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A Perspective on the Requirements of Ni-rich Cathode Surface Modifications for Application in Lithium-ion Batteries and All-Solid-State Lithium-ion Batteries

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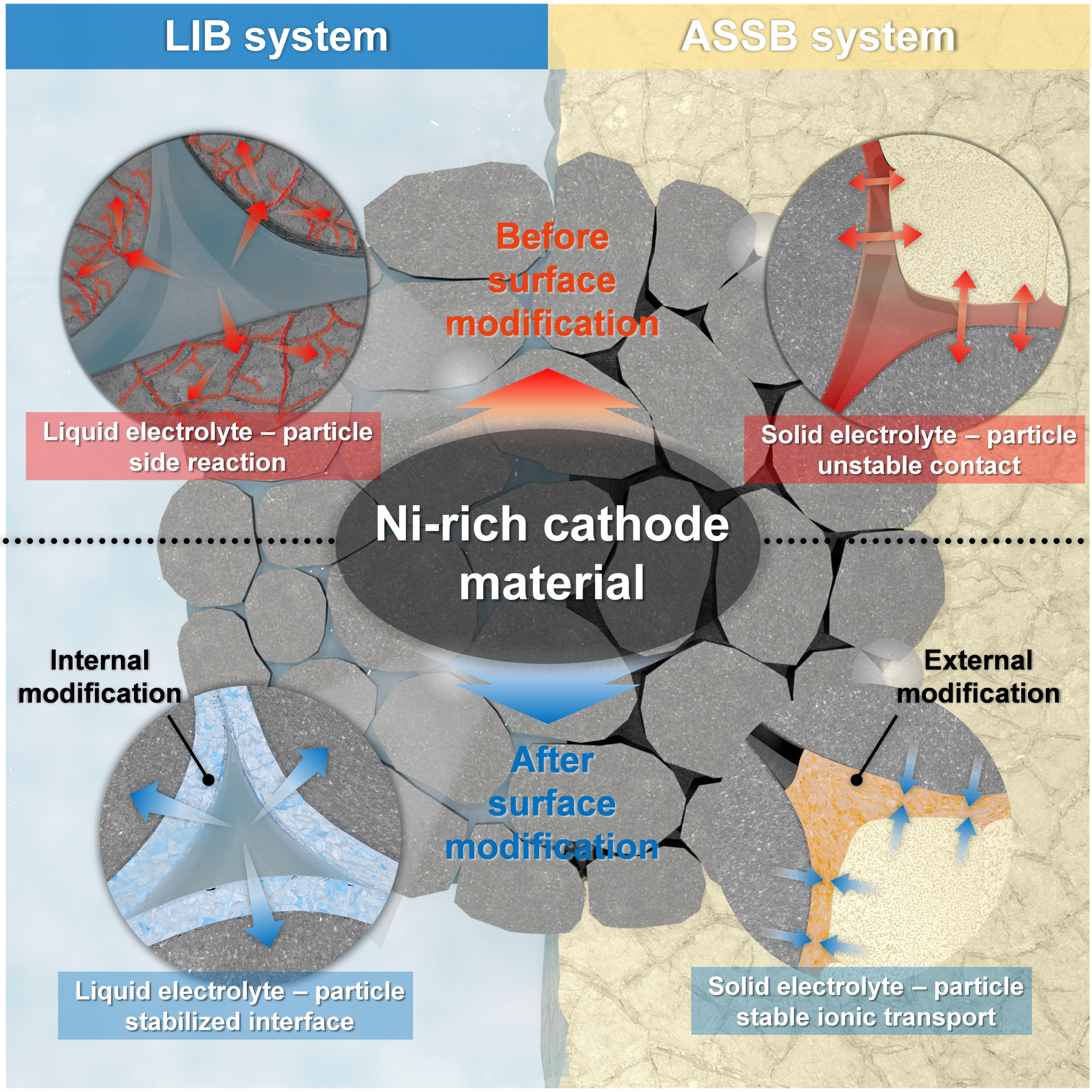

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The increasing adoption of Ni-rich cathode active materials in commercial liquid electrolyte Lithium-ion batteries (LIBs) is testament to the improvements in the cathode stability through various surface modification strategies. The development of a deeper understanding of the cathode/electrolyte interface in LIBs has resulted in coatings capable of mitigating both surface and bulk cathode degradation mechanisms. However, due to increasing demands for safe and high energy density cells, a large portion of the research has now shifted towards applying Ni-rich cathode active materials in inherently safer all-solid-state Lithium-ion batteries (ASSLBs), with the resulting cathode surface modification strategies evolving differently. In this regard, a review outlining the surface modification strategies of Ni-rich cathode materials applied in both LIB and ASSLB systems is provided. Within, a review of the traditional, advanced and specialized surface modification strategies of each system is discussed, along with a final perspective on the likely future direction of research regarding the design of system-specific Ni-rich cathode-based surface modification strategies.

1. Introduction

Lithium-ion batteries (LIBs) have evolved beyond their initial applications in mobile electronics, becoming essential in the realm of electric vehicles and electrical energy storage systems.[1,2] The escalating requirements for high energy/power density and thermal stability underscore the critical significance of advanced LIB technology.[3,4] Currently, LIBs, which are often cells configured with a combination of a graphite anode component and a layered NCM (Nickel-Cobalt-Manganese) cathode component, offer a gravimetric energy density of 260 $\mathrm{Wh\,kg^{-1}}$ and a volumetric energy density of 780 $\mathrm{Wh\,L^{-1}}$.[5,6] While the energy density of current LIBs has improved by approximately 160% compared to LIBs from 30 years ago,[2] the market demands batteries with even higher energy density. In response to these demands, there has been a recent surge in interest in Ni-rich layered cathode materials. This is because the Ni-rich layered cathode materials ($LiNi_{1-x}M_xO_2$; $x \leq 0.3$; M = Co, Mn, Al, etc.) exhibit a relatively higher achievable specific capacity (~200 $\mathrm{mAh\,g^{-1}}$) compared to other materials such as $LiCoO_2$ (~140 $\mathrm{mAh\,g^{-1}}$),[7] $LiFePO_4$ (~140 $\mathrm{mAh\,g^{-1}}$),[8] and $LiMn_2O_4$ (~120 $\mathrm{mAh\,g^{-1}}$).[9]

Ni-rich layered cathode materials achieve a high specific capacity by utilizing over 70% of available lithium at high operating voltages (~4.3 V vs Li^+/Li). On the flip side, since more than 0.7 mols of lithium exits the cathode material during the charging process, the Ni-rich layered cathode materials undergo structural instability and are prone to irreversible transformations, leading to rapid performance degradation.[10] During the charging process, the extraction of lithium creates vacancies, generating a high repulsive force between the oxygen slabs.[11] This structural instability prompts the migration of Ni ions into Li vacancies, because of the similarity in ionic radius between divalent nickel ions (0.69 Å) and lithium ions (0.76 Å), which is well known to be an irreversible transition.[12] This induces the formation of an NiO-like structure during the charge/discharge process which inhibits the lithium ion transport at the cathode surface, accelerating the capacity fading.[13,14] Additionally, the extraction of lithium ions from the cathode materials induces mechanical strain, leading to anisotropic lattice volume changes along the c-axis. This leads consequently to the formation of microcracks and particle breakage, resulting in void space.[15,16]

To combat the degradation of Ni-rich layered cathode materials, one predominant strategy is surface coating for interfacial stabilization, which is known to be effective for improving capacity retention, rate capability and thermal stability.[17,18] However, the strategies are addressed differently in systems employing liquid electrolytes, such as traditional LIBs, and those using solid electrolytes, like all-solid-state lithium-ion batteries (ASSLBs). Direct comparison of surface modification in these two systems is required to further develop a better understanding of their associated differences, overlaps and inherent needs and to encourage a focus on system-specific surface modification research.

Initially, to mitigate the degradation of Ni-rich layered cathode materials in LIBs systems, coatings were specifically engineered with the primary objective of establishing a physical barrier to prevent direct contact between the cathode material particles and the electrolyte at the surface of the secondary particle.[19,20] However, considering that Ni-rich layered cathode materials consist of particles containing many primary particles that agglomerate into larger secondary particles,[21] the evolution of strategies has led to the development of coating approaches that go beyond simply coating the surface of individual secondary particles. These strategies involve coating all surfaces, including individual primary particles, as the electrolyte interacts with every interface of the primary particles, not just the surface of the simple secondary particles.[22,23] Furthermore, there have been recent reports on

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coatings even capable of addressing mechanical cracking issues.[24,25]

In contrast to liquid electrolyte systems where all particles form interfaces with the electrolyte, coating strategies for ASSLBs have evolved differently. Initially, similar to LIBs, the emphasis was on stabilizing the interface between Ni-rich layered cathode materials and the solid electrolyte to enhance lithium-ion diffusivity.[26,27] Despite the development of solid electrolytes with ion conductivity comparable to liquid electrolytes,[28] issues arose due to poor contact at the interface between cathode materials and the solid electrolyte. This prompted research efforts to concentrate on developing thin and uniform coating layers, addressing contact issues.[29] Additionally, studies were conducted to mitigate cracking, aiming to enhance ion conductivity.[30] With specialized coating strategies, which effectively establish contact between cathode materials and the solid electrolyte (SE), progress has been made on continuously suppressing the interfacial resistance.[31,32]

Herein, this review outlines coating strategies to mitigate the degradation of Ni-rich layered cathode materials in LIBs and ASSLBs systems. The coatings are categorized into traditional, advanced, and specialized methods based on the electrolyte type employed. Lastly, the review provides a perspective on future directions for designing system-specific Ni-rich cathode-based surface modifications with superior performance.

2. Liquid-Electrolyte Systems

2.1. Traditional Cathode Surface Modification with Liquid-Based Electrolyte

Initially, coatings for liquid electrolyte systems were developed to serve as a physical barrier, preventing direct contact between cathode material particles and the electrolyte on the surface of the secondary particle. When the interface is completely coated, it can effectively prevent degradation caused by the electrolyte, such as the well-known ′hydrogen fluoride (HF) attack′.[19] This attack results from the decomposition of $LiPF_6$ salt due to the presence of water, as shown in Figure 1a. Consequently, with coating, the dissolution of transition metals into the electrolyte can be minimized, thereby preventing oxygen evolution reactions and enhancing the structural integrity of the cathode material particle.[20] Moreover, the use of a physical barrier between the cathode material and external contaminants, such as CO_2 and H_2O, can effectively enhance the stability of the material.[33,34] This barrier prevents degradation pathways, such

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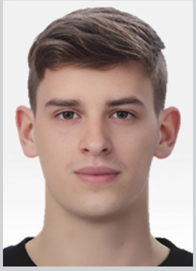

Tom James Embleton is a postdoctoral researcher in the Department of Smart Green Technology Convergence Engineering at Pukyong National University (Republic of Korea), from where he received his PhD. During his PhD, he contributed to the development of Ni-rich cathode materials for application in traditional Li-ion battery systems and all-solid-state Li-ion battery systems. His current research is focused on developing cathode materials and electrode systems for future iterations of the Li-ion battery technology.

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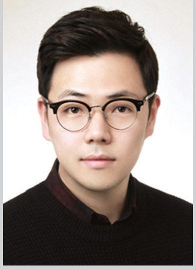

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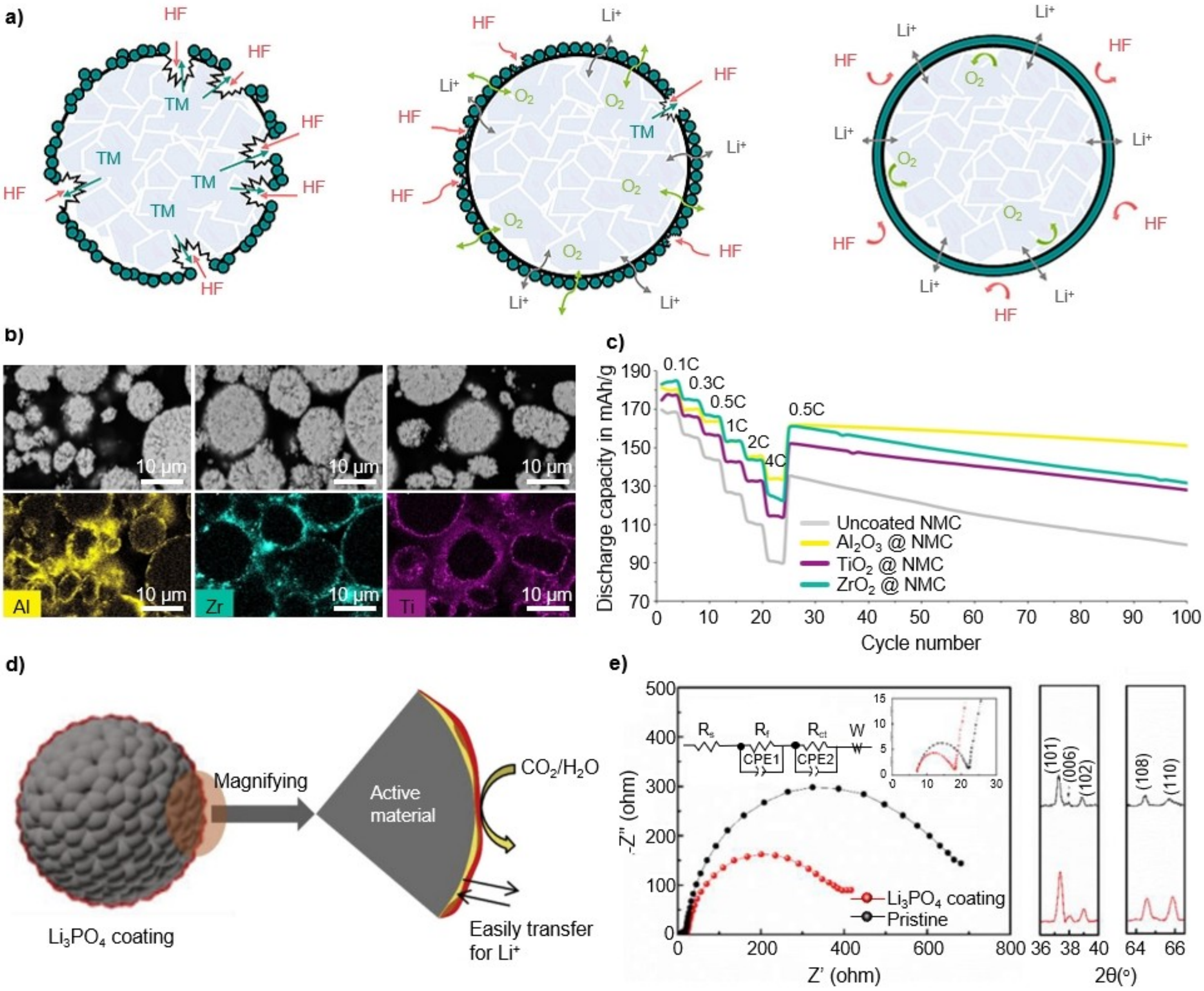

Figure 1. a) The HF attack and corresponding transition metal (TM) dissolution associated with non-uniform surface modification, uniform particulate surface modification, and uniform thin film surface modification. [Reproduced from Ref.[19] Copyright (2020), with permission from Wiley], b) Cross sectional Scanning Electron Microscopy (SEM) images of dry process Al_2O_3-coated, ZrO_2-coated, and TiO_2-coated $LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2$ with c) corresponding electrochemical rate and cycle data. [Reproduced from Ref.[49] Copyright (2021), with permission from Wiley], d) Schematic of Li_3PO_4 coated cathode material with e) EIS and XRD data after 100 cycles. [Reproduced from Ref.[52] Copyright (2018), with permission from Elsevier].

as lithium leaching and the formation of lithium residuals.[35–37] In addition to their protective properties, the coatings must meet or surpass the ionic transference and electric conductivity capabilities of a typical cathode material in order to maintain charge movement at the surface of the cathode and avoid reductions in reaction rate. Therefore, researchers have developed coatings that mimic the characteristics of conventional cathode materials, such as metal-oxide and metal-phosphate coatings.[38–47] These coatings are being explored for their stability, ionic conductivity, and electrical conductivity.[48]

Herzog et al. utilized a dry coating technique to apply nanostructured Al_2O_3, ZrO_2, and TiO_2 onto $LiNi_{0.7}Mn_{0.15}Co_{0.15}O_2$ cathode material in order to examine the varying impacts of these metal-oxides (Figure 1b).[49] The group attributed the effectiveness of the coating layers at higher cycling rates to the physical properties of the coatings, such as porosity and thickness. They also attributed the poor rate performance of the pristine material to the buildup of a rate-limiting cathode electrolyte interface (CEI) layer. The study also mentioned the HF scavenging effect of the three coatings as a protective mechanism. This emphasized that physical barrier protection is not the only mechanism, and that chemical protection is also at work and improves the cycling over 100 cycles (Figure 1c). Although there appeared a general improvement against mechanical failure, the secondary particles still experienced cracking after 250 cycles. This cracking was determined to be caused by the infiltration of liquid electrolyte into the secondary particle, which conventional coating methods traditionally overlooked. Lithium-phosphate and other phosphates have also been proposed for their high ionic conductivity and stability.[50,51] Zhu et al. successfully implemented a lithium reactive metal-phosphate coating, specifically Li_3PO_4, on the cathode material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.[52] This coating used surface lithium to effectively achieve a uniform coating of the

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secondary particle. This was demonstrated by the reduced residual lithium detected on the coated surface. The study referenced the high ionic conductivity of the Li_3PO_4 coating layer, as demonstrated in electrochemical impedance spectroscopy data following 100 cycles (Figure 1d). As expected of traditional coatings, the presence of the Li_3PO_4 interfacial layer acted as a physical barrier resulting in a significant reduction in HF reactions and thereby providing protection to the surface structure of the cathode material, resulting in lower resistances and improved layered structure of the active material after 100 cycles (Figure 1e).

Despite the fact that these valuable attempts to create an interfacial barrier between the active material and the liquid electrolyte undoubtedly pushed the boundaries of research and understanding, it was quickly determined that solving interfacial issues at the secondary particle surface would not solve the instability issues of Ni-rich polycrystal materials. Without absolute and uninterrupted coverage of the polycrystal surface, the majority of the surface area remains uncovered and vulnerable to the intrusive liquid electrolyte. To overcome this, new coating technologies and methodologies were required.

2.2. Advanced Cathode Surface Modification with Liquid-Based Electrolyte

The infiltration of liquid electrolyte into the Ni-rich secondary particle has been recognized as a significant factor contributing to cathode degradation (Figure 2a).[53–55] The electrolyte infiltrates the secondary particle structure during electrochemical evaluation because of the anisotropic shrink of the lattice.[56] Electrolyte-related attacks can lead to the formation of NiO-like structures and CEI layers within the particles (Figure 2b).[57,58] This leads to the destabilization of the particle structure and eventual cracking of the secondary particle after prolonged cycles. The cracking of the cathode particles signals the beginning of the serious deterioration for the cathode.[23,59] The increased surface area resulting from the cracks facilitates ongoing side reactions with the electrolyte and the separation of cathode material fragments.[60] Advanced internally diffusive coatings are now widely used to protect surfaces from such internal degradation.[55,61,62] These coatings effectively prevent the negative side effects of penetration of electrolytes and contaminants into the internal structure of cathode material secondary particles. The internal coating layer provides a physical barrier on the surface of the internal primary particles, effectively preventing both external and internal chemical degradation. Numerous advanced internally diffusive coatings have been developed, exhibiting common properties consistently reported in the literature.[63–65] The coatings should naturally cover the internal grain boundaries of the cathode material. Furthermore, it is important for the coating to possess adequate lithium-ion conductivity due to the restriction of ion movement within the grain boundaries caused by the potential absence of electrolyte after material modification.

Embleton et al. found that contaminants including H_2O and CO_2, which are known to degrade cathode material with a high nickel content, can migrate into the voids within secondary particles (Figure 2c).[22] This migration leads to degradation of both the surface and bulk of the cathode material. A thin layer of lithium-cobalt-oxide with a low weight percentage was applied to protect the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$. This layer infused into the structure, preserving the rate capabilities by leveraging the properties of $LiCoO_2$. Furthermore, the utilization of advanced coating techniques, such as atomic layer deposition, enables precise manipulation of the surface modification layer's thickness and morphology, leading to notable enhancements in the performance of specific coatings.[66] Cheng et al. observed that, post-atomic layer deposition (ALD), infusion into the grain boundaries of the surface modification material can occur during annealing (Figure 2f). The presence of grain boundaries and a controlled, thin surface coating led to a notable decrease in cation mixing in the cathode, both at the surface of secondary particles and internally at the primary particle surface.[17] This was determined by comparing the electrochemical performance of the material with both the standard surface coating and the infused coating, highlighting the importance of a diffusive buffer layer when it comes to chemical protection of polycrystalline Ni-rich cathodes (Figure 2d–e). The use of ALD also allows for the precise control over the morphology and thickness of these layers, addressing the challenges related to achieving uniformity in conventional solution coating methods.

According to the current literature, advanced coatings of Ni-rich materials in traditional LIB systems are now capable of preventing chemical degradation both at the secondary particle surface and additionally at the internal primary particle surface. The necessity for this has already been extensively highlighted by the current literature. The relevance of such coatings should increase linearly with the demand for increased Nickel concentrations in Ni-rich polycrystalline active materials, due to the corresponding increase in capacity fade related to cation mixing interactions which come hand-in-hand. Therefore, protection from, or altogether prevention against electrolyte infiltration of polycrystalline Ni-rich active materials will certainly remain as a design heuristic for future coatings.

2.3. Specialized Cathode Surface Modification with Liquid-Based Electrolyte

The current research trend in traditional lithium-ion batteries (LIBs) surface modification focuses on addressing mechanical cracking issues while also enhancing or maintaining the physical barrier concept employed in traditional coating methods. Novel research has emerged in the form of self-healing coating mechanisms, which involve the application of complex polymers to the cathode material.[67,68] These polymers aim to rapidly repair surface defects caused by mechanical strain. In their study, Yang et al. introduced a self-adaptive polymer named polyrotaxane-co-poly(acrylic acid) (Figure 3a). This polymer was applied as a coating on $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$.[24] The coating included a slide ring polymer that accommodated the dynamic volume changes of the lattice during charge and

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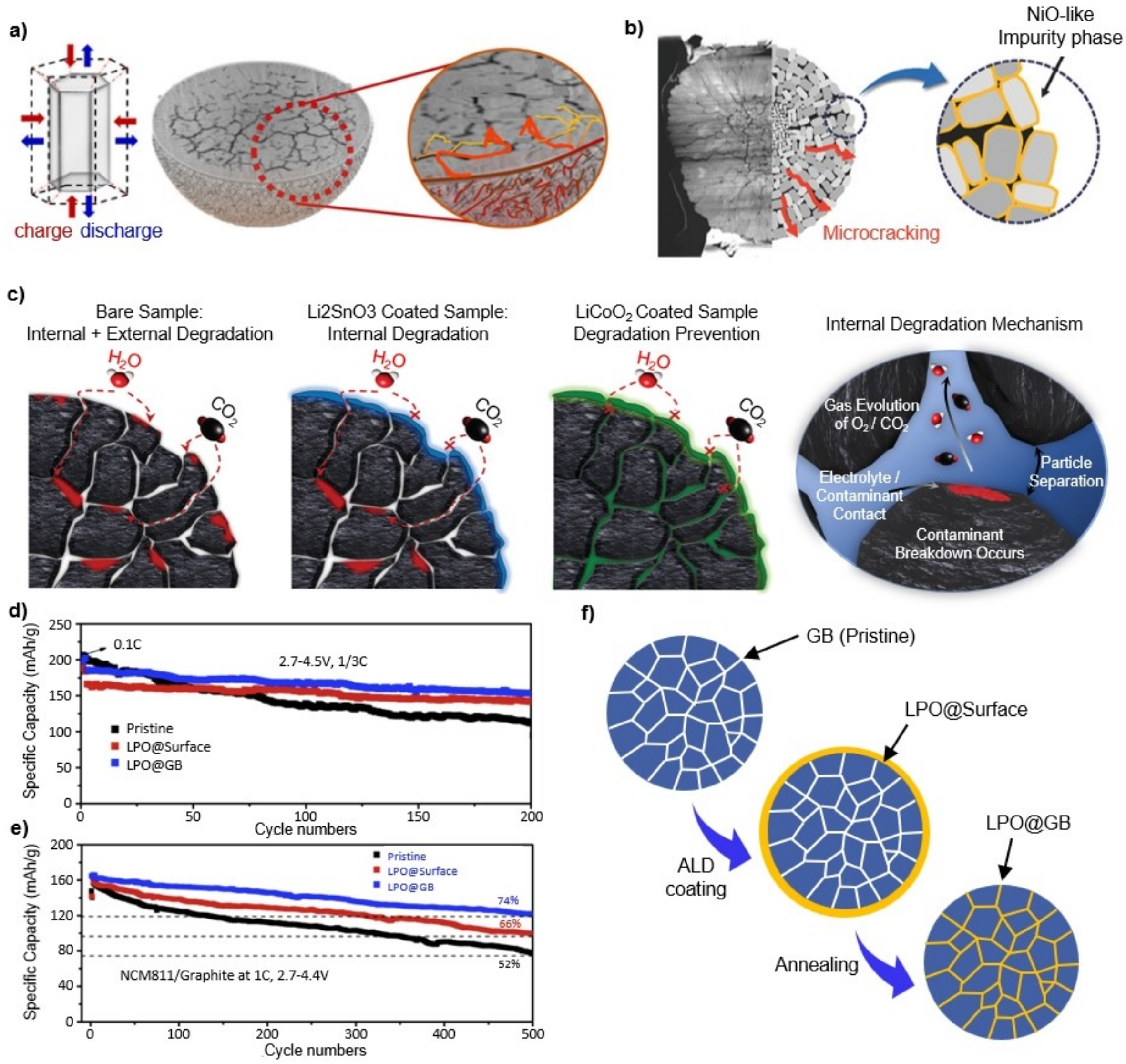

Figure 2. a) Schematic of Ni-rich cathode lattice volume change and the associated internal cracking and electrolyte penetration. [Reproduced from Ref.[23] Copyright (2018), with permission from American Chemical Society], b) Schematic of crack-induced internal NiO rocksalt phase growth. [Reproduced from Ref.[60] Copyright (2018), with permission from Wiley], c) Schematic of comparison between traditional coating and advanced coating prevention mechanisms for ambient air compounds. [Reproduced from Ref.[22] Copyright (2023), with permission from Wiley], d) Electrochemical cycle analysis of the half cells and e) full cells of bare-, outer surface LPO coated-, and grain boundary coated- NCM811 alongside f) the schematic highlighting the effects of atomic layer deposition (ALD) surface coating followed by annealing to provide tightly engineered grain boundary and surface coated material. [Reproduced from Ref.[17] Copyright (2019), with permission from Elsevier]

discharge. Additionally, the coating effectively prevented surface side reactions by creating a physiochemical barrier at the interface. Kim et al. also conducted a strengthening surface modification experiment on an NCA cathode material (Figure 3b).[69] Their research findings indicated that the internal coating functioned as an adhesive, effectively maintaining the mechanical integrity of the particle and resulting in prolonged cycling without the propagation of cracks. Further research is being conducted to investigate the mechanism by which such internal diffusive coatings resolve mechanical issues in Ni-rich cathode material secondary particles. The application of a lithium-borate (LBO) coating of a high Li-conductivity to $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ led to the filling of grain boundary voids (Figure 3c). These LBO-filled voids were able to accommodate the anisotropic shrinkage of the cathode material (Figure 3d) during electrochemical evaluation which was reflected by the electrochemical performance at standard temperatures (Figure 3e), high temperatures (Figure 3g) and at all rates tested (Figure 3f).[70] Ongoing research on protective mechanisms against mechanical degradation in Ni-rich cathode of traditional LIB systems will further highlight the significance of these emerging coatings, motivating researchers to adopt cathode surface modifications that account for the electrolyte propensity to infiltrate the secondary structure.

The mechanical degradation routes of Ni-rich cathode materials, such as cracking, can be attributed mainly to the

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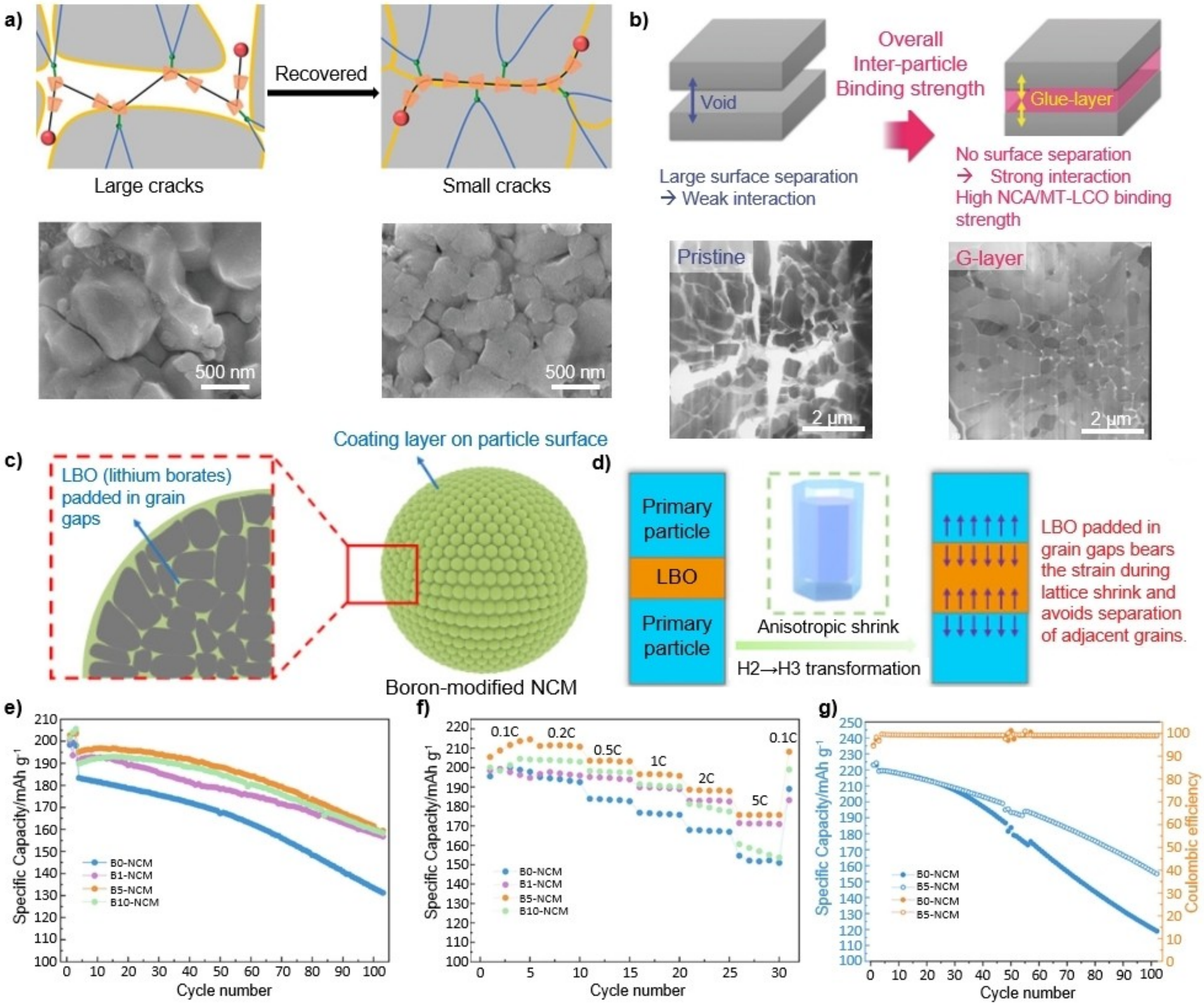

Figure 3. a) Schematic of self-healing polymer with corresponding scanning electron microscopy (SEM) images highlighting the cracks in the uncoated sample. [Reproduced from Ref.[24] Copyright (2022), with permission from Wiley], b) Schematic showing the mechanical strength improvements to the Ni-rich cathode after application of internally diffusive coating layer and the corresponding effects on the cycled cathode material after 300 cycles via scanning electron microscopy (SEM). [Reproduced from Ref.[69] Copyright (2016), with permission from Wiley], c) Schematic showing the infiltration of lithium borate coatings with d) the current understanding of their mechanical padding effect to control the strain and electrochemical analysis showing e) standard 25 °C cycling at various LBO wt.% at 1 C, f) rate test analysis of LBO coated samples of varying wt.% and g) 60 °C temperature performance cycle testing at 1C [Reproduced from Ref.[70] Copyright (2022), with permission from Elsevier].

anisotropic shrink of the lattice during charge. This results in an influx of electrolyte into the secondary particle and hence coating of all primary particles should be considered as vital in order to protect them from unwanted interfacial reactions. This coating should additionally provide mechanical strength to the particle in order to minimize the formation of cracks themselves, or minimize the resulting damage and degradation caused by particle cracking. Coatings where this can be achieved are now capable of achieving structural enhancements that were previously associated mostly with bulk alterations such as ion-substitution. Coatings that can achieve these properties are likely to dominate polycrystal coating modifications, particularly as demand for exceedingly high-performance Ni-rich active materials increases, with these materials naturally being required to accommodate for more strain.

3. Solid-Electrolyte Systems

3.1. Traditional Cathode Surface Modification with Solid-Based Electrolyte

All-solid-state batteries have gained considerable attention due to their superior safety and energy density compared to conventional LIBs.[71] Although the systems clearly differ, their approaches to surface modification concepts initially shared similarities. The degradation mechanism of solid-state batteries, while chemically distinct from that of LIBs, involves lithium

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transfer between the solid electrolyte and the cathode material at the interface. Therefore, the physical barrier coating method was utilized similarly, focusing on lithium-ion diffusive coatings as the primary candidates. The conductivity of lithium-ions through these coatings becomes more important in solid-state-electrolyte systems, as the solid-phase nature of the electrolyte and its lower ductility reduces its ability to penetrate and transfer ions to the cathode material.[72] Solid-state systems often use lithium-containing coatings, such as lithium-metal-oxides, lithium-phosphates, and lithium-metal-alloys, which are being studied to different extents.[26,27,73–75] Additionally, sulfide-based electrolytes, popularized by their high ionic conductivity, are limited by their chemical stability and lack of compatibility with cathodes containing a high proportion of Nickel.[76] Accounting for this, surfaces that are chemically reactive and responsible for releasing/accepting electrons during redox reactions, such as the Ni-rich cathode material, should be coated with materials that possess high ionic conductivity and low electrical conductivity.

Lithium-metal-based ionic compounds, such as $Li_{0.35}La_{0.5}Sr_{0.05}TiO_3$, have been utilized as a result (Figure 4a).[77] The material acts as a physical barrier between the cathode and Li_6PS_5Cl (LPSCl) electrolyte. By limiting the formation of the breakdown compounds of the LPSCl electrolyte, the issue of poor ionic conductivity can be circumvented. As a result, the cells exhibit a capacity retention of 91.5% after undergoing 850 cycles. The application of a thin layer of a novel halide electrolyte has proven to be a valuable coating strategy. Halide

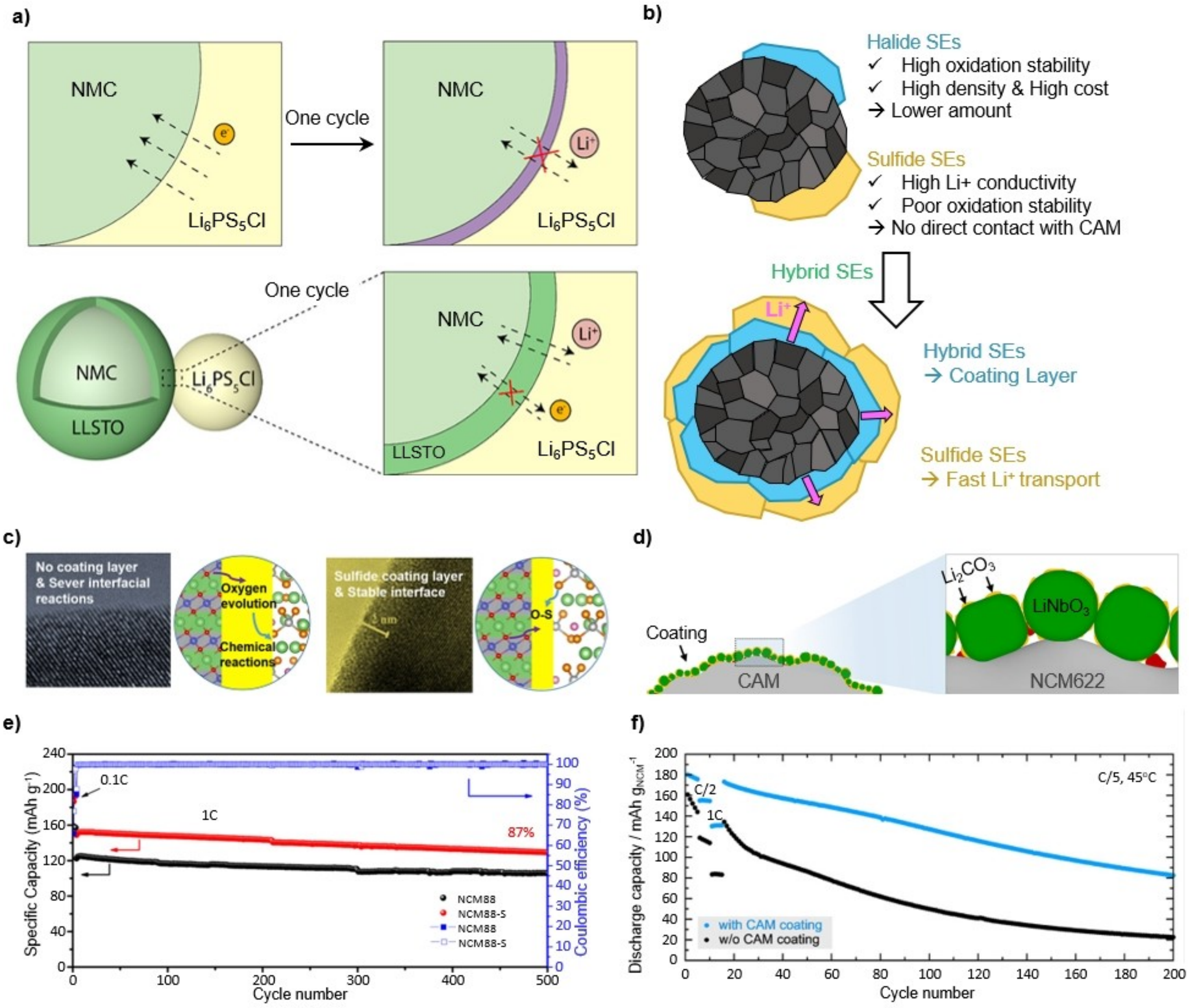

Figure 4. a) Schematic of the electrolyte oxidation at the cathode material interface and the repulsion of this mechanism through physical barrier coating of $Li_{0.35}La_{0.5}Sr_{0.05}TiO_3$. [Reproduced from Ref.[77] Copyright (2019), with permission from American Chemical Society], b) Schematic depicting the issues of sulfide-based solid electrolytes when in contact with NCM cathode material and their stable relationship followed by the proposed halide electrolyte coating system. [Reproduced from Ref.[78] Copyright (2022), with permission from Elsevier], c) Low magnification Transmission Electron Microscopy (TEM) of the NCM88 sample with schematic of interfacial layer with and without sulfide coating along with e) the corresponding electrochemical cycling analysis at 1C over 500 cycles. [Reproduced from Ref.[79] Copyright (2022), with permission from Elsevier], d) Example of the microstructure for the $Li_2CO_3/LiNbO_3$ coating with nanoparticles and f) related electrochemical cycling analysis showing the coating effect at 0.2C over 200 cycles. [Reproduced from Ref.[80] Copyright (2021), with permission from American Chemical Society].

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electrolytes are known for their high ionic conductivity and exceptional stability when used with Ni-rich cathode materials (Figure 4b). Kim et al. achieved a successful coating of an Yttrium-Chloride based halide electrolyte onto an $LiNi_{0.88}Co_{0.11}Al_{0.01}O_2$ cathode material.[78] This coating resulted in a notable enhancement in discharge capacity and rate capabilities. The separation of the unstable sulfide-electrolyte from the Ni-rich cathode material using a stable solid electrolyte interface is a highly promising surface modification technique for solid-state systems. This method is particularly important for maintaining the ionic conductivity of the cathode composite. Various surface protection methods have also been explored to address the instability of the electrolyte. For instance, one approach involves incorporating sulfur-based interlayers into sulfur-based electrolytes to mitigate chemical reactions during cell cycling (Figure 4c).[79] This resulted in large improvements to the discharge capacity over 500 cycles at 1C compared to the uncoated sample (Figure 4e). Another approach involved a traditional $LiNbO_3$ coating, with Li_2CO_3 present on the surface as an ion-conductor and insulator capable of reducing the voltage present at the LPSCl electrolyte interface (Figure 4d).[80] The improvements to the extended cycling over 200 cycles at 0.2C were significant and clearly highlight the requirements for a chemically protective buffer layer (Figure 4f).

The initial inroads into the coating of Ni-rich cathode materials for application in ASSLBs highlighted the differences in the degradation of not only the active material, but of the composite material including SE. The poor voltage range of the sulfide solid electrolytes resulted in coatings that focused significantly more on both the active material degradation and the electrolyte degradation, with many researchers opting to insulate their active material to prevent direct electron transfer to the SE. Additionally, this type of protective surface layer research adopted particularly different coatings to those typically associated with the traditional LIB systems, with most coatings opting to maximize the ionic conductivity through the application of coating layers consisting of more compatible solid electrolytes. This trend highlights the requirement for the coating layer to maintain a substantial ionic conductivity in the ASSLB system, as this system is less capable of adapting to any electrochemically-induced decreases in ionic conductivity such as an ionically resistive CEI layer, or poor active material/electrolyte contact.

3.2. Advanced Cathode Surface Modification with Solid-Based Electrolyte

Over time, it was determined that the degradation mechanisms of ASSLBs differ greatly from conventional systems, necessitating surface modifications with distinct properties. The degradation mechanisms in solid electrolyte-based systems are known to result from resistances caused by insufficient contact between the solid electrolyte and the cathode material, as well as resistances associated with stable contact between the unstable solid electrolyte and the Ni-rich cathode material. Hence, the coating should ensure effective contact with the solid electrolyte, while preventing direct contact between the cathode material and the electrolyte interface.

Lithium-phosphates exhibit stability in sulfide-based solid electrolyte systems, as previously stated. Lee et al. successfully obtained an optimal coating of Li_3PO_4 by ensuring that the thickness and uniformity of the surface coating were thin and free of defects using an ethoxide-based precursor (Figure 5a). The 3 nm-thick coating obstructed the interface between the $LiNi_{0.82}Co_{0.12}Mn_{0.06}O_2$ cathode material and the LPSCl electrolyte, preventing the dissolution of transition metals. The presence of phosphorus in the coating led to extended cyclability by further suppressing side reactions associated with oxygen exchange between the cathode and electrolyte (Figure 5b).[81] Negi et al. conducted a study where they implemented a surface modification technique using a composite $Al_2O_3/LiAlO_2$ on $Ni_{0.70}Co_{0.15}Mn_{0.15}$.[29] One sample was subjected to further annealing, while another sample received only the coating treatment. Two samples were obtained: the standard coated sample, which exhibited a non-uniform and porous structure, and the annealed coating sample, which displayed a dense and uniform surface coverage (Figure 5c). The enhanced performance of the annealed coating can be attributed to its thin and uniform layer, which facilitates preferential contacts with the solid electrolyte as shown by the scanning electron microscopy (SEM) (Figure 5d). Additionally, the migration of lithium ions from the bulk NCM material into the coated layer resulted in the formation of a dual coating layer consisting of Al_2O_3 and $LiAlO_2$. The enhanced coating performance emphasizes the significance of the ionic rate capability of the surface modified interface in solid electrolyte-based systems.

Advanced coating research into the surface modification of Ni-rich cathode active materials applied in ASSLBs highlights the importance of a thin and uniform coating layer due to the nature of the solid electrolyte, which has poorer contact with the active material. Achieving contact improvement at the interface between the active material and the solid electrolyte is therefore vital. Firstly, as established by the traditional coatings, the solid electrolyte and the coated active material must provide a chemical buffer, in order to prevent SE degradation and maintain Li^+ conductivity across the interface. Additionally, the contact between the coated layer and the solid electrolyte must be maximized through a thin and uniform coating layer. An uninterrupted area for Li^+ movement across the interface appears to verifiably improve the performance, whilst the benefits of a thin layer seem obvious, as the lithium-ion movement through these stable materials is usually slower than within the solid electrolyte itself. However, despite efforts to ensure uniform contact of the coating layer with the SE, further research is required to ensure that these contacts can be maintained throughout the electrochemical evaluation of the cells.

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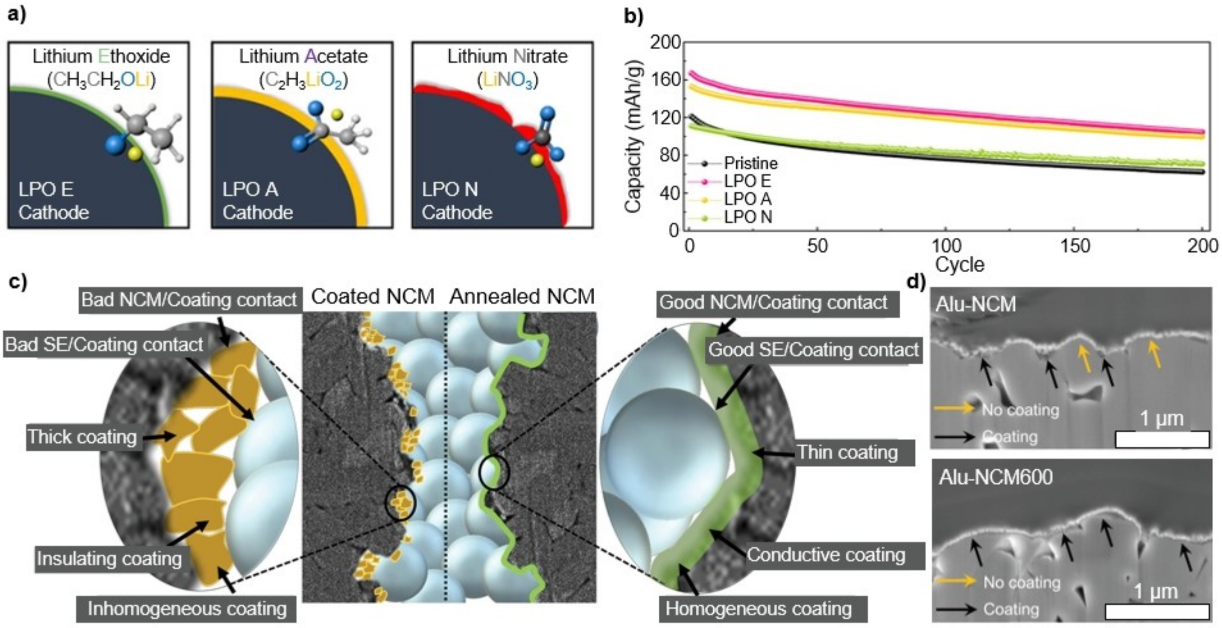

Figure 5. a) Schematic and b) corresponding cycle data for lithium phosphate coatings prepared by different precursors to modify the coated morphology. [Reproduced from Ref.[81] Copyright (2023), with permission from American Chemical Society], c) Schematic showing the influence of coating morphology on the contact between the cathode material and the solid electrolyte with d) scanning electron microscopy (SEM) images of the Alu-coated NCM powder before and after additional annealing, highlighting the increased contact. [Reproduced from Ref.[29] Copyright (2023), with permission from Wiley].

3.3. Specialized Cathode Surface Modification with Solid-Based Electrolyte

Perhaps most importantly of all, the coatings need to maintain high ionic conductivity over the interface throughout the lifetime of the cell. A pristine polycrystal active material may crack upon cycling and, unlike in the liquid electrolyte system, the solid electrolyte will not rush to fill the new space. Therefore, the influence of the electrolyte phase on the ionic isolation of cracked cathode particles cannot be overlooked.[30] Additionally, the solid electrolyte and cathode material can lose or gain contact due to various factors, such as the mechanical properties of the electrolyte, cell pressures, and interface engineering at the cathode material surface.[82] This has led to the widespread adoption of cathode material surface modifications that ensure proper contact with the solid electrolyte throughout electrochemical cycling. Various techniques, including atomic layer deposition and annealing, have been utilized to achieve precise engineering of the active material coating/SE interface.[83–85] Surface modification strategies, such as sticky binder-like coatings or highly conductive and stable solid electrolyte coatings, have demonstrated considerable potential in recent studies.[31,86] These strategies can be employed alongside additives or pressure controls to achieve the desired outcome.

Figure 6a demonstrates that if cracking occurs in the ASSLBs system, the fragmented material will remain isolated indefinitely. Preventing cracking and promoting ion mobility at the grain boundaries is a valid advanced coating technique for solid-electrolyte-based cathode systems with lower ductility. In this case, applying internally diffusive coatings in the solid-state system, that can function as ion transporters, will help to overcome isolation of active material particles upon cracking.[72] Hence, research associated with the grain boundary infusion of coatings applied in ASSLBs is often associated with the infusion of highly lithium-ion conductive materials.[87,88] Liang et al. synthesized a cathode material, $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, with a gradient oxy-thiophosphate coating (Figure 6b).[89] The surface modification of Ni-rich cathode material, including infusion into the grain boundaries, facilitated efficient ion-mobility both at the surface and within the secondary particle of the Ni-rich cathode material. The improvement in ionic conductivity can be indirectly represented through the significant rate capability enhancements that were observed. Furthermore, surface modifications can be used to directly alter the cathode material and solid electrolyte, leading to the formation of shared structures at the interface. This establishes a unique and mutually beneficial relationship between the cathode material and the solid electrolyte. Su et al. demonstrated the efficacy of an aluminum-glycerol-based coating in suppressing interfacial side reactions and improving the interfacial contact between the solid electrolyte and coating layer on the cathode material (Figure 6c).[90] Force displacement experiments were used to determine the elasticity and adhesion of the modified sample. SEM analysis further shows the effect of this coating, with the coated sample exhibiting greatly improved interfacial contact after cycling (Figure 6d). These properties were found to have a significant impact on the coated sample's increased capacity retention and coulombic efficiency due to the surface modification maintaining contact with the solid electrolyte (Figure 6e–f).

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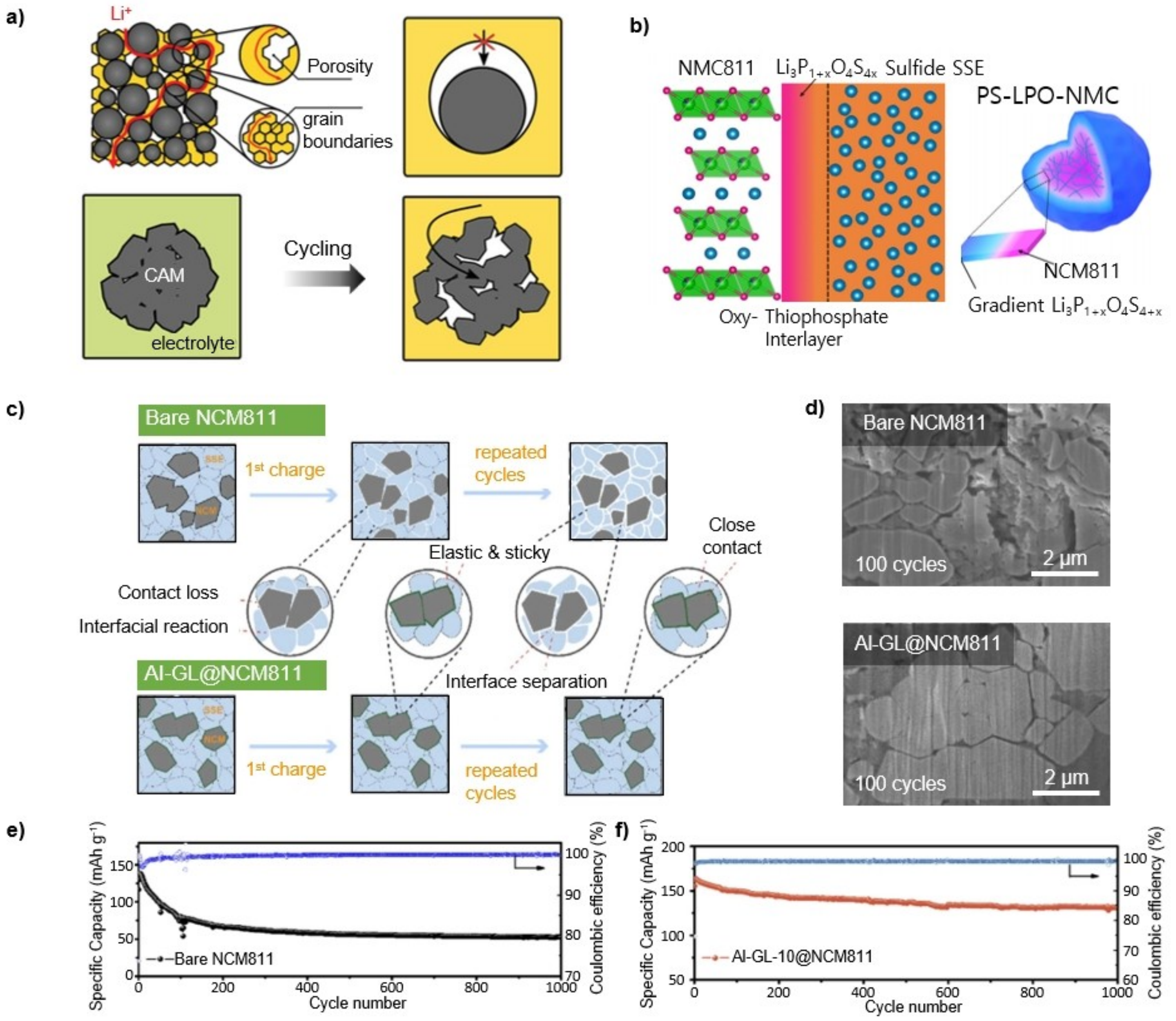

Figure 6. a) Schematic of the critical contact-associated resistance inducing points of the solid-state electrolyte system including the direct solid electrolyte/cathode material contacts and the isolation of cathode material during cracking. [Reproduced from Ref.[30] Copyright (2022), with permission from Wiley], b) Schematic of the chemically shared structure coating of oxy-thiophosphate on NCM, with internal grain boundary coating for increased mechanical integrity and improved ionic conductivity. [Reproduced from Ref.[89] Copyright (2023), with permission from Springer Nature], c) Schematic representing the contact loss of the uncoated cathode material and solid electrolyte during cycling, compared with the maintained contact of the Al-GL coated sample. d) SEM images of the cathode composite after 100 cycles are provided with the uncoated showing significantly more detachment than the coated. The corresponding electrochemical analysis of e) bare NCM811 and f) Al-GL-10-coated NCM811 samples over extended cycling have been included [Reproduced from Ref.[90] Copyright (2023), with permission from Elsevier].

The expansion and contraction of the polycrystalline Ni-rich cathode active materials can affect the performance in two main ways. Standard secondary particle interfaces can be lost as the cathode's contraction creates dead space during the charge which the solid electrolyte, by nature, is less capable of filling. Overcoming this is vital in the ASSLB system and has to be a key consideration of future coating techniques. Internal coatings in solid-state electrolyte systems can be focused to enhance the ionic conductivity of the cathode's secondary particle as infiltration of electrolyte is less likely, as the solid electrolyte cannot easily rush to fill pores left by cracked active material polycrystal particles. Furthermore, prevention of this altogether may be achieved through enhancing the mechanical strength and limiting the cracking of Ni-rich active material in the ASSLB system.

4. Summary and Outlook

The development of advanced coatings for both traditional LIBs systems and modern ASSLBs systems absolutely must consider the specific characteristics of each system, particularly the phase and nature of the electrolyte, as this factor plays a crucial role in determining the degradation pathway. Figure 7 illustrates the surface modification requirements for liquid electrolyte systems and solid electrolyte systems, outlining the desired properties for each. In a conventional LIB system, it is necessary to have

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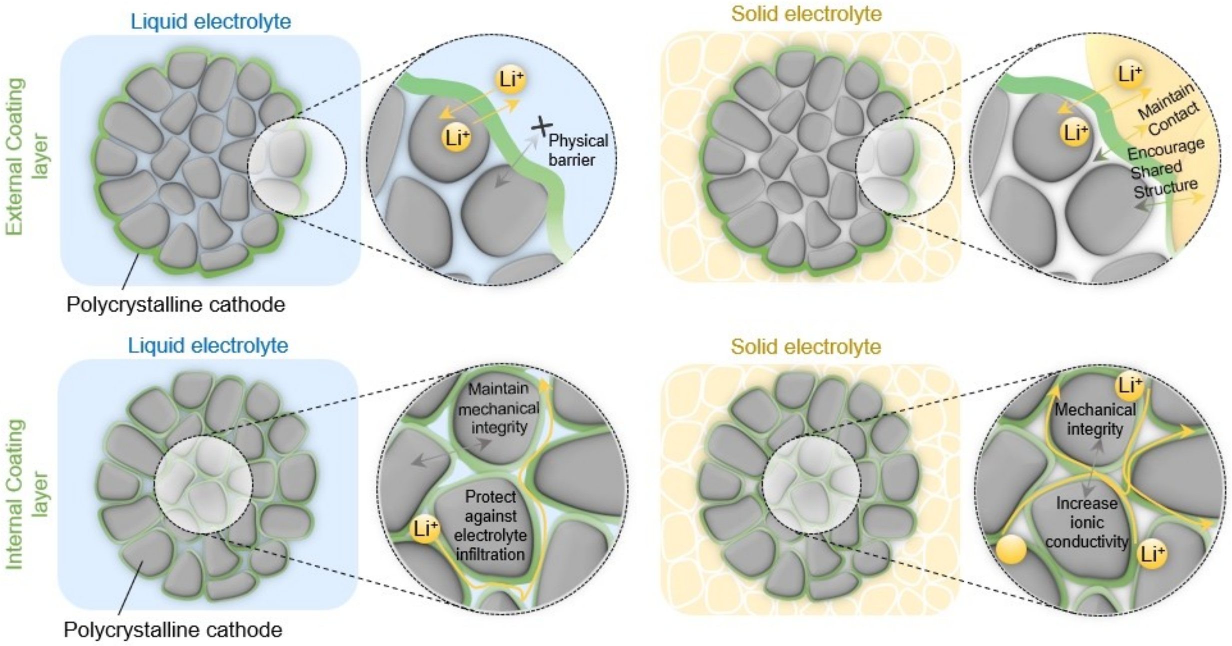

Figure 7. Schematic summarizing the required properties of surface modifications for both liquid and solid electrolyte systems, considering traditional secondary particle protections and advanced internally diffusive protection.

both internal and external protection mechanisms. This is because of the liquid electrolyte's propensity to penetrate the secondary particle structure, leading to the formation of rock salt NiO on the internal primary particles. This leads to crack propagation which, in this system, is capable of propagating from both the center and surface of the particle. To enhance mechanical integrity, mitigate oxygen evolution, and fill void spaces, applying internally infused coatings can result in a stronger Ni-rich cathode material.

The solid electrolyte system typically includes an unstable electrolyte. Therefore, the surface modification approach should prioritize an ionically conductive material with lower electrical conductivity. This will maximize the ion movement whilst also reducing the voltage at the cathode material / electrolyte interface and protect the solid electrolyte. Unlike in the LIB system, maximizing the contact between the less ductile solid electrolyte and the surface modification layer is crucial and should be carefully engineered to ensure optimal contact throughout the cycling process. Maintaining contacts throughout cycling can be achieved through ensuring the integrity of the secondary particle and through promoting surface contact at the NCM/SE interface. It is for this reason that internally infused coatings and functional surface coatings alike will likely receive great attention in the coming iterations.

In summary, as Ni-rich cathode materials are applied in more diverse systems, the surface modification strategies will require specific tailoring to control the cathode material degradation routes and to accommodate for the degradation routes related to the applied system. The content of this perspective paper should serve to highlight the evolutionary process of Ni-rich cathode surface modification research in these two systems, and help inspire future works and ideas on the topic. The authors of this concept paper hope that this study can contribute to readers understanding of the differences and overlaps in Ni-rich cathode electrodes of LIBs and ASSLBs and the respective requirements for their cathode material surface modifications.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Ni-rich layered cathode materials · Surface modification · Lithium-ion batteries · All-solid-state lithium-ion batteries

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