. In contrast to typical surface modification processes with additional high-temperature sintering, a one-step wet chemical treatment was designed to decorate LCO with  $\text{LiBH}_4$  or  $\text{LiAlH}_4$  in a tetrahydrofuran (THF) solution. The modified LCO demonstrated a remarkably enhanced rate and cycling stability under high voltage, which were largely attributed to the generation of a more robust CEI and more stable B-O and Al-O bonds.

In particular, for Li-rich cathode materials, a series of surface treatments with  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_3\cdot\text{H}_2\text{O}$ , urea, or acid compounds are usually applied to modify the surface structure. Metal/oxygen vacancies and the spinel/rock salt phase will be artificially created on the cathode surface, which are conducive to electrochemical performance. Specifically, when modifying  $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$  via a multifunctional urea treatment, the *in situ* construction of oxygen vacancies, the spinel structure, and a N-doped carbon layer can be obtained simultaneously<sup>[179]</sup>. It has been well proved that oxygen vacancies can induce the generation of a self-built charge field to facilitate  $\text{Li}^+$  transport and reversible oxygen evolution, the spinel phase with fast 3D  $\text{Li}^+$  diffusion paths can also enhance ionic conductivity. Simultaneously, the N-doped carbon layer is able to protect active particles from HF attack from electrolyte decomposition. Other surface treatments are similar regarding their underlying working mechanism.

Recently, Peng and co-workers<sup>[36]</sup> developed a facile interface engineering via an ultrasonic treatment with oleic acid (OA) for a pristine Li-rich Mn-based cathode material. Note that  $\text{H}^+$  from OA can exchange with  $\text{Li}^+$  in the lithium oxide material, resulting in the formation of not only lithium defects but also a uniform organic coating layer on the cathode material surface by OA polymerization. The following calcination process further induces the generation of transition metal and oxygen vacancies, as well as surface reconstruction layer, including spinel phase  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  and a carbon coating layer. It is well established that both cation/anion defects and *in situ* surface reconstruction play a prominent role in improving the structural and electrochemical stability of lithium oxide cathode materials, as mentioned above. Additionally, the innovative and scalable strategy can be applied to other kinds of layered cathode materials. As a result, superior electrochemical performance, including improved initial CE, ameliorative voltage and capacity decay during cycles, as well as outstanding rate capability, can be achieved.

## CONCLUSIONS AND OUTLOOK

In this review, we have systematically discussed four representative oxide cathode materials, namely, layered lithium cobalt oxides, lithium ternary oxides, Li-rich oxides, and spinel lithium (nickel) manganese oxides. Generally, these materials exhibit diverse electrochemical behavior based on the intrinsically distinct crystal structures. In order to achieve high energy density, working at a raised cutoff voltage has been an important trend. However, these cathodes often suffer from unsatisfactory structural and electrochemical stability simultaneously, which is mainly due to the resulting fragile surface and interface under a high operating voltage. In the process of summarizing recent research progress on high-voltage lithium oxide cathode materials, a series of universal surface/interface modification strategies have been considered, including surface coating, electrolyte regulation, binder design, and special surface treatments. Their specific mechanisms of electrochemical improvement have also been investigated in detail to obtain a better understanding of high-voltage oxide cathode materials with high energy density.

Primarily, surface coating is the most efficient and simple modification, which has been proved to effectively improve the stability of not only the surface of active materials but also the interface between the electrode and electrolyte. In particular, coating materials (like fluorides, phosphates, polymers, and so on), methods (like wet-chemical, coprecipitation, sol-gel, ALD, and so on), and working mechanisms (like physically insulating electrodes from electrolytes, scavenging HF, constructing stable electrode/electrolyte interphase, and so on) have been summarized and discussed in detail. Note that synergetic surface modifications with several coating materials have also been attempted and can further promote the electrochemical performance improvement for high-performance LIBs with lithium oxide cathodes under high voltages. Simultaneously, some novel coating species and techniques of surface modification should be developed to achieve a better balance between cost and performance for practical applications in the future.

Considering the interfacial instability from side reactions between the electrode and electrolyte accompanied by electrolyte decomposition and structural degradation, electrolyte regulation is well known to be applied as a highly efficient modification strategy. Generally, studies on high-voltage electrolyte systems focus on two aspects. The first is introducing functional additives into traditional electrolyte systems. When charging to a high working voltage, the electrolyte additives will be preferentially oxidized to help generate a more stable CEI/SEI, inhibit the subsequent electrolyte decomposition and suppress the detrimental structure transformation and parasitic side reactions, thus causing the improved electrochemical performance. The second is designing novel electrolyte systems to meet the ever-increasing demand for high-voltage operation, which has also proved to be feasible. It is noteworthy that LHCEs take into full account several factors, including ionic conductivity, viscosity, oxidation stability, and cost, which are able to significantly improve significant interfacial issues and enhance electrochemical performance.

Furthermore, a novel functional binder design has also been developed as a feasible modification strategy recently, which is expected to play a significant part in consolidating the electrode itself and therefore enhancing the comprehensive electrochemical performance. At present, extensive research is still devoted to optimizing binder structure and uncovering the underlying working mechanism for high-voltage lithium oxide cathode materials. In particular, novel aqueous binders are usually cost-efficient and eco-friendly. Additionally, some binders with superior high-voltage tolerant capability are beneficial to the structural and electrochemical performance of advanced LIBs with lithium oxide cathodes under high-voltage operation. In contrast, some binders have the ability to coordinate with transition metal ions of active materials, which can reduce the dissolution of transition metal ions and thus lead to improved energy storage capability.

Finally, special surface treatments have been regarded as another widely reported modification strategy in recent years. Generally, surface treatments with special chemical agents like acids have the ability to change the surface structure in a certain content and obtain improved electrochemical performance for lithium oxide materials. In particular, for Li-rich oxide cathode materials, surface treatments through acids or amine are applied to realize surface recondition and specific oxygen vacancy formation, further are beneficial to relieve a series of harmful side reactions during cycling and realize high-performance LIBs.

So far, there is no doubt that significant improvements in structural and electrochemical stability with the high-voltage operation have been achieved for commonly used lithium oxide cathode materials. Nevertheless, consistent efforts are still required for next-generation LIBs with both high energy density and long cycle life. As a consequence, definite development directions in the future can be proposed. These mainly involve the following aspects: (1) In the perspective of cathode materials, it is indispensable to optimize the existing oxides and develop innovative active materials with high lithium storage performance and stable crystal structure. For example, considering the limited capacity, developing novel cobalt-free and nickel-rich oxide materials like  $\text{LiNi}_{0.9}\text{Mn}_{0.1}\text{O}_2$  is urgent and attractive. This is able to not only improve the reversible capacity but also reduce cost. However, poor rate and cyclic capability need to be further enhanced by various modification strategies. In addition, layered Li-rich oxide materials can deliver ultrahigh specific capacity with cation and anion redox, which should be further developed for next-generation LIBs with high energy and power density during cycling. (2) In order to successfully achieve advanced LIBs with superior electrochemical performance under the growing cutoff voltage, other battery compositions like electrolyte, separator, and binder should be optimized to ensure high compatibility with cathode and anode. High-voltage electrolyte systems such as LHCEs and novel functional binders like polymers should be designed in the future. (3) It is expected that rational combinations of multiple modification strategy are promising to further upgrade the electrochemical performance of next-generation LIBs. Meanwhile, the simplified and environmental modification process will be more conducive to large-

scale applications in the future. (4) Advanced characterization techniques are also vitally important. More in-depth theoretical and experimental studies will be carried out to pursue more insight into the underlying mechanism of performance deterioration for various lithium oxide cathode materials under high-voltage operation during cycling. Subsequently, the corresponding performance improvements will be more targeted and efficient. In particular, recently, artificial intelligence, including machine learning, has been devoted to materials science, which can predict, design, and research new energy materials and battery systems with vast development potential.

## DECLARATIONS

### Authors' contributions

Conceived the manuscript: Heng YL, Wu XL

Wrote and reviewed the manuscript: Heng YL, Wu XL

Contributed to the discussion of the manuscript: Heng YL, Gu ZY, Guo JZ, Wang XT, Zhao XX, Wu XL

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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