Review Article
Air/Water Stability Problems and Solutions for Lithium Batteries

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Recently, lithium-ion batteries (LIBs) have faced bottlenecks in terms of energy/power density and safety issues caused by flammable electrolytes. In this regard, all-solid-state batteries (ASSBs) may be one of the most promising solutions. However, many key battery materials (such as solid electrolytes (SEs), cathodes, and anodes) are unstable to air/water, which greatly limits their production, storage, transportation, practical applications, and the development of ASSBs. Herein, the research status on air/water stability of SEs, cathodes, and anodes is reviewed. The mechanisms for their air/water instability are revealed in details. The corresponding modification methods are also proposed, with emphasis on the construction strategies of air/water stable protective layers, including ex situ coatings and in situ reactions. Moreover, the application of air/water-stable protective layers in ASSBs is discussed correspondingly. Last but not least, the advantages and disadvantages of various protective layer construction strategies are analyzed, in which their applications in practical production are prospected.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in consumer electronics, powered vehicles, large-scale energy storage, and many other fields, but face bottlenecks in energy/power density and safety issues caused by flammable liquid electrolytes [1, 2]. In this regard, all-solid-state batteries (ASSBs) may be one of the most promising solutions. However, many key battery materials (such as solid electrolytes (SEs), cathodes, and anodes) are unstable to air/water, which greatly limits their production, storage, transportation, practical applications, and the development of ASSBs. Herein, the research status on air/water stability of SEs, cathodes, and anodes is reviewed. The mechanisms for their air/water instability are revealed in details. The corresponding modification methods are also proposed, with emphasis on the construction strategies of air/water stable protective layers, including ex situ coatings and in situ reactions. Moreover, the application of air/water-stable protective layers in ASSBs is discussed correspondingly. Last but not least, the advantages and disadvantages of various protective layer construction strategies are analyzed, in which their applications in practical production are prospected.

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Therefore, sulfide SEs, Ni-rich layered cathode materials, and LMA need to be strictly controlled and maintained in an inert environment during actual storage, processing, and application, which will undoubtedly result in higher industrial costs [37]. Therefore, it is important to construct air/water-stable protective layers on their surfaces by suitable techniques to reduce their reactivity with ambient air to enhance their stability in air and reduce the environmental cost of their storage and processing. At the same time, it does not have a large negative impact on the subsequent electrochemical performance, which is of great practical importance to promote their application in ASSBs.

In this paper, the research progress on the air/water stability of SEs, cathodes, and anodes is summarized from the aspects of structural stability and construction of air/water-stable protective layers on their surfaces and provides a systematic and overall understanding for the research of SEs, cathodes, and anodes. First, the essential causes of their structural instability are revealed separately, and several methods for constructing air/water-stable protective layers are introduced. Moreover, the application of air/water-stable protective layers in ASSBs is discussed correspondingly. Finally, the development prospects of air/water-stable protective layers are prospected.

2. Air/Water Instability of SEs

Among all kinds of SEs, sulfide SEs have remarkable ductile property and highest ionic conductivity (10⁻² S/cm at room temperature), making them ideal SE candidates for ASSBs [38]. However, most SEs face the problem of air instability [39, 40]. For oxide-based SEs, they slowly react with humid air through Li⁺/H⁺ exchange to form LiOH and Li₂CO₃ on the surface, which enlarges the interfacial resistance [41–43]. Similarly, halide SEs (LiₓInCl₃, etc.) are also sensitive to air/water; when LiₓInCl₃ is exposed to humid air, it first becomes crystalline hydrate and then decomposes into InO₃, HCl, and LiCl [44, 45]. Although polymer SEs (PEO, etc.) are chemically stable to water and air, they are easily oxidized in a pure O₂ environment during cycling [46, 47]. Most notably, almost all conventional sulfide SEs are intrinsically unstable and react violently with air/water to release toxic H₂S gas, which results in their structure being destroyed and Li⁺ conductivity decreasing [15, 16, 48]. This greatly hinders the practical application of sulfide SEs in ASSBs, making the production, storage, transportation, and battery assembly processes very complicated and heavily dependent on inert atmosphere or drying chamber, which significantly increases the production cost. In this section, the air/water instability mechanism and the characterization of air/water stability of sulfide SEs will be introduced, and the corresponding modification strategies will be proposed.

2.1. Mechanisms of Air/Water Instability of Sulfide SEs

So far, the most convincing and widely accepted mechanism is the Hard and Soft Acid and Bases (HSAB) theory [48], in which the radii and polarizabilities of hard acids and bases are generally smaller than those of soft acids and bases. Hard acids and hard bases are bonded mainly by coulombic forces, while soft acids and soft bases are bonded mainly by covalent bonds. Therefore, hard acids preferentially combine with hard bases, and soft acids preferentially combine with soft bases. Based on the HSAB theory, the central atom P of most sulfide SEs is a hard acid, which is easier to form P–O bond with hard base O in air or moisture than soft base S. Meanwhile, S tends to bond with hydrogen in the air, resulting in the generation of H₂S gas and the attenuation of air stability of sulfide SEs [49]. Muramatsu et al. [50] studied air/water instability and structural changes of the LiₓS-PₓSₓ system in moist air (Figure 1). Figure 1(a) shows the structural change of 67LiₓS-33PₓSₓ glass in air by means of Raman spectroscopy. Results show that the PₓSₓ−4 ion, which is the major structural unit of 67LiₓS-33PₓSₓ glass, decomposed to form OH and SH groups by reacting with H₂O molecules in air. OH groups indicate the generation of LiOH, which coats the material surface and deteriorates its ionic conductivity. The SH group was further hydrolyzed to form the OH group and H₂S. In contrast, PₓSₓ−4 ions showed the best structural stability; no distinct peaks associated with OH or SH were observed after exposure in humid air for 24 hours (Figures 1(a), 1(c), and 1(d)) [50].

2.2. Characterization of Air/Water Stability of Sulfide SEs

The air/water stability reflects the chemical stability of SEs materials in humid ambient air. Air/water-stable SEs do not react with any air components such as N₂, O₂, CO₂, and H₂O and maintain their physicochemical properties. Therefore, air stability characterization of sulfide SEs can be based on macroscopic chemical reaction phenomena (i.e., changes in H₂S gas generation [50, 51], morphology [52], and mass [53] change with exposure time), microchemical composition and structure. The generation amount of H₂S gas has generally been regarded as a critical index for evaluating the air stability and possibility for practical application of sulfide SEs. The H₂S gas generation amount was calculated from the concentration detected by the H₂S sensor during exposure to a controlled atmospheric environment. The total generation amount of H₂S gas (V) can be calculated by [51]

\[ V = \frac{C \times L \times 10^{-6}}{m}, \]

where V denotes the total generation amount of H₂S (cm³ g⁻¹) normalized by weight m of sulfide electrolyte sample (g), C denotes the recorded value of H₂S concentration (ppm), and L is the volume of desiccator (cm³).

Recently, Lu et al. [14] designed and developed a H₂S gas detection system (Figure 2(a)) to measure the total H₂S generation amount and to evaluate the air/water stability of LiₓSn₁₋ₓAs₁₋ₓS₄ (LSAS). More specifically, nitrogen gas with constant RH and temperature was blown into the bottle containing sulfide SE powder (e.g., Li₀.₅Sn₁.₇P₁.₄₄S₁.₇Cl₀.₃ (LSPSC), LiₓPS₁ₓ (LPS), LiₓSnS₄ (LSS), and Li₃.₈₇Sₓ–y₋₄As₀.₅₁S₄ (LSAS)). The generated H₂S gas was blown out instantaneously by the flowing nitrogen gas, which was then detected by the H₂S sensor. Figure 2(b) shows the
curves of the total generation amount of H$_2$S as a function of exposure time $t$, which is calculated by Equation (1). At the final exposure time $t = 300$ min, the total generation amounts of H$_2$S for LSPSC, LPS, LSS, and LSAS are 48.818, 94.962, 13.130, and 5.931 cm$^3$ g$^{-1}$, respectively, following the order of LPS > LSPSC > LSS > LSAS. By calculating the first-order derivative of total H$_2$S generation amount to time, the H$_2$S generation rate can be obtained, as shown in Figure 2(c).

Sulfide SEs exhibit hygroscopicity and undergo a hydrolysis reaction when exposed to humid air, which not only produces toxic H$_2$S gas but also leads to changes in morphology and quality. Morphological changes can be captured by optical photographs or scanning electron microscopy (SEM) images. Furthermore, the mass change with exposure time can be recorded by thermogravimetric analysis (TGA) technique [53]. For example, Lu et al. [14] obtained time-lapse serial images of four typical sulfide SE powders (LSPSC, LPS, LSS, and LSAS) during exposure to a humid N$_2$ (100% RH) environment, which accurately records their morphological evolution (Figure 3(a)). It can be seen from Figure 3(a) that LSPSC and LPS have large volume changes and obvious color changes, while LSS and LSAS only absorb H$_2$O molecules without hydrolysis/chemical reactions. Tufail et al. [54] performed ex situ SEM characterization for the particles of glass ceramics Li$_2$P$_2$S$_{11}$ and Li$_{6.95}$Zr$_{0.05}$P$_2$S$_{10.8}$O$_{0.1}$I$_{0.4}$ electrolyte. When exposed to humid air, the morphology of the Li$_2$P$_2$S$_{11}$ glass-ceramics became porous and underwent structural degradation, while the Li$_{6.95}$Zr$_{0.05}$P$_2$S$_{10.8}$O$_{0.1}$I$_{0.4}$ electrolyte with enhanced air stability maintained its morphology without significant changes (Figure 3(b)). Zhao et al. [53] investigated the reactivity of Li$_8$PS$_3$I (LPSI) and Sn-substituted LPSI-20Sn with O$_2$ by exposing these two SEs to pure oxygen atmosphere and monitored the mass change with exposure time in TGA apparatus. The mass of LPSI increased by 1.12% after exposure to pure oxygen for 10h, while LPSI-20Sn just increased by 0.35% after exposure to the same atmosphere for 20h.

The microscopic chemical composition and structural characterization of sulfide samples before and after exposure to air are beneficial to identify the air stability of various sulfide SEs and to understand the mechanism of structural degradation and chemical reactions. In addition to the commonly used characterization methods for materials research (such as X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS)), some advanced characterization methods such as solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR), synchrotron radiation sources (e.g., X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS)) have been applied to study the air/water stability of sulfide SEs.

In this review, the reported data obtained from air/water stability test of various sulfide SEs are summarized in Table 1. The air/water stability of the modified sulfide SEs was significantly improved, which can be confirmed by the depressed generation amount of H$_2$S gas and minor structural degradation. Two obvious conclusions can be drawn from Table 1: (1) a larger surface area of sulfide samples
exposed to the atmosphere contributes to stronger hydrolysis reaction and more \( \text{H}_2\text{S} \) gas generation. (2) Higher relative humidity (to which the sulfide sample is exposed) contributes to more \( \text{H}_2\text{S} \) gas generation.

## 2.3. Strategies to Enhance Air/Water Stability of Sulfide SEs

### 2.3.1. Elemental/Oxide Doping

To address this essential issue, researchers have developed a number of strategies to improve the air/water stability of sulfide SEs, mainly based on the HSAB theory [48]. According to HSAB theory, sulfur is a softer base than oxygen and binds more readily to soft acids (e.g., As and Sn). Therefore, proper elemental doping of sulfide SEs can effectively reduce O erosion, thereby helping to maintain the good electrochemical performance of ASSBs. For example, Sahu et al. [48] selected soft acid As and Sn as the central atoms and synthesized a new sulfide SE \( \text{Li}_{3.833}\text{Sn}_{0.833}\text{As}_{0.166}\text{S}_4 \) by partial substitution of \( \text{Li}_4\text{SnS}_4 \) with \( \text{Li}_4\text{AsS}_4 \). The ionic conductivity of this SE reaches \( 1.39 \times 10^{-3} \, \text{S cm}^{-1} \) at room temperature, with a high air/water stability in humid air. Many more studies reported similar elemental doping strategies to improve the air/water stability of sulfide SEs, such as \( \text{Li}_3\text{SbS}_4 \) [61], \( \text{Li}_{3.8}\text{Sb}_0.2\text{Sn}_0.8\text{S}_4 \) [59], \( \text{Li}_{10}\text{Ge} \left( \text{P}_{0.925}\text{Sb}_{0.075}\right)\text{S}_12 \) [56], \( \text{Li}_6\text{PS}_5\text{I}-20\%\text{Sn} \) [53], and \( \text{Li}_4\text{Cu}_2\text{Ge}_3\text{S}_{12} \) [65]. Furthermore, doping oxides (e.g., \( \text{P}_2\text{O}_5 \) [66], \( \text{ZnO} \) [67], and \( \text{LiNbO}_3 \) [52]) can also effectively improve the air/water stability of sulfide SEs. However, the sulfide SEs modified by the above strategies are still far from practical application conditions, as the range of humidity they can withstand is limited to dry environments of less than 3% RH [56]. Recently, an essentially air/water stable sulfide SE has been developed by complete revolution of synthetic methods. Lu et al. [14] proposed the first gas-phase synthesis of sulfide SEs with excellent air/water stability in atmospheric environments. The entire synthesis process from raw materials to final products does not require a glovebox, and it can be done in one step, which is obviously different from the complex and multistep synthesis of sulfides in traditional glovebox, which greatly improves the yield, time efficiency, and cost reduction. Moreover, Lu et al. [14] exploited 50 combinations of doping elements and concentrations to improve the ionic conductivity of gas-phase-synthesized sulfide SE up to 3 mS/cm, which holds the world record for ionic conductivity of air-stable sulfide SEs.

### 2.3.2. Construction of Surface Protective Layer

Recently, a new method has been proposed to construct a protective layer by surface modification to protect sulfide SEs from

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**Figure 2:** The moisture stability of LSPSC, LPS, LSS, and LSAS when exposed to the atmosphere of 100% RH and 100% vol \( \text{N}_2 \). (a) The specially designed equipment for the detection of \( \text{H}_2\text{S} \) gas generated from sulfide SEs samples. (b) The total \( \text{H}_2\text{S} \) generation amount of LSPSC, LPS, LSS, and LSAS as a function of exposure time. (c) The generation rate of \( \text{H}_2\text{S} \), i.e., the first-order derivative of curves in Figure 2(b). Reproduced with permission [14]. Copyright 2021, Wiley-VCH Verlag GmbH.
air/water. Jung et al. [68] synthesized a novel core-shell structured sulfide SE Li₆PS₅Cl with a 50 nm-thick oxysulfide nanolayer, by environmental mechanical alloying with controlled oxygen partial pressure (Figure 4(a)). The oxysulfide nanospheres prevent atmospheric degradation of Li₆PS₅Cl surfaces and significantly improve their air/water stability. A higher ionic conductivity of $2\times10^{-3}$ S cm$^{-1}$ was maintained after air exposure for 30 min under 35% RH at 25°C (Figures 4(b) and 4(c)).

In addition to core-shell structure, the preparation of sulfide composite SEs by combining polymers with sulfide materials can also improve the air/water stability of sulfide SEs. Recently, Li et al. [63] prepared an air/water-stable sulfide composite electrolyte composed of β-Li,P₅S₁₁ and poly(glycidyl methacrylate) (PGMA) through a controlled interfacial reaction between the polymer and Li₆PS₅Cl (Figure 5(a)). The PGMA-LPS50% sample showed no obvious structural change after 20 minutes of air exposure, indicating a retarded diffusion of oxygen and moisture by polymer matrix, and thus a significantly improved air/water stability of sulfide SEs (Figures 5(b) and 5(c)). Tan et al. [62] synthesized thin, flexible, and air/water-stable solid Li₇P₃S₁₁/polystyrene-block-polyethylene-ran-butylene-block-polystyrene (SEBS) composite electrolyte films by combining sulfide Li₇P₃S₁₁ with SEBS(Figure 5(d)), in which the use of hydrophobic polymer SEBS significantly improved the moisture stability of the films in air (50–55% RH) (Figure 5(e)). Li et al. [64] prepared a unique sulfide composite electrolyte with great air/water stability by combining inorganic sulfide Li₇PS₆ and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer(Figure 5(f)). In this composite structure, the PVDF-HFP polymer matrix protects the Li₇PS₆ sulfide SE from humid air (Figures 5(g) and 5(h)). LiFePO₄ (LFP)//Li₇PS₆@PVDF-HFP//Li cells delivered an outstanding specific capacity of 160 mAh g$^{-1}$ over 150 cycles.

Unlike embedding sulfide particles into polymers, Wang et al. [69] prepared a highly conductive 3D composite by in situ polymerizing poly(ethylene glycol)methyl ether acrylate [P (PEGMEA)] within a self-supported 3D porous Li-argyrodite (Li₆PS₅Cl) skeleton. The 3D composite exhibits an ionic conductivity of $4\times10^{-4}$ S cm$^{-1}$ at room temperature. Meanwhile, the inferior solid–solid electrolyte/electrode interface is integrated via in situ polymerization, which significantly reduced the interfacial resistance. More importantly, the LiCoO₂/Li ASSB based on the 3D composite delivers a high capacity of 133 mAh g$^{-1}$ (3.0–4.3 V versus Li$^+$/Li) at 0.2°C and also demonstrates excellent long cycle life. Moreover, the as-prepared LiNi₀.₈Mn₀.₁Co₀.₁O₂ (NCM811)3D
<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Testing set-up or characterization method</th>
<th>Sample mass and morphology</th>
<th>Exposure atmosphere (relative humidity and temperature)</th>
<th>Exposure time (min)</th>
<th>Amounts of $H_2S$ ($cm^3 \cdot g^{-1}$)</th>
<th>Classification</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$67$Li$_2$S·$33$P$_2$S$_5$</td>
<td>A sealed desiccator ($2000$ cm$^3$) with a fan</td>
<td>$100$ mg (pellet)</td>
<td>48–51%, 24–25°C</td>
<td>1</td>
<td>2</td>
<td>Glass</td>
<td>[50]</td>
</tr>
<tr>
<td>$75$Li$_2$S·$25$P$_2$S$_5$</td>
<td>Sealed desiccator ($2000$ cm$^3$) with a fan</td>
<td>$100$ mg (pellet)</td>
<td>48–51%, 24–25°C</td>
<td>1</td>
<td>0.01</td>
<td>Glass</td>
<td>[50]</td>
</tr>
<tr>
<td>$75$Li$_2$S·$25$P$_2$S$_5$</td>
<td>A sealed desiccator ($2000$ cm$^3$) with a fan</td>
<td>$100$ mg (pellet)</td>
<td>48–51%, 24–25°C</td>
<td>1</td>
<td>0.2</td>
<td>Glass-ceramic</td>
<td>[50]</td>
</tr>
<tr>
<td>$\beta$-Li$_3$PS$_4$</td>
<td>A sealed desiccator ($2000$ cm$^3$)</td>
<td>XRD</td>
<td>- (powder)</td>
<td>10%</td>
<td>1440 (overnight)</td>
<td>Crystal</td>
<td>[55]</td>
</tr>
<tr>
<td>LPSI-20$^{10}$Sn</td>
<td>A sealed desiccator ($18600$ cm$^3$)</td>
<td>$350$ mg (powder)</td>
<td>1–3%</td>
<td>24 h</td>
<td>&lt;0.053</td>
<td>Crystal</td>
<td>[56]</td>
</tr>
<tr>
<td>Li$<em>{10}$GeP$</em>{0.8}$Sn$_{0.2}$S$_3$J$_3$ ($x = 0.75$)</td>
<td>A closed container ($2.5$ L) with a small electric fan</td>
<td>Aqueous solution (100 mg:1 mL)</td>
<td>—</td>
<td>60</td>
<td>Almost 0</td>
<td>Crystal</td>
<td>[58]</td>
</tr>
<tr>
<td>Li$<em>{3.83}$Sn$</em>{0.83}$As$_{0.166}$S$_4$</td>
<td>XRD</td>
<td>- (powder)</td>
<td>80%, 17.8°C</td>
<td>48 h</td>
<td>—</td>
<td>Crystal</td>
<td>[48]</td>
</tr>
<tr>
<td>Li$_2$Li$_4$Sn$_4$</td>
<td>EXAFS</td>
<td>- (powder)</td>
<td>Dry air, 30°C</td>
<td>24 h</td>
<td>—</td>
<td>Glass</td>
<td>[57]</td>
</tr>
<tr>
<td>Li$_4$Sn$_4$ (solution processed)</td>
<td></td>
<td>A closed desiccator ($2000$ cm$^3$) with a small electric fan</td>
<td>50 mg (powder)</td>
<td>70%, 20–22°C</td>
<td>40</td>
<td>0.25</td>
<td>Crystal</td>
</tr>
<tr>
<td>Li$<em>{3.8}$Sn$</em>{0.8}$Sb$_{0.2}$S$_4$</td>
<td>A closed space ($900$ cm$^3$)</td>
<td>- (powder)</td>
<td>60%, 22°C</td>
<td>&gt;100</td>
<td>Almost 0</td>
<td>Crystal</td>
<td>[59]</td>
</tr>
<tr>
<td>Li$<em>{3.8}$Sn$</em>{0.8}$Sb$_{0.2}$S$_4$</td>
<td>A closed space ($900$ cm$^3$)</td>
<td>- (powder)</td>
<td>50%, RT</td>
<td>—</td>
<td>Almost 0</td>
<td>Crystal</td>
<td>[60]</td>
</tr>
<tr>
<td>Li$_4$Sb$_4$</td>
<td>A container with flowing air</td>
<td>50 mg (powder)</td>
<td>70%, RT</td>
<td>950</td>
<td>&lt;1</td>
<td>Glass</td>
<td>[61]</td>
</tr>
<tr>
<td>Li$<em>4$P$</em>{0.1}$S$_{1.9}$5%SEBS</td>
<td>An air-filled desiccator ($0.31$ ft$^3$) with a fan</td>
<td>$100$ mg (membrane)</td>
<td>50–55%, 22–24°C</td>
<td>10</td>
<td>12.5</td>
<td>Composite</td>
<td>[62]</td>
</tr>
<tr>
<td>PGMA-50%Li$_3$PS$_4$</td>
<td>In situ XRD</td>
<td>- (membrane)</td>
<td>20%, RT</td>
<td>20</td>
<td>—</td>
<td>Composite</td>
<td>[63]</td>
</tr>
<tr>
<td>Li$_3$PS$_4$/PVDF-HFP SCE</td>
<td>XRD, Raman</td>
<td>Ambient air</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Composite</td>
<td>[64]</td>
</tr>
</tbody>
</table>
composite Li ASSB exhibits a reversible discharge capacity of 157 mAh g\(^{-1}\) with a high cut-off voltage of 4.5 V at 0.1°C and outstanding capacity retention of 84% after 90 cycles. Therefore, the 3D composite provides both high ionic conductivity and good interfacial compatibility, laying the foundation for achieving high-energy-density ASSBs. However, there is still a lack of a general method to protect all types of sulfide SEs from water erosion.

To solve this problem, Xu et al. [15] innovatively designed a superhydrophobic surface layer on the surface of sulfide SE with both water-repellent and Li\(^+\) conductive properties (Figure 6(a)). The hydrophobic protective layer was spray coated onto the Li\(_6\)PS\(_5\)Cl membrane, consisting of Li\(_{1.4}\)Al\(_{0.4}\)Ti\(_{1.6}\)(PO\(_4\))\(_3\) (LATP) nanoparticles and fluorinated polysiloxane (F-POS) prepared by hydrolysis and condensation reactions (Figure 6(a) (iii)). When water droplets adhere to the bare membrane surface, the membrane with superhydrophobic surface exhibits a unique water-repellent effect (Figure 6(a) (v)). Further, the surface of the F-POS@LATP-coated Li\(_6\)PS\(_5\)Cl membrane did not change significantly even under the high humidity environment of 70% RH by water jetting (Figures 6(b) and 6(c)). By contrast, bare Li\(_6\)PS\(_5\)Cl membrane immediately changed color after contacting water. The ASSBs assembled using the water-jetted F-POS@LATP-coated Li\(_6\)PS\(_5\)Cl membrane exhibited almost the same electrochemical performance as the unexposed bare Li\(_6\)PS\(_5\)Cl membrane (Figure 6(d)). In contrast, the ASSBs assembled with the bare Li\(_6\)PS\(_5\)Cl membrane that had been jetted with water did not work properly due to structural damage and the ionic conductivity was completely reduced (Figure 6(e)). It is worth noting that this post-processing method is applicable to all types of water-sensitive SEs.

This section summarizes the researches on the air stability of sulfide SEs reported in recent years and summarizes the methods to improve the air/water stability of sulfide SEs: (1) elemental/oxide doping and (2) construction of surface protective layer. Sulfide SEs are sensitive to air/water because they contain air/water-sensitive S\(^2\)- ions and oxygenophilic P atoms. This sensitivity leads to structural decay and emission of toxic H\(_2\)S, which results in a reduction of ionic conductivity and electrochemical cycling capacity. Therefore, an element/metal oxide doping strategy from the reaction source is an effective method to improve the air/water stability of sulfide SEs. The key of protecting sulfide-based SEs is to avoid S and O contact as much as possible. According to the HSAB theory, sulfur is softer than oxygen and easily combines with soft acids such as As and Sn. Therefore, suitable elemental (e.g., O) doping can effectively reduce the attack of O and help maintain the good electrochemical
Figure 5: (a) Schematic illustration of the preparation process of PGMA-LPS hybrid membranes. XRD patterns of (b) LPS and (c) PGMA-LPS50% after exposure to air. Reproduced with permission [63]. Copyright 2019, Elsevier. (d) $H_2S$ amount released as a function of exposure time for pristine $Li_7P_3S_{11}$ and composite with hydrophobic SEBS polymer. (e) Surface changes of bare $Li_7P_3S_{11}$ and composite electrolyte films before and after immersion in water. Reproduced with permission [62]. Copyright 2019, American Chemical Society. (f, g) (f) XRD patterns and (g) Raman spectra of $Li_7PS_6$/$PVDF-HFP$/$LiTFSI$, $PVDF$/$LiTFSI$, $PVDF$-$HFP$, and pure $Li_7PS_6$. Reproduced with permission [64]. Copyright 2020, American Chemical Society.
In addition, the introduction of some soft acids (e.g., As, Sn, and Sb) into the sulfide SEs to stably combine with S can also effectively inhibit the generation of H₂S and improve the air stability of the electrolyte. However, the substitution of oxygen for sulfur reduces the ionic conductivity of sulfide SEs because of the smaller electronegativity and larger ionic radius of S²⁻, which is favorable for the migration of lithium ions. Moreover, soft acid substitution introduced toxicity issues with new elements, and the stability of solvent/binder reactions beyond air stability was not assessed. Therefore, researchers proposed [66, 67] a codoping strategy of oxides (e.g., ZnO and P₂O₅) to enhance the performance of sulfide SEs comprehensively, improving the air stability of sulfide SEs while maintaining a high ionic conductivity.
conductivity. Although these modification strategies are effective in a certain degree, the range of humidity they can withstand is limited to dry environments of less than 3% RH, which is still far from the requirements of practical production, storage, and transportation.

To address the limitations of the element/oxide doping strategy, researchers proposed [68] to construct a protective layer on the surface of sulfide SEs to address the air stability of sulfide SEs in high-humidity environments. Since the hydrolysis reaction of sulfide SEs with moisture first occurs on the surface of the sulfide, an oxysulfide-coated Li₆PS₅Cl with a core-shell structure can be synthesized by an ambient mechanical alloying method with controlled oxygen partial pressure to resist chemical attack by O₂, water molecules, and even organic solvents. Besides constructing the core-shell structure, another method was also proposed [62–64, 69] to construct composite SEs by combining sulfide SEs with polymers to well protect sulfide SEs from air/water. The composite SEs combine the excellent room-temperature ionic conductivity of sulfide SEs with the mechanical flexibility of polymer SEs, thus enabling ultrathin films with high ionic conductivity and mass-production capabilities. However, due to the complex interactions between sulfide SEs and organic solvents/polymers, the ionic conductivity may be seriously reduced. Therefore, extensive efforts are required in the future to finely tune the ratio of sulfide and polymer SEs for optimized performance of composite SEs. To solve the above problem, a superhydrophobic protective layer with both waterproof and ion-conducting properties was designed [15]. This protective layer was sprayed coated onto Li₆PS₅Cl membrane, consisting of LATP nanoparticles and F-POS prepared by hydrolysis and condensation reactions. Notably, this modification strategy is a posttreatment method that can be applied to any air/water unstable materials. In conclusion, both strategies of element/oxide doping and the construction of surface protective layers have achieved significant progress in improving the air/water stability of sulfide SEs. However, there are still many challenges for large-scale production and practical application of sulfide SEs, especially the improvement of ionic conductivity.

3. Air/Water Instability of Cathodes

Ni-rich layered cathode materials, especially LiNiₓCo₀.₅Mn₀.₅O₂ (NMC) and LiNiₓCo₀.₅Al₀.₅O₂ (NCA), have become one of the most practical and promising cathode materials for LIBs due to their high energy density, large discharge capacity, and low cost [25]. However, during the production, storage and application of Ni-rich cathode materials (Ni contents ≥ 70%), their highly reactive surfaces almost inevitably react with H₂O and CO₂ in the ambient air to form electrochemically inert residual lithium compounds such as Li₂CO₃ and LiOH (Figure 7(a)), which hinder the practical production and application of Ni-rich cathodes [70–74]. These surface residual lithium compounds will lead to not only deterioration of the capacity retention capability but also high pH of the electrode coating slurry and the sequential gelation of slurry during the electrode preparation process [28, 75, 76]. As a result, large amounts of gas will be generated during cycling, and the electrochemical performance of LIBs will be deteriorated [77–79]. In this section, Ni-rich cathode materials will be taken as an example to introduce the air/water instability mechanisms and characterization of air/water stability of cathodes. The corresponding modification strategies will also be proposed.

3.1. Mechanisms of Air/Water Instability of Ni-Rich Cathodes

At present, the surface degradation mechanism of Ni-rich cathode materials exposed to humid air is majorly classified into two types: redox reaction mechanism and proton-lithium exchange mechanism. In a redox mechanism, the surface degradation of Ni-rich cathodes occurs when exposed to ambient air as the highly chemically active Ni₃⁺ is reduced to the more stable Ni²⁺, resulting in the release of lattice oxygen and the formation of residual lithium compounds on the surface. Due to the loss of surface lattice lithium, NiO-like rock-salt phase layers and delithium layers are also produced. By comparing the surface impurity content of LiNiₓC₀.₅Mn₀.₅O₂ with different Ni contents, Noh et al. [80] found that more carbonates and hydroxides grew on the surface of the cathode with higher Ni content, indicating that the formation of residual lithium compounds on the surface is closely related to surface Ni ions. Similarly, Qian et al. [73] calculated by density functional theory (DFT) to find that with the increase of Ni content, both the charge transfer ability of nickel and the adsorption energy for water increase. This result suggests that Li₂CO₃ tends to grow on the surface of Ni-rich cathodes (Figure 7(b)). Chemically active Ni₃⁺ tends to convert to Ni²⁺ because this alleviates the local lattice distortion of the Ni-O octahedra, while also releasing some of the residual stress and reducing the system energy [81]. In addition, the highly reactive oxygen species will be accelerated with the reduction reaction of Ni₃⁺ [82]. As a result, when the Ni-rich layered cathode materials are exposed to the atmosphere, the reactive oxygen species on the surface will react with H₂O and CO₂ in the air to form species such as hydroxyl and carbonate, while releasing lattice oxygen to generate oxygen. The previously formed hydroxyl and carbonate substances will further react with Li⁺ in the host material to produce residual lithium compounds (mainly LiOH and Li₂CO₃). At the same time, the structure changes from the original layered structure to a NiO-like rock salt structure [73, 83]. Based on the above research results, the generation of hydroxyl and carbonate species should proceed through the following reaction pathways in the redox reaction mechanism:

\[
\text{Ni}^{3+} + \text{O}^2- (\text{lattice}) \rightarrow \text{Ni}^{2+} + \text{O}^- \quad (2)
\]

\[
\text{O}^- + \text{O}^- \rightarrow \text{O}^2- (\text{active}) + \text{O} \quad (3)
\]

\[
\text{O}^2- (\text{active}) + \text{CO}_2 \rightarrow \text{CO}_3^{2-} \quad (4)
\]

\[
\text{O}^2- (\text{active}) + \text{H}_2\text{O} \rightarrow 2\text{OH}^- \quad (5)
\]

\[
\text{O} + \text{O} \rightarrow \text{O}_2 \quad (6)
\]

Different from the redox mechanism, in the proton-lithium
exchange mechanism, the residual lithium compounds are formed by the H\(^+\) released from the surface adsorbed water molecules exchanged with the outward-migrating Li\(^+\) and occupying Li\(^+\) sites. Theoretically, this mechanism usually occurs in the near-surface region along with redox reactions [84, 85]. Shkrob et al. [84] investigated the effect of exposure to humid air on the structure and electrochemical performance of LiNi\(_{0.5}\)-Co\(_{0.2}\)-Mn\(_{0.3}\)O\(_2\) (NCM523) and showed that Li\(_2\)CO\(_3\) and LiOH species were formed on the surface of NCM523 after being maintained at 100% relative humidity for 2 months, along with the capacity loss, which can be attributed to the H\(^+\)/Li\(^+\) cation exchange mechanism that occurs in transition metal oxides after moisture exposure. Similar results for LiNi\(_{0.33}\)-Mn\(_{0.33}\)-Co\(_{0.33}\)O\(_2\) (NCM333) and LiNi\(_{0.4}\)-Mn\(_{0.4}\)-Co\(_{0.2}\)O\(_2\) (NMC442) exposed to humid air were also reported by Haik et al. [86]. Furthermore, Faenza et al. [87] demonstrated that the formation of the Li\(_2\)CO\(_3\) surface layer requires the presence of both H\(_2\)O and CO\(_2\) to occur. The above literature study shows that in the proton-lithium exchange mechanism, the formation of LiOH and Li\(_2\)CO\(_3\) proceeds through the following reaction pathways:

\[
\text{Li}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{LiOH} \tag{7}
\]

\[
\text{LiOH} + \text{CO}_2 \rightarrow \text{LiHCO}_3 \tag{8}
\]

\[
\text{LiOH} + \text{LiHCO}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \tag{9}
\]

3.2. Characterization of Air/Water Stability of Ni-Rich Cathodes. Owing to the high sensitivity of Ni-rich cathode materials to moisture and CO\(_2\) in ambient air, residual lithium compounds

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**Figure 7:** (a) Schematic illustration of NMC811 exposed to ambient air. Reproduced with permission [88]. Copyright 2020, Elsevier. (b) Surface morphology evolution of NCM333, NCM622, NCM701515, and NCM811 samples after air exposure for 0, 10, 20, and 45 days under 45% RH at 25°C. Reproduced with permission [73]. Copyright 2019, Royal Society of Chemistry.
(e.g., LiOH and Li$_2$CO$_3$) are prone to form on the surface, subsequently inducing the detrimental subsurface phase transformation. Therefore, the identification and quantification of the surface reaction products of Ni-rich cathodes are crucial for evaluating the air/water stability of Ni-rich cathode materials before and after modification. The characterization of surface stability of Ni-rich cathode materials in ambient air/water has been focusing on morphological and compositional changes when exposed to humid air or immersed in water. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are commonly used to reveal the microstructure of Ni-rich cathode materials and assess structural damage. In addition, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and EDX (energy dispersive X-ray) are also widely used in analyzing the composition of Ni-rich cathode materials.

Ni-rich cathode materials exposed to ambient air may lead to severe surface degradation, depleting Li$^+$ in the host material, and further leading to the formation of impurities such as residual lithium compounds. Morphological changes of Ni-rich cathode materials can be captured by scanning electron microscopy (SEM) images. For example, Wei et al. [89] tested the surface topography evolution of bare NCM811 and octadecyl phosphate- (OPA-) passivated NCM811 materials exposed to ambient air (RH~60%–70%) for 7 and 14 days by SEM. Some white feathery adventitious species appeared on the surface of bare NCM811 after 7 days of ambient air exposure, and the amount of white feathery species increased significantly when the air exposure period was increased to 14 days (Figure 8 (a1–c1)). In sharp contrast, the surface of OPA-NCM811 barely changed during exposure to the same ambient air for 14 days, indicating that OPA-SAM passivation effectively suppressed the degradation reaction between NCM811 and ambient air (Figure 8 (a2–c2)).

The chemical composition and crystal structure of surface impurities can be tested and analyzed by FT-IR, XPS, and XRD before and after exposure of the Ni-rich cathode material to ambient air. Wei et al. [89] further used FT-IR, XPS, and XRD methods to analyze the surface chemical properties and crystal structures of bare NCM811 and OPA-NCM811 samples before and after exposure to ambient air for 7 and 14 days. As shown in Figure 9(a) (i), distinctive characteristic peaks at 861 and 1419 cm$^{-1}$ appeared on the FT-IR spectrum of bare NCM811 sample after exposure to ambient air for 7 days, which may be attributed to Li$_2$CO$_3$ peak. The peak intensity increased as the air exposure time increased to 14 days, and XPS results provide more detailed information of the surface chemistry. The C1s XPS spectrum of bare NCM811 contains CO$_3^{2-}$ (289.8 eV) mainly from carbonate, C=O (286.6 eV), and C-C (284.8 eV) as adventitious carbon (Figure 9(b) (i)). O1s peak contains impurities (531.9 eV), which can be attributed to O$_2^-$, O$^2-$, and CO$_3^{2-}$ from lithium carbonate species, and from M-O (M=Ni, Co, and Mn) bonds in the NCM lattice (Figure 9(b) (ii)). As air exposure time increases, the peak intensity of lithium carbonate species increases, while the O lattice signal decreases due to the formation of residual lithium species covering the surface of NCM811. XRD patterns show that the (003) peak of bare NCM811 shifts to lower $2\theta$ angles after 14 days of exposure in ambient air (Figure 9(d) (i)), indicating structural expansion along the c-axis. This should be caused by the loss of Li from a layered structure during the chemical reaction of NCM811 and ambient air. In sharp contrast, FT-IR (Figure 9(a) (ii)) and XPS (Figures 9(b) (ii)–9(c) (ii)) spectra of OAP-NCM811 show no impurity signal during the 14-day exposure to ambient air, and no structural changes were observed from XRD (Figure 9(d) (iii)). These results indicate that the hydrophobic OPA-SAM is chemically stable during air exposure and thus can effectively suppress the unfavorable chemical reaction between NCM811 and ambient air. Furthermore, Raman and EDX mapping are also useful to analyze the composition of Ni-rich surface after exposure to the atmosphere.

3.3. Strategies to Enhance Air/Water Stability of Ni-Rich Cathodes

3.3.1. Elemental Doping. To address the above-mentioned problems, numerous strategies have been adopted to modify Ni-rich cathode materials, among which doping is one of the most important and effective strategies to improve its air/water stability. Air/water stability can be significantly improved by incorporating small amounts of cation or anion atoms in the lattice of Ni-rich cathode materials. The introduction of multiple dopants into the lattice of Ni-rich cathode materials can significantly improve the air/water stability of the materials, generally including cationic doping (e.g., Al [90–97], Mg [98], Zr [99–101], Ti [102–105], Nb [106], and B [107–110]) and anionic doping (e.g., F [111, 112], Cl

![Figure 8: SEM images of bare NCM811 and OPA-NCM811 after different air exposure durations: the fresh (a1) bare NCM811 and (a2) OPA-NCM811, the 7-day air-exposed (b1) bare NCM811 and (b2) OPA-NCM811, and the 14-day air-exposed (c1) bare NCM811 and (c2) OPA-NCM811. Reproduced with permission [89]. Copyright 2019, American Chemical Society.]
Figure 9: (a) (i-ii) FT-IR spectra of (i) bare NCM811 and (ii) OPA-NCM811 materials after being exposed for 0, 7, and 14 days. C1s and O1s XPS spectra of (b) the bare NCM811 and (c) OPA-NCM811 materials after being exposed for 0, 7, and 14 days. (d) XRD patterns of (i) bare NCM811 and (ii) OPA-NCM811 materials after being exposed for 0, 7, and 14 days. Reproduced with permission [89]. Copyright 2019, American Chemical Society.
of Ni-rich cathode materials include metallic oxides (e.g., Mg and Zr are usually recognized to be the most promising elements due to their low cost.

The effects of cationic doping can generally be divided into two categories. One is to form strong covalent bonds between doping cations and lattice oxygen to enhance the lattice structure and suppress the loss of lattice oxygen. For instance, You et al. [90] successfully incorporated few of Al$^{3+}$ into the surface lattice of LiNi$_{0.95}$Co$_{0.05}$O$_2$ by sintering a mixture of LiOH and precursors coated with Al(OH)$_3$ at high temperatures. Compared with the pristine LiNi$_{0.94}$Co$_{0.06}$O$_2$, Al-doped LiNi$_{0.94}$Co$_{0.06}$O$_2$ exhibits higher capacity retention and superior cycling stability after 30 days of exposure to humid air. The doping of Al significantly suppresses the unfavorable chemical reaction between LiNi$_{0.94}$Co$_{0.06}$O$_2$ and H$_2$O/CO$_2$ in the air, which is attributed to the enhanced surface stability of the lattice by strong Al-O covalent bonds. Furthermore, some high-valent cations are doped to reduce the content of surface-active Ni$^{2+}$ (reduced to stable Ni$^{2+}$ to maintain charge balance). Similarly, Lai et al. [115] introduced a small amount of Zr$^{4+}$ ions into Ni-rich LiNi$_{0.815}$Co$_{0.15}$Al$_{0.035}$O$_2$ (NCA) cathode material via a one-step solid state method, which effectively alleviated the air sensitivity of the NCA cathode material. The as-prepared Zr$^{4+}$-modified NCA cathode exhibited good storage performance, with a significant increase in capacity retention from 72.3% to 96.9% after exposure to ambient air conditions for 10 d. The reason why Zr$^{4+}$ ions exhibit excellent storage performance is mainly because Zr$^{4+}$ ions suppress the formation of residual lithium compounds and the disorder of cations during exposure to ambient air, thereby effectively slowing down the increase of polarization and impedance. Moreover, anion doping can also effectively enhance the stability of the oxygen lattice, thereby improving the structural stability of the Ni-rich cathode materials. Effective doping can improve the stability and construction of Ni-rich layered cathode materials, limiting the formation of microcracks and the conversion of Ni$^{2+}$ ions to the Li layer, resulting in excellent air/water stability and superior thermal stability. However, doping only delays the onset of the degradation process of Ni-rich cathode materials exposed to ambient air, and does not significantly suppress oxygen loss. Therefore, the doping strategy cannot completely solve the surface parasitic reaction between the cathode and the electrolyte, and the released gas may swell the battery and cause a safety accident.

3.4. Construction of Cathode Surface Protective Layer. The construction of a surface protective layer is another widely used modification method for Ni-rich cathode materials, which is aimed at isolating H$_2$O/CO$_2$ in the air, avoiding the formation of residual lithium compounds on surface, and improving its air/water stability. At the same time, they can also act as a physical barrier to prevent the direct contact of Ni-rich cathode with the organic electrolyte to suppress side reactions, thereby improving the cycle life, safety performance, and energy density of the battery. Typically, the materials used to construct a protective layer on the surface of Ni-rich cathode materials include metallic oxides (e.g., MnO$_2$ [116], TiO$_2$ [117], Al$_2$O$_3$ [118–120], ZnO [121, 122], and ZrO$_2$ [123]), phosphates (e.g., (NH$_4$)$_2$HPO$_4$ [124], AlPO$_4$ [125, 126], and ZrP$_2$O$_7$ [127]), fluorides (e.g., AlF$_3$ [128, 129] and LiF [130]), fast ionic conductors (e.g., Li$_2$MnO$_3$ [131], LiAlO$_2$ [119, 132, 133], Li$_3$PO$_4$ [134–136], Li$_2$ZrO$_3$ [137], and LiPON [138]), organic hydrophobic polymers (e.g., octadecyl phosphate (OPA) [89] and hydride terminated polydimethyloxsiloxane (HTPDMS) [139]), conductive polymers (e.g., polypyrrole (PVP) [140], polyaniline (PANI) [140], permeable poly(3,4-ethylenedioxythiophene) (PEDOT) [141, 142], and poly-3-hydroxymethyl-1”-methyloxetane (PHMO) [143]), and other materials. So far, the methods of constructing air/water-stable protective layers on Ni-rich cathode surface are mainly divided into two categories, namely ex situ and in situ construction.

3.4.1. Ex Situ Formation of Cathode Protection Layer. The ex situ construction of surface protective layer is to physically form a protective layer on the surface of Ni-rich cathode material by means of coating, without reacting with the residual lithium compounds. For example, Zhang et al. [131] constructed a Li$_{0.5}$Mn$_{0.5}$O$_2$ protective layer on the surface of Ni-rich cathode material LiNi$_{0.8}$Co$_{0.15}$Mn$_{0.05}$O$_2$ (NCM0) by a liquid precipitation method. The protective layer blocks the damage of H$_2$O/CO$_2$ in the air to NCM0 and inhibits the generation of residual lithium compounds (e.g., Li$_2$CO$_3$) on surface, significantly improving the air/water stability of NCM0 (Figures 10(a) and 10(b)). Compared with the pristine material NCM0, the cycling stability of LiNi$_{0.8}$Co$_{0.15}$Mn$_{0.05}$O$_2$@Li$_{0.5}$Mn$_{0.5}$O$_2$ (NCM1) modified by Li$_2$MnO$_3$ was significantly improved, and good electrochemical performance was maintained even after 2 months of exposure to ambient air (Figure 10(c)). In addition, Oh et al. [144] successfully constructed a surface protective layer by coating the surface of Ni-rich layered oxide LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.1}$O$_2$ with chemically inert Mn-rich spinel LiMn$_{1.9}$Al$_{0.1}$O$_4$. The spinel LiMn$_{1.9}$Al$_{0.1}$O$_4$ protective layer improved the air/water stability of LiNi$_{0.7}$Co$_{0.15}$Mn$_{0.1}$O$_2$ and maintained a high capacity even after being exposed to air for one month (Figures 10(d) and 10(e)). Moreover, Zhao et al. [116] successfully constructed a protective layer composed of MnO$_2$ nanoparticles on the surface of Ni-rich layered oxide LiNi$_{0.5}$Co$_{0.15}$Al$_{0.35}$O$_2$ by wet chemical method. The MnO$_2$ layer not only blocks the penetration of external air but also consumes the residual lithium compounds on the surface of LiNi$_{0.5}$Co$_{0.15}$Al$_{0.35}$O$_2$, thus improving its chemical stability (Figure 10(f)). Compared with the pristine sample, the Ni-rich cathode material LiNi$_{0.5}$Co$_{0.15}$Al$_{0.35}$O$_2$ modified by MnO$_2$ still has a high capacity retention after 40 days of exposure to ambient air (Figure 10(g)). Furthermore, TiO$_2$ has been used as a very competitive protective layer to improve the air/water instability of Ni-rich cathode materials due to its abundance, structural stability, and electrochemical inertness [117]. Mo et al. [117] constructed a protective layer consisting of TiO$_2$ nanoparticles (labeled as NCM@TO$_2$-x (x = 1, 2, 3) on the surface of Ni-rich cathode material LiNi$_{0.5}$Co$_{0.15}$Mn$_{0.35}$O$_2$ (NCM622) by a wet chemical coating method, which significantly decreased its air/water sensitivity (Figure 10(h)). Compared with the pristine
NCM622, the capacity retention of the NCM@TO2-2 sample is significantly improved (Figure 10(i)). In addition to the above-mentioned protective layer dielectrics, many other metal oxides (e.g., Al2O3 [118, 120], ZnO [121, 122], and ZrO2 [123]) have also been used to build protective layers on the surface of Ni-rich cathodes to reduce air/water sensitivity.

Conventional cladding methods usually cannot obtain a uniform thickness of the protective layer. In addition, some parts of the coating in certain areas are too thick, which blocks lithium ion diffusion, increases the impedance, and reduces the discharge capacity. Therefore, there is an urgent need to develop a new coating technology to construct a uniform and adjustable protective layer. Atomic layer deposition...
(ALD) is a vapor-phase method of growing thin films that allows precise control of coating thickness at the atomic level, resulting in uniform coating layers. For example, Yan et al. [145] used ALD technology to build a thin and uniform LiPO 4 protective layer on the surface of Ni-rich cathode material LiNi 0.8Co 0.15Mn 0.05O 2 (NCM), which significantly improved the structure and interface stability of NCM and its long-term capacity/voltage cycling stability. Similarly, Xie et al. [146] designed and synthesized a stable and strong LiAlF 4 protective layer that conducts Li ions on the surface of Ni-rich cathode material NCM811 using ALD, which significantly improved the long-term capacity retention of NCM811. The NCM811 cathode material modified by LiAlF 4 can achieve good cycling stability for 300 cycles, and the capacity retention rate per cycle is higher than 99.9%. However, ALD precursors are often metal-organic compounds with high cost and slow deposition rates, making them unsuitable for large-scale industrial production. Compared to ALD, magnetron sputtering is less costly and faster, suitable for coating on the outermost layer of cathode materials. Yang et al. [138] prepared an ultrathin lithium phosphonium nitride (LiPON) film on the surface of LiNi 0.8Co 0.15Mn 0.05O 2 (NCM) cathode by magnetron sputtering, which effectively suppressed the interfacial degradation between electrode and electrolyte. This significantly improved the stability of the overall particle surface structure for lower impedance, longer cycle life, and better safety of the whole battery. Most notably, such an NCM-LiPON-based 1.3-Ah pouch cell delivers an energy density of 364.4 Wh kg⁻¹ (based on cathode and anode materials), along with the retention of 80.0% over 745 cycles at 0.5 C-rate, which is 1.3 times longer than the bare one. The air/water stability data for various protective layers formed ex situ on Ni-rich cathodes are summarized in Table 2.

3.4.2. In Situ Formation of Cathode Protection Layer. Moreover, in situ construction of the surface protective layer is to form on Ni-rich cathode material surface simultaneously through chemical reaction between the medium and residual lithium compounds, thereby eliminating surface impurities and forming a protective layer on the surface to block H 2O/CO 2 in the air. For example, Ryu et al. [124] converted Li residues on the surface of Ni-rich cathode material LiNi 0.8Co 0.15Mn 0.05O 2 (NMC811) into a Li 3PO 4 nanoprotective layer by a simple phosphate ((NH 4) 2HPO 4) treatment, thus improving the air/water stability of NCM811 (Figure 11(a)). Compared with pristine NCM811, the electrochemical performance (cycling performance and rate capability) of the phosphate-modified NCM811 was significantly improved after storage under harsh environmental conditions (Figure 11(a) (ii)). This improved stability was attributable to the phosphate treatment, which eliminated Li residues from the surface of NCM811, inhibited the formation of undesirable impurities such as LiOH and Li 2CO 3, and formed a thin Li 3PO 4 nanolayer in situ on its surface, mitigating the parasitic reaction between NCM811 and the electrolyte. In addition, Li 3PO 4 provided an effective protective barrier for the penetration of H 2O and CO 2 into the particle agglomerates under a humid air environment, thereby suppressing the loss of particle integrity. Moreover, phosphates such as AlPO 4 [125], ZrP 2O 7 [127], MnPO 4 [147], Ni 3 (PO 4) 2 [148], Co 3 (PO 4) 2 [149], and FePO 4 [150] can be used for the modification of Ni-rich cathode materials and can equally function as a favorable protective layer.

In order to inhibit the formation of residual lithium compounds, the in situ construction of a tightly packed hydrophobic protective layer on the surface of Ni-rich cathode can effectively prevent the erosion of water. For instance, Gu et al. [89] successfully solved the inherent air/water sensitivity of NCM811 by forming a thin and uniform octadecyl phosphate (OPA) self-assembled monolayer (SAM) in situ on the surface of Ni-rich cathode NCM811 particles via a simple wet chemical process (Figure 11(b)). Compared to the original NCM811, the OPA-NCM811 material exhibited a dramatic change in contact angle from fully wetted to 85.5° and still had a high capacity retention after 14 days of exposure to 60% RH ambient air (99.6% after 200 cycles vs. 87.4% for the NCM811 sample) (Figure 11(b) (v)). Similarly, the hydride terminated polydimethylsiloxane (HTPDS) can in situ form an ultrathin HTPDS hydrophobic protective layer on the surface of Ni-rich cathode material LiNi 0.82Co 0.15Al 0.03O 2 (NCA) (Figure 11(c)) [139]. This protective layer is formed by hydrogen bonding tightly to the hydroxyl groups on the surface of the NCA. The HTPDS protective layer can not only prevent NCA from adsorbing H 2O and CO 2 in the environment but also has excellent lithium ion transport ability. Furthermore, the HTPDS-modified NCA material still exhibited similar electrochemical performance to the fresh pristine material after 14 days of storage in ambient air (Figure 11(c) (ix)). However, the hydrophobic protective layer can only improve the storage performance of Ni-rich cathode materials in humid air but fails to improve the electrochemical performance of the battery.

Different from the above protective layer materials, the conductive polymer protective layer can not only improve the air/water sensitivity of Ni-rich cathode material but also be oxidized and polymerized to form a network or three-dimensional protective layer structure to improve the electron transfer and diffusion coefficient of Li⁺. Gan et al. [140] successfully constructed a uniform and thin PANI conductive protective layer (NCM811@PANI–PVP) on the surface of NCM811 through the bonding between polyvinylpyrrolidone (PVP) and polyaniline (PANI) molecules (Figure 12(a)). The conductive PANI protective layer can not only greatly inhibit the side reactions between the electrode and the organic electrolyte but also act as a fast channel for electron conduction, resulting in a significant improvement in the electrochemical performance of NCM811@PANI–PVP. Compared with pristine NCM811, NCM811@PANI–PVP exhibits excellent rate capability and superior cycling stability (Figure 12(a) (iv-v)).

Besides the construction of surface protective layer by liquid-solid reaction mentioned above, gas-solid reaction can also be used to remove surface impurities and construct a suitable protective layer in situ on the surface of Ni-rich cathode materials, which basically avoids the generation of waste water. For example, Kim et al. [151] developed a simple and innovative sublimation-induced
<table>
<thead>
<tr>
<th>Type of Ni-rich cathodes</th>
<th>Protective layer</th>
<th>Fabrication method</th>
<th>Layer thickness</th>
<th>Air/water stability</th>
<th>Capacity retention of pristine (B)</th>
<th>Capacity retention of coated cathodes (A)</th>
<th>Improved capacity retention (A–B)</th>
<th>Rate/current/cycle</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>Li$_2$MnO$_3$</td>
<td>Liquid precipitation method</td>
<td>—</td>
<td>2 months</td>
<td>62%</td>
<td>79%</td>
<td>17%</td>
<td>1 C/100 cycles</td>
<td>[131]</td>
</tr>
<tr>
<td>LiNi$<em>{0.7}$Co$</em>{0.15}$Mn$_{0.15}$O$_2$</td>
<td>LiMn$<em>{1.2}$Al$</em>{0.1}$O$_4$</td>
<td>Wet chemical method</td>
<td>—</td>
<td>1 months</td>
<td>68%</td>
<td>80%</td>
<td>12%</td>
<td>0.3 C/200 cycles</td>
<td>[144]</td>
</tr>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
<td>MnO$_2$</td>
<td>Wet chemical method</td>
<td>10 nm</td>
<td>40 days</td>
<td>70.3%</td>
<td>87.1%</td>
<td>16.8</td>
<td>1 C/100 cycles</td>
<td>[116]</td>
</tr>
<tr>
<td>LiNi$<em>{0.6}$Co$</em>{0.2}$Mn$_{0.2}$O$_2$</td>
<td>TiO$_2$</td>
<td>Wet chemical method</td>
<td>14 nm</td>
<td>—</td>
<td>78%</td>
<td>96%</td>
<td>18%</td>
<td>5 C/200 cycles</td>
<td>[117]</td>
</tr>
<tr>
<td>LiNi$<em>{0.76}$Mn$</em>{0.14}$Co$_{0.10}$O$_2$</td>
<td>Li$_3$PO$_4$</td>
<td>ALD</td>
<td>—10 nm</td>
<td>—</td>
<td>79%</td>
<td>91.6%</td>
<td>12.6%</td>
<td>0.5 C/200 cycles</td>
<td>[145]</td>
</tr>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.1}$Mn$_{0.1}$O$_2$</td>
<td>LiAlF$_4$</td>
<td>ALD</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.25 C/300 cycles</td>
<td>[146]</td>
</tr>
<tr>
<td>LiNi$<em>{0.8}$Co$</em>{0.1}$Mn$_{0.1}$O$_2$</td>
<td>LiPON</td>
<td>Magnetron sputtering</td>
<td>10 nm</td>
<td>—</td>
<td>80% (221 cycles)</td>
<td>80% (288 cycles)</td>
<td>—</td>
<td>0.5 C/221 cycles/228 cycles</td>
<td>[138]</td>
</tr>
</tbody>
</table>

**Table 2:** Air/water stability data for protective layers formed ex situ on Ni-rich cathodes.
**Figure 11:** (a) (i) Schematic illustration of the surface changes of bare NCM811 and phosphate-modified NCM811 stored in humid air. (ii) Cycling performance of NCM and P-NCM (0.5) before and after subject to ASST. Reproduced with permission [124]. Copyright 2019, Elsevier. (b) (i) Schematic illustration of the preparation process of SAM-passivated NCM811. (ii) SFG vibrational spectra of bare and OPA-passivated NCM811 materials. (iii, iv) Contact angles of water drop on the (iii) bare and (iv) OPA-passivated NCM811 pellets. (v) Cycle performance of bare NCM811 and OPA-NCM811 materials. Reproduced with permission [89]. Copyright 2019, American Chemical Society. (c) (i) The skeleton symbol of HTPDMS. (ii) The particle model of NCA. (iii) The model of the binding process of HTPDMS to hydroxyl groups on the NCA surface via hydrogen bonding. (iv) The schematic illustration of the air stability of HTPDMS-modified NCA. (v) Schematic illustration of the lithium ion transport process in the HTPDMS-modified NCA. (Vi, Vii) Static water contact angle of (vi) pristine and (vii) HTPDMS-modified NCA. (viii) XRD patterns of pristine and HTPDMS-modified NCA. (ix) Cycling performance of pristine and HTPDMS-modified NCA before and after 14 days of storage in ambient air. Reproduced with permission [139]. Copyright 2021, Elsevier.
gas-reacting (SIGR) process (Figure 12(b)). The gas-phase sulfur (S) reacts with the remaining lithium compounds on the surface of the Ni-rich cathode material NCM811 at a low temperature of 300°C to generate a Li$_2$S$_x$O$_y$ protective layer in situ (Figure 12(b) (i)). Furthermore, the SIGR process helps the Li$_2$S$_x$O$_y$ coating to be uniformly distributed on the surface of the secondary and primary particles. As a consequence, the SIGR-treated NCM811 exhibits better cycling stability, which is mainly owed to the Li$_2$S$_x$O$_y$ protective layer and the suppressed (de) lithiation process of anisotropic volume change (Figure 12(b) (ii-iii)). The air/water stability data for various protective layers formed in situ on Ni-rich cathodes are summarized in Table 3.
<table>
<thead>
<tr>
<th>Type of Ni-rich cathodes</th>
<th>Protective layer</th>
<th>Agent</th>
<th>Layer thickness</th>
<th>Air/water stability</th>
<th>Capacity retention of pristine (B)</th>
<th>Capacity retention of coated cathodes (A)</th>
<th>Improved capacity retention (A–B)</th>
<th>Rate/current/cycle</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>Li_{3}PO_{4}</td>
<td>(NH_{4})<em>{2}HPO</em>{4}</td>
<td>3 nm</td>
<td>100 h (70% RH)</td>
<td>55%</td>
<td>77%</td>
<td>22%</td>
<td>95 mA g^{-1}/50 cycles</td>
<td>[124]</td>
</tr>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>OPA</td>
<td>Octadecyl phosphonic acid (OPA)/THF</td>
<td>2.6 nm</td>
<td>14 days (60% ~70%RH)</td>
<td>52.38%</td>
<td>89.69%</td>
<td>37.31%</td>
<td>0.5 C/197 cycles</td>
<td>[89]</td>
</tr>
<tr>
<td>LiNi_{0.82}Co_{0.15}Al_{0.03}O_{2}</td>
<td>HTPDMS</td>
<td>Hydride-terminated polydimethylsiloxane (HTPDMS)</td>
<td>10 um</td>
<td>14 days</td>
<td>63.9%</td>
<td>75.4%</td>
<td>11.5%</td>
<td>2 C/150 cycles</td>
<td>[139]</td>
</tr>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>PANI–PVP</td>
<td>Polyaniline (PANI)</td>
<td>5-7 nm</td>
<td>—</td>
<td>66.3%</td>
<td>88.7%</td>
<td>22.4%</td>
<td>200 mA g^{-1}/100 cycles</td>
<td>[140]</td>
</tr>
<tr>
<td>LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2}</td>
<td>Li_{x}S_{y}O_{z}</td>
<td>Gas-phase sulfur (S)</td>
<td>15-20 nm</td>
<td>—</td>
<td>70.1%</td>
<td>83.8%</td>
<td>13.7%</td>
<td>0.1 C/200 cycles</td>
<td>[151]</td>
</tr>
</tbody>
</table>
This section summarizes the researches on air stability of Ni-rich cathode materials reported in recent years and the corresponding methods for improvements: (1) elemental doping and (2) construction of surface protective layer. The surface degradation of Ni-rich layered oxides exposed to ambient air is driven by the reduction of chemically active Ni$^{3+}$ to more stable Ni$^{2+}$, resulting in the release of lattice oxygen and the formation of surface residual lithium compounds. Therefore, adding a small amount of cation or anion atoms into the lattice of Ni-rich cathode materials through elemental doping strategy can significantly improve the air/water stability. The main purpose of cation doping is to improve the air/water stability of Ni-rich cathode materials from the aspect of structural stability. First, doping cations (Al$^{3+}$) in Ni-rich cathode materials can form strong covalent bonds with lattice oxygen, enhance the lattice structure, and suppress the loss of lattice oxygen. Secondly, doping with some high-valence cations (Zr$^{4+}$) can reduce the content of active Ni$^{3+}$ on the surface of Ni-rich cathode materials (reduced to stable Ni$^{2+}$ to maintain charge balance) and can also play a role in suppressing the loss of lattice oxygen. Moreover, anion doping can also effectively enhance the stability of oxygen lattice, thereby improving the structural stability of Ni-rich cathode materials. However, elemental doping strategy can only retard the degradation process of Ni-rich cathode materials exposed to humid air and cannot fundamentally solve the occurrence of interfacial side reactions, let alone effectively improve the electrochemical performance of the battery.

Notably, constructing various surface protection layers on Ni-rich cathode materials can not only effectively improve the stability of Ni-rich cathode materials in ambient air but also protect Ni-rich cathode materials from HF erosion and harmful side reactions with electrolyte at high potentials, thus significantly improving the electrochemical performance of Ni-rich cathode materials. First, a series of chemically stable metal oxides (e.g., MnO$_2$ and TiO$_2$), layered LiMnO$_2$, and spinel LiMn$_{1.9}$Al$_{0.1}$O$_4$ protective layers are formed on the surface of Ni-rich cathode materials by ex situ coating, which effectively inhibits the generation of residual lithium compounds on the surface of Ni-rich cathode materials. However, the above-mentioned conventional cladding methods generally fail to obtain a uniform thickness of the protective layer. Furthermore, some parts of the coating in some areas are too thick, which hinders the diffusion of Li$^+$, increases the interface resistance, and reduces the discharge capacity. Uniform and controllable ultrathin Li$_2$PO$_3$ and LiPON protective layers were successfully constructed on the surface of Ni-rich cathode materials by ALD and magnetron sputtering technology, which solved the problem of uneven coating and improved ionic conductivity. Secondly, a protective layer is formed in situ on the surface of Ni-rich cathode materials through the chemical reaction between the medium and the residual lithium compound, thereby eliminating surface impurities and blocking H$_2$O/CO$_2$ in the air. Since moisture is one of the necessary conditions for the formation of residual lithium compounds, the in situ construction of a tightly packed hydrophobic protective layer (e.g., OPA and HTPDMS) on the surface of Ni-rich cathode can significantly improve its air/water stability. However, the organic hydrophobic protective layer can only improve the storage performance of Ni-rich cathode material in humid air but cannot effectively improve its electrochemical performance. This is because the hydrophobic protective layer may dissolve into the organic electrolyte during long-term cycling. It may also be oxidized at high voltages, thus reducing the electrochemical performance of the cell, such as cell swelling, thick solid electrolyte interface (SEI) layer, and increased polarization. Fortunately, the application of conductive polymer protective layer (PANI-PVP) solves the above problems. This layer can not only improve the air/water sensitivity of Ni-rich cathode material but also be oxidized and polymerized to form a network or three-dimensional protective layer structure to improve the electron transfer and diffusion coefficient of Li$^+$. Although the coating strategy has many advantages, its disadvantages are also very obvious. For example, the coating technology is relatively complex and difficult to achieve a uniform coating [64, 152, 153]. Specifically, the physical parameters of coatings, such as coating materials, size, thickness, uniformity, density, and conductivity, have a significant influence on the electrochemical behavior of Ni-rich cathode materials. Three aspects can be helpful solutions: (1) select a more suitable surface coating layer that combines high lithium ion conductivity and electronic conductivity; (2) select a more suitable coating path to achieve uniform coating; (3) accurate control of coating process for mass production.

4. Moisture/Water Instability of Anodes

As we all know, LMA is the most promising anode materials for LIBs due to its high theoretical capacity (3860 mAh g$^{-1}$), low density (0.59 g/cm$^3$), and the lowest electrochemical reaction potential (-3.04 V vs. SHE) [17–19, 30–33]. However, the practical application of LMA is hindered by moisture/water instability due to the high reactivity of Li metal. When LMA comes into contact with moisture/water, it will react violently with H$_2$O, burning and releasing large amounts of heat and gas, causing serious safety accidents. Therefore, there are high requirements for the production, storage, and transportation of LMA, which will undoubtedly increase the manufacturing cost significantly [154–156]. In this section, LMA will be taken as the main example to introduce the moisture/water instability mechanism and the characterization of air/water stability of anode, and the corresponding modification strategies will be proposed.

4.1. Mechanisms of Air/Water Instability of LMA. Since Li metal itself is a highly reactive alkali metal, its surface will be immediately corroded after exposure to ambient moisture/water, forming a passivation layer composed primarily of LiOH, Li$_2$CO$_3$, and Li$_3$N [157]. Specifically, Li reacts with O$_2$ and N$_2$ to form Li$_2$O and Li$_3$N, both of which readily absorb moisture from the air to form LiOH to further react with CO$_2$ to form Li$_2$CO$_3$ [158]. In addition, Li metal reacts violently with H$_2$O, burning and releasing a lot of heat and H$_2$. Therefore, if the Li metal battery has packaging leakage...
and moisture infiltration during transportation and use, serious safety hazards such as burning or even explosion may occur. At the same time, various uncontrollable adverse reactions caused by the exposure of Li metal surface to air will generate heterogeneous contaminants and uneven surfaces, making the interfacial electron/ionic current densities uneven and aggravating the growth of lithium dendrites [159]. Moreover, during the cycling process, the continuous growth of lithium dendrites will penetrate the separator and cause a short circuit to generate Joule heating, which eventually leads to thermal runaway of the battery [160]. As a result, the operation of Li metal usually requires a high-purity inert atmosphere such as an argon-filled glove box, which is costly and difficult to operate, seriously hindering the development of high-energy density lithium metal batteries (LMBs).

4.2. Characterization of Air/Water Stability of LMA. The identification and quantification of reaction products on Li metals are crucial for evaluating the air/water stability of LMA before and after modification. The characterization of surface stability of LMA in ambient air/water has been focusing on morphological and compositional changes when exposed to the atmosphere or immersed in water. In general, the color and volume changes of Li metal can be observed by visual observation, while scanning electron microscopy (SEM) is frequently used to study the morphology evolution of Li surface. Furthermore, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Raman spectra, and EDX (energy dispersive X-ray) are widely used for composition analysis.

SEM is frequently used to study the surface morphology evolution of LMA. Observations of Li metal after exposure to air for different times provide the temporal evolution of Li surface corrosion. For example, Ma et al. [161] examined the air stability of the prepared 100nm thick graphene film deposited LMA (gLi-100) by time-lapse photography. When exposed to ambient air with a relative humidity of 45–60% at room temperature for 6 h, bare Li turned blue-gray, indicating severe surface corrosion. In contrast, the surface of gLi-100 maintained an overall unchanged appearance and texture, which confirmed the good protection of the graphene coating against air moisture (Figure 13(a)). Postcycle SEM analysis of batteries cycled in “moist” electrolyte or open system is used to evaluate the effectiveness of the protective layer against attack from air/water and electrolyte. For example, Liao et al. [162] characterized the surface morphologies of GeCl₄-THF-treated Li and pristine Li by SEM after 25 cycles in a humid Li₂O₂ battery (RH 45%) (Figure 13(b)). The originally smooth pristine Li surface evolved into “hills” after 25 cycles, while the surface of the treated Li remained smooth and dense.

XRD is the main method to study the phase and crystal structure of substances. XRD can detect Li surface oxidation products such as LiOH, Li₂CO₃, and Li₃N crystals. Furthermore, in situ XRD measurements can reveal various crystal-line oxidation products generated in real time. For example, Shen et al. [163] investigated the real-time structural change information of GF-LiF-treated Li and bare Li exposed to ambient air (RH~10%) by in situ XRD measurements to analyze the entire oxidation process. The in situ XRD measurements show a change in the positions and intensities of all peaks for bare Li, as well as a gradual increase in the peak intensities associated with LiOH, indicating a continuous reaction between Li and ambient H₂O. In contrast, the XRD spectrum of GF-LiF-treated Li did not change significantly during its exposure to ambient conditions (Figure 13(c)).

XPS provides quantitative elemental analysis of the sample surface with analysis depths of 8–10 nm. For example, Liang et al. [164] studied the chemical composition of Li metal surface coatings treated with SiCl₄/THF solution by analyzing Li 1s, Si 2p, and S 2p XPS spectra (Figure 13(d)). Furthermore, FTIR spectroscopy, Raman, and EDX mapping are also useful to analyze the composition of Li surface after exposure to the atmosphere.

4.3. Construction of Anode Surface Protective Layer. Various strategies have been proposed to address the moisture/water instability of lithium metal anode, among which the construction of moisture/water-stable protective layer on the surface of the LMA is one of the most widely used and effective strategies. Choose an appropriate material to form a dense, hydrophobic, and high-ionic-conductivity protective layer on the LMA surface through ex situ coating or in situ reaction, which can block contaminants without increasing interfacial resistance (such as LiPSs, humid air or even water), thereby improving the corrosion resistance of the LMA.

4.3.1. Ex Situ Formation of Anode Surface Protective Layer. Ex situ construction of surface protection layers is a simple method to prepare moisture/water stable LMAs. Under the premise of vacuum, inert substances are deposited on the surface of LMA to form an ultrathin conformal protective layer with a controllable thickness, which can easily and effectively process Li foil samples, thereby physically isolating the contact between LMA and moisture/water. Common deposition techniques include chemical vapor deposition (CVD), atomic layer deposition (ALD), molecular layer deposition (MLD), and physical vapor deposition (PVD) (e.g., magnetron sputtering and vacuum thermal vapor deposition).

CVD is a method of producing thin films by chemically reacting gaseous or vaporous substances on the surface of a substrate. For example, Ma et al. [161] achieved a moisture/water-resistant LMA by implementing a wax-assisted transfer protocol to passivate the LMA surface with high-quality CVD graphene films (Figure 14(a)). The 100 nm thick graphene film (gLi-100) has good hydrophobicity, which can well protect Li metal from moisture/water erosion. After exposure to humid air for 6 h, bare Li metal surface corroded severely and turned blue-gray, while the gLi-100 surface showed no obvious change or LiOH peak (Figure 14(a) (ii–iv)). Moreover, this conductive and mechanically robust graphene protective layer can act as an SEI, which can effectively dissipate local surface charges, guiding homogeneous lithium plating/stripping, and suppress lithium dendrite growth. Li-air batteries fabricated
with gLi-100 exhibited excellent cycling performance up to 2300 hours (Figure 14(a) (v-vi)). This passivation method of LMA by CVD of conductive and inert graphene films provides a practical solution for the preparation of moisture/water-stable LMAs, which can even be extended to other moisture/water-sensitive materials.

Unlike the continuous reaction of CVD, ALD has the characteristics of self-limiting and layer-by-layer deposition growth, which can precisely control the coating thickness and ensure the consistency of the deposited layer in thickness and composition. Noked et al. [165] used ALD to deposit an Al2O3 protective layer on LMA surface to block direct contact of lithium metal with air, sulfide, and organic solvents, thus significantly improving the moisture/water stability of LMA (Figure 14(b)). A protective layer of Al2O3 with 14 nm thickness allows LMA to retain its metallic

Figure 13: (a) Serial optical images of the bare-Li and gLi-100 anodes exposed to air for 6 h. Reproduced with permission [161]. Copyright 2021, Wiley-VCH Verlag GmbH. (b) (i, ii) SEM images of the pristine (i) and protected (ii) Li anode in Li-O2 cells after 25 cycles in the humid O2. Reproduced with permission [162]. Copyright 2018, Wiley-VCH Verlag GmbH. (c) (i, ii) All in situ XRD patterns of (i) pristine Li metal and (ii) GF-LiF-Li at every scan. Reproduced with permission [163]. Copyright 2019, Nature Publishing Group. (d) (i-iii) XPS analysis for the surface of Li treated with SiCl4/THF solution. Reproduced with permission [164]. Copyright 2019, Wiley-VCH Verlag GmbH.
Figure 14: (a) (i) Schematic illustration of the process of preparing graphene films on Li foil. (ii) Serial optical images of the bare-Li and gLi-100 anodes exposed to air for 6 h. Time-lapse XRD patterns of (iii) bare Li and (iv) gLi-100 exposed to air. The cyclic charge/discharge profiles of (v) bare-Li||Ru@CNT and (vi) gLi-100||Ru@CNT cells. Reproduced with permission [161]. Copyright 2021, Wiley-VCH Verlag GmbH. (b) (i) Schematic illustration of the ALD Al₂O₃-protected Li against H₂O and polysulfide corrosion. (ii) Series optical images of bare Li and Li@ZrEG anodes exposed to an atmosphere of 40% RH at 25°C for 6 h. Reproduced with permission [165]. Copyright 2015, American Chemical Society. (c) (i) Illustration of a protective zircon coating on a Li metal anode. (ii) Optical images of bare Li and zircon-coated Li metal after exposure to air at different time intervals. Electrochemical performance of Li-O₂ battery with a (iii) Li@25ZrEG anode and (iv) bare Li metal anode. Reproduced with permission [166]. Copyright 2019, Wiley-VCH Verlag GmbH.
luster after exposure to 40% relative-humidity (RH) air for 20 hours (Figure 14(b) (ii)). Similar to ALD, MLD is also able to precisely control the thickness and composition of the film at the atomic level. Adair et al. [166] used MLD to form a nano-scale zircone protective layer on the surface of LMA, which significantly improved the moisture/water stability and electrochemical performance of LMA (Figure 14(c)). Compared to pristine LMA, zircone-protected LMA can be stored stably in ambient air for 6 hours without any surface changes, which can be owed to the fact that the zircone-protected layer can act as a physical/chemical barrier to protect LMA from air or moisture erosion (Figure 14(c) (ii)). Furthermore, zircone-protected LMA exhibits excellent cycling performance in Li-O₂ batteries, which is 10 times better than that of pure LMA (Figure 14(c) (iii-iv)).

PVD is a method of vaporizing the coating material by physical methods (such as evaporation and sputtering) and depositing a film on substrate surface. The most widespread PVD processes are vacuum thermal vapor deposition and magnetron sputtering, both of which can deposit uniform coatings of controlled thickness directly on LMA surface. Vacuum thermal vapor deposition is a technique in which the target is heated and evaporated under vacuum conditions, causing a large number of atoms and molecules to vaporize and eventually be deposited on the substrate surface. Xu et al. [167] used vacuum evaporation deposition technology to form a mixed interfacial phase film composed of fullerene (C₆₀) and magnesium metal bilayers on the surface of lithium foil, thereby successfully preparing a moisture/water stable and dendrite-free LMA, Mg@C₆₀@Li (Figure 15(a)). The hydrophobic C₆₀ film has a contact angle of 97.1°, making the LMA resistant to moist air (Figure 15(a) (ii-iii)). The Mg thin film provides LMA with low lithium deposition/stripping overpotential, which ensures better electrochemical stability and cycle life of LMA. Due to this unique hybridization interface, Mg@C₆₀@LMA still showed no significant peaks of LiOH after being exposed to humid air (30% RH) for 12 h compared to untreated Li foil and Li foil treated with Mg metal only (Figure 15(a) (iv-v)). Furthermore, the batteries assembled with Mg@C₆₀@LMA and commercial LiFePO₄ cathodes exhibited longer cycle life and higher capacity retention (Figure 15(a) (vi)). Compared with pristine LMA, Mg@C₆₀@LMA still exhibits excellent electrochemical performance after being exposed to humid air (30% RH) for more than 12 h (Figure 15(a) (vii)).

Magnetron sputtering is a technique for depositing a target onto an object surface by means of a plasma, which allows the sputtering time to be controlled to regulate the thickness of the coating. Liu et al. [168] deposited a 2 μm thick and dense lithium phosphorus oxyxinitride (LiPON) protective layer on the surface of LMA by magnetron sputtering technique (Figure 15(b)). It is worth noting that when LMA with locally deposited LiPON was exposed to the atmosphere at room temperature for up to 10 days, the uncovered LMA turned into dull gray-black, while the protected LMA still maintaining its initial metallic luster (Figure 15(b) (ii)). This indicates that the LiPON protective layer could protect LMA from side effects of O₂, H₂O, and even N₂ in air. Although LMAs prepared by the above-mentioned deposition techniques have good moisture/water stability, these techniques usually require large specialized equipment and expensive targets as well as high maintenance costs, making them unsuitable for large-scale industrial production. Therefore, there is a need to develop simpler, cost-effective, and mass-producible methods for ex situ formation of protective layers.

Compared with the deposition technology mentioned above, the liquid coating process is simpler to operate and less expensive, which provides a simple and effective method for ex situ construction of a protective layer on LMA surface. For instance, Zhang et al. [160] proposed a simple dip coating method, in which lithium metal was immersed in a wax-PEO solution, followed by heating and drying to remove solvent and to form a blend polymer protective layer on LMA surface (noted as Li-wax-PEO) (Figure 16(a)). Since wax is an inert sealing material with good chemical stability, electrical insulation, and hydrophobicity, Li metal sealed with wax has excellent moisture/water stability, and the wax coating also prevents corrosion of LMA by electrolyte. On the other hand, the ion-conductive PEO provides a pathway for the homogeneous deposition of Li⁺, thus ensuring the long-term cycling stability of the Li-wax-PEO anode. After exposure to air at 70% RH for 24 hours, the surface of Li-wax-PEO had almost no change, while the pristine Li metal surface was immediately corroded, whose color also changed from silver to blue (Figure 16(a) (ii)). This indicates that the dense wax composite coating significantly improved the air stability of LMA. Moreover, when water was dropped on Li-wax-PEO surface or when Li-wax-PEO was immersed in water, no violent reaction such as fire occurred, confirming its excellent waterproof performances (Figure 16(a) (iii)). Furthermore, the electrochemical behavior of Li-wax-PEO hardly changes whether it is exposed to air or immersed in water (Figure 16(a) (iv)). Both symmetric and lithium-sulfur batteries using Li-wax-PEO as the anode exhibit excellent cycling performance (Figure 16(a) (vi-vii)). Similarly, a hydrophobic and ionically conductive ethylene-vinyl acetate (EVA) copolymer bifunctional protective layer was formed on LMA surface by dip coating, which can simultaneously improve the moisture/water resistance and electrochemical cycling stability of LMA (Figure 16(b)) [169]. On the one hand, EVA can easily interact with lithium salts to improve Li ion conductivities because of the high concentration of ester polar groups. On the other hand, the methylene and methyl groups make EVA obtain better hydrophobicity, which can effectively protect LMA from the corrosion of humid air. The EVA-coated LMA showed no obvious change whether it was exposed to air at 35% RH for 5 hours or immersed in water (Figure 16(b) (ii-iii)), confirming its outstanding air stability and waterproof performance. It is worth mentioning that the Li|NCM cells assembled with EVA-protected LMA exhibited more stable cycling performance compared with the pristine LMA (Figure 16(b) (iv)). Although this simple liquid coating process has the advantages of simple operation, low cost, and wide selection of coating materials, the resulting protective layer is relatively thick (micrometer scale), which may lead to greatly
Figure 15: (a) (i) Schematic illustration of the preparation process of depositing fullerenes (C60) and magnesium metal successively on lithium foil by vacuum evaporation deposition technique. (ii, iii) Contact angle of water droplets on a bare glass sheet and a glass sheet with 100-nm C60. XRD patterns of (iv) fresh anodes and (v) anodes after exposure to air at 30% RH for 12 h. (vi) Cycling performances of the fresh Mg@C60@Li//LFP full cells (LFP loading of 15–16 mg cm\(^{-2}\)). (vii) Cycling performance of LFP full cells using Mg@C60@Li anodes after exposure to air at 30% RH for 12 h. Reproduced with permission [167]. Copyright 2019, Wiley-VCH Verlag GmbH. (b) (i) SEM images of LiPON layer deposited on lithium electrode: side-view image. (ii) Optical image of LiPON@Li metal during atmospheric exposure at room temperature after 10 days. The red square shows the size of LiPON layer. Both the length and width of LiPON@Li metal were about 6 cm. Reproduced with permission [168]. Copyright 2018, American Chemical Society.
Figure 16: (a) (i) Diagram of the functions of the wax-PEO coating. (ii) SEM images and corresponding optical photographs of pristine Li and Li-wax-PEO before and after air exposure. (iii) Photographs of pristine Li and Li-wax-PEO contact to water, and corresponding SEM images. The stripping profiles of Li-wax-PEO before and after (iv) exposure to air at 70% RH for 24 h and (v) soaked in water. (vi) Voltage-time curves of cells with Li and Li-PEO-wax anodes. (vii) Comparison of the cycling performance of lithium-sulfur cells with Li and Li-wax-PEO anodes. Reproduced with permission [160]. Copyright 2019, Elsevier. (b) (i) Schematic diagrams of lithium-ion surface deposition on lithium metal coated with EVA layer. (ii, iii) The stability of lithium metal anodes with and without EVA coating layer in (ii) humid air (35% RH) and (iii) water. (iv) Cycling performance of pristine Li|NCM and LMCA|NCM cells at 0.1 C. Reproduced with permission [169]. Copyright 2020, Elsevier.
reduced ionic conductivity and energy density. Notably, liquid coating methods (such as dip/spray/spin coating, which can be easily integrated into existing cell fabrication processes) hold the most promise for large-scale production of moisture/water-stable LMA. The air/water stability data for various protective layers formed ex situ on LMA are summarized in Table 4.

4.3.2. In Situ Formation of Anode Protection Layer. In addition to ex situ methods, protective layers can also be constructed on LMA surfaces by in situ reactions. Passivation of highly active Li metal with gas or liquid to form various functional protective layers on Li metal surface can inhibit moisture/water erosion and lithium dendrite growth, thereby improving the moisture/water stability of LMA and the electrochemical performance of batteries. Recently, Liang et al. [164] reported the in situ construction of air-stable LiSiSy protective layers on LMA surfaces using a solution method (Figure 17(a)). The LiSiSy layer was fabricated by a simple two-step solution reaction process using a chemical reaction between Li, Li2S8, and silicon tetrachloride (SiCl4) (Figure 17(a) (ii)). Theoretically, the composition of the LiSiSy layer is chemically inert, difficult to penetrate even by dry air, and has excellent oxidation resistance. This indicates that the LiSiSy protective layer can effectively prevent the erosion of LMA by external moisture/water. According to thermal gravimetric analysis (TGA) (Figure 17(a) (iii)), the Li-LiSiSy films showed little weight change during exposure to dry air (25°C) for 24 hours. In stark contrast, under the same conditions, the bare Li foil gained 1.1% weight after 6 hours of exposure. These results clearly show that the LiSiSy protective layer has excellent air stability. Furthermore, the time-of-flight secondary ion mass spectrometry (TOF-SIMS) mapping images and elemental depth distribution of Li-LiSiSy further demonstrate the superior stability of LiSiSy layer in air (30% RH) (Figure 17(a) (iv-vi)). Besides, the LiSi material with Li2O layer also has excellent air stability. For instance, Zhao et al. [174] used low-cost SiO or SiO2 mixed with Li metal to reduce its activity and used a one-pot metallurgical process to prepare Li2Si/LiO composites (Figure 17(b)). The stable Li2O matrix wrapped the uniformly dispersed active LiSi nanodomain surface, which significantly improved the air stability of Li metal. The capacity fading of Li2Si/Li2O composite is almost negligible in dry air, and its capacity is still up to 1240 mAh g⁻¹ after being exposed to an environment with 40% RH for 6h (Figure 17(b) (iv)). The excellent air stability of the Li2Si/Li2O composite material reduces the requirements for the industrial battery manufacturing environment, and the relatively low-cost raw materials can also reduce the battery manufacturing cost. Such chemical passivation methods generally utilize a simple reaction to in situ generate a dense and air-stable inorganic protective layer on Li metal surface. In addition to the above-mentioned inorganic protective layers, polymer protective layers or composite protective layers can also be constructed on LMA surface by in situ reaction. The interfacial layer was prepared by an in situ reaction between lithium metal and a polymer composed of PEO and urethrapyrimidine (UPy) (Figure 18(a)). After LiPEO-UPy was exposed to air at 30% RH for 30 min, the surface color hardly changed, while the bare Li foil turned black within 1 minute (Figure 18(a) (ii)), indicating that the LiPEO-UPy coating has better air stability. Moreover, this self-stabilizing and strongly adhesive supramolecular polymer can serve as a stable artificial SEI layer, which not only significantly inhibits the growth of lithium dendrites, but also effectively prevents side reactions between lithium metal and organic electrolyte (Figure 18(a) (iv)). Furthermore, LiPEO-UPy@Li|NCM full cells also exhibit superior electrochemical performance (Figure 18(a) (iii)). Similarly, Gao et al. [176] reported a PAN polymer-in-salt electrolyte that facilitates the generation of a stable interphase layer against a LMA owing to the high concentration of lithium salt. This interfacial layer effectively suppresses uncontrollable parasitic reactions, thereby enabling long-term, dendrite-free plating/stripping of LMA and improving battery safety. In addition, Jiang et al. [177] reported a facile method for in situ construction of a poly (tetramethylene ether glycol) (PTMEG)-Li/Sn alloy hybrid protective layer on LMA surface to improve performance and moisture stability (Figure 18(b)). The process simply immerses Li metal into a solution of SnCl4 in tetrahydrofuran (THF), where SnCl4 is directly reduced to form a Li-Sn alloy layer upon contact with Li metal (Figure 18(b) (i)). The Lewis acid SnCl4 and the resulting LiCl4 can further act as a nucleophile to initiate ring-opening polymerization of THF to PTMEG. Besides, the presence of propylene oxide (PO) in solution can also accelerate the polymerization reaction to higher molecular-weight polymers. PTMEG exhibits excellent hydrophobicity due to the higher content of alkyl groups in the main chain backbone and retains the original color even in a humid environment (78% relative humidity) after exposing the treated lithium metal for 24 h (Figure 18(b) (ii)), and the XRD pattern does not show the corresponding peak of oxide, indicating that the Li metal protected by PTMEG-Li/Sn alloy has excellent air stability. In addition, this hybrid protective layer exhibits fast Li⁺ conductivity and good electrochemical cycling stability due to the strong affinity of Li in Li-S alloys as well as C-O bonds in polymers. Surprisingly, the Li-S cells and Li-LiFePO4 cells assembled using the treated LMA still exhibited good cycling stability even after exposure to a humid environment (25°C, 78% RH) for 3h (Figure 18(b) (iii-iv)). Similar to the polymer/lithium alloy composite protective layer, the in situ formed inorganic composite protective layer can also well improve the air/moisture stability of LMA. For instance, a 1.5 μm thick germanium-based composite protective layer can be formed on the LMA surface by a rapid spontaneous reaction between lithium metal and GeCl4/tetrahydrofuran (THF) vapor (Figure 18(c)) [162]. The protective layer is composed of amorphous germanium (Ge, GeOx) and lithium compounds (Li2CO3, LiOH, Li2O, and LiCl). The two protective layer compositions of amorphous germanium and lithium compounds are functionally complementary. The electronically insulating lithium compound suppresses electrolyte
Table 4: Air/water stability data for protective layers formed ex situ on LMA.

<table>
<thead>
<tr>
<th>Protective layer</th>
<th>Fabrication method</th>
<th>Layer thickness</th>
<th>Air/water stability</th>
<th>Electrolyte</th>
<th>CE or symmetric cell performance</th>
<th>Reference</th>
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<tr>
<td>Graphene</td>
<td>CVD</td>
<td>100 nm</td>
<td>6h</td>
<td>LiTFSI/DME-DOL+1% LiNO₃</td>
<td>1 mA cm⁻²/1 mAh cm⁻²/1200 h; 5 mA cm⁻²/1 mAh cm⁻²/120 h</td>
<td>[161]</td>
</tr>
<tr>
<td>h-BN</td>
<td>CVD</td>
<td>0.35–3.5 nm</td>
<td>15 min</td>
<td>LiPF₆/EC-DEC</td>
<td>CE of 95–97%/1 mA cm⁻²/3 and 5 mAh cm⁻²/50 cycles</td>
<td>[170]</td>
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<tr>
<td>Al₂O₃</td>
<td>ALD</td>
<td>14 nm</td>
<td>20 h (40% RH)</td>
<td>LiTFSI/DME-DOL+1% LiNO₃</td>
<td>—</td>
<td>[165]</td>
</tr>
<tr>
<td>C₆₀&amp;Mg</td>
<td>Vacuum evaporation deposition</td>
<td>100 nm</td>
<td>12 h (30% RH)</td>
<td>LiPF₆/EC-DEC-EMC</td>
<td>1 mA cm⁻²/1 mAh cm⁻²/550 h; 3 mA cm⁻²/1 mAh cm⁻²/180 h</td>
<td>[167]</td>
</tr>
<tr>
<td>LiPON</td>
<td>Magnetron sputtering</td>
<td>2 μm</td>
<td>240 h</td>
<td>LiPF₆/EC-DEC</td>
<td>CE of 98.06%</td>
<td>[168]</td>
</tr>
<tr>
<td>Li₃PO₄</td>
<td>Magnetron sputtering</td>
<td>30 nm</td>
<td>1 min</td>
<td>LiPF₆/EC-DEC-DMC</td>
<td>0.5 mA cm⁻²/0.5 mAh cm⁻²/900 h; 1 mA cm⁻²/1 mAh cm⁻²/300 h</td>
<td>[171]</td>
</tr>
<tr>
<td>Wax-PEO</td>
<td>Dip coating</td>
<td>4 μm</td>
<td>24 h (70% RH) and water stability</td>
<td>LiTFSI/DME-DOL+1% LiNO₃</td>
<td>1 mA cm⁻²/1 mAh cm⁻²/500 h; 1 mA cm⁻²/3 mAh cm⁻²/280 h; 3 mA cm⁻²/1 mAh cm⁻²/155 h</td>
<td>[160]</td>
</tr>
<tr>
<td>EVA</td>
<td>Dip coating</td>
<td>120 nm</td>
<td>5 h (35% RH)</td>
<td>LiPF₆/EC-DEC</td>
<td>0.5 mA cm⁻²/1 mAh cm⁻²/650 h</td>
<td>[169]</td>
</tr>
<tr>
<td>PVA</td>
<td>Dip coating</td>
<td>0.33 μm</td>
<td>15 min (65% RH)</td>
<td>LiTFSI/DME-DOL+4% LiNO₃</td>
<td>CE of 98.3%/2 mA cm⁻²/1 mAh cm⁻²/630 cycles; CE of 98.4%/2 mA cm⁻²/2 mAh cm⁻²/320 cycles; CE of 98.5%/2 mA cm⁻²/3 mAh cm⁻²/220 cycles</td>
<td>[172]</td>
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<td>PVDF-HFP</td>
<td>Dip coating</td>
<td>25 μm</td>
<td>48 h (30% RH) and water stability</td>
<td>LiTFSI/DME-DOL</td>
<td>0.5 mA cm⁻²/0.5 mAh cm⁻²/500 h</td>
<td>[173]</td>
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Figure 17: (a) Schematic illustration of the in situ formation process of Li-Li$_x$Si$_y$. (ii) XPS spectra of Li-Li$_x$Si$_y$-1 electrodes after ambient air exposure for 5 h. (iii) TGA curves of bare Li and Li-Li$_x$Si$_y$-1 anodes in air with time (inset: schematic illustration of the Li$_x$Si$_y$ layer blocking air). (iv) TOF-SIMS secondary ion images of air-exposed Li-Li$_x$Si$_y$-1 anodes before and after Cs$^+$ consecutive sputtering for 300 s. (v) Depth profile of various secondary ion species obtained by sputtering. (vi) The 3D images of the sputtered volume corresponding to the depth profiles in (v). Reproduced with permission [164]. Copyright 2019, Wiley-VCH Verlag GmbH. (b) (i) The different behaviors of Li$_x$Si/Li$_x$O composite and Li$_x$Si/Li$_x$O core shell NPs exposed to ambient air. (ii, iii) SEM images of (ii) ball-milled SiO NPs and (iii) thermal lithiated SiO NPs. (iv) The remaining capacity of lithiated SiO NPs exposed to ambient air at approximately 40% RH for different times. Reproduced with permission [174]. Copyright 2016, Natl Acad Sciences.
Figure 18: (a) (i) Schematic illustration of the process of preparing PEO-UPy coating on Li metal surface. (ii) Series optical photographs of bare Li and LiPEO-UPy@Li anodes exposed to humid air. (iii) Cycling performance of full cells assembled using bare Li and LiPEO-UPy@Li anodes with NCM cathodes at 1C. (iv) Li stripping/plating behavior for bare Li and LiPEO-UPy@Li anodes. Reproduced with permission [175]. Copyright 2020, Wiley-VCH Verlag GmbH. (b) (i) Reaction mechanism of PTMEG-Li/Sn alloy layer formation. (ii) Series optical photographs of the pristine Li and treated Li exposed to humid air at 78% RH for 24 h. (iii) Electrochemical performance of a Li battery using the treated Li exposed to air for 3 h at 0.1 C. Reproduced with permission [177]. Copyright 2019, Wiley-VCH Verlag GmbH. (c) (i) Schematic illustration of the formation procedure of the protected Li foils. (ii) Schematic diagram of lithium plating/deposition with a germanium-based composite protective layer in a dry or moist environment. (iii) Surface changes and (iv) XRD patterns of pristine and protected lithium after 1 hour immersion in solutions with different H2O contents. (v) Galvanostatic cycling curves of pristine Li and protected Li symmetrical cells. (vi) Discharge/charge curves of Li-O2 cells using pristine and protected Li anodes exposed to humid air at 45% RH. (vii) Schematic illustration of a Li-O2 cell operating with pristine Li and GeCl4-THF-treated Li anodes exposed to a humid air environment. Reproduced with permission [162]. Copyright 2018, Wiley-VCH Verlag GmbH.
decomposition and lithiation of Ge/GeOₓ, while the germanium composition can effectively prevent dendrite penetration and water attack (Figure 18(c) (ii)). Compared with the pristine Li foil, the protected Li foil surface did not change from the beginning to the end after being immersed in H₂O-containing "moist" electrolytes for 1 h, and no obvious LiOH peak appeared, confirming that the germanium-based composite protective layer has excellent waterproof performance (Figure 18(c) (iii-iv)). Moreover, this composite protective layer allows stable cycling of LMA in Li-symmetric cells and Li-O₂ cells, especially in "moist" electrolytes (containing 1000 ppm H₂O) and humid O₂ atmospheres (45% RH) (Figure 18(c) (v-vii)). This approach can be easily translated into existing manufacturing processes, thereby facilitating the development of LMBs. The air/water stability data for various protective layers formed in situ on LMA are summarized in Table 5.

This section summarizes the researches on the moisture/water stability of LMA reported in recent years and the main methods for constructing protective layers on LAM surfaces: (1) ex situ coating and (2) in situ reaction. The ex situ or in situ formed protective layer not only keeps the LMA stable when exposed to air or even water but also resists the growth of Li dendrites during cycling, inspiring low-cost large-scale fabrication of moisture/water stable and interfacial-stable LMAs. Ex situ coating methods can produce various functional thin films. Ultrathin protective layers (e.g., graphene, Al₂O₃, zircon, and Mg@C₆₀, LiPON) with precisely tunable properties can be fabricated by vapor deposition technologies (such as CVD, ALD, MLD, and PVD), which can significantly improve the moisture/water stability and electrochemical performance of LMA. However, the vapor deposition process is time-consuming and requires high vacuum, making it difficult to be implemented on a large scale. Based on this, a liquid coating process [160, 169] was proposed to solve the above problems. Compared with the deposition technology, the simple liquid coating process (e.g., dip coating, spray coating, and spin coating) has the advantages of simple operation, low cost, and wide selection of coating materials, which can be easily integrated into existing battery fabrication processes and hold the great promise for large-scale production of moisture/water-stable/safe LMA. However, the hydrophobic protective layers of wax-PEO and EVA prepared by liquid coating process are typically too thick (micrometer scale), reducing the ionic conductivity and energy density of the whole battery. Therefore, uniform regulation of the liquid-coating thickness and creation of ion transport pathways are crucial to synchronously improve the moisture/water stability and electrochemical performance of LMA.

In addition, the in situ formation of protective layers on Li metal surfaces via spontaneous reaction with Li metal by gas or solution treatment is another effective method to improve the moisture/water stability of LMA. The in situ formed protective layer will bind more tightly to the lithium metal than the ex situ formed protective layer because of the stronger chemical bonding. Surface conditioning with solutions or their vapors is convenient, timely, and easy to carry out and transferrable to industrial scale. Moisture/water-stable inorganic protective layers such as Li₅SiSₓ and Li₅Si/Li₂O are constructed on Li metal surfaces by in situ reactions, which effectively prevent parasitic side effects in the surrounding environment. However, the Li₅SiSₓ and Li₅Si/Li₂O inorganic coatings prepared by solution and one-pot metallurgical processes are not uniform, and the presence of defects, grain boundaries, and pores in the coatings significantly reduces the shear modulus, ionic conductivity, and Li⁺ selectivity. Compared with inorganic coatings, polymer coatings (e.g., LiPEO-Upy, PAN) are more flexible and elastic and thus more adaptable to volume changes during lithium plating/striping. Furthermore, polymers can be made into uniform films by dip coating, spin coating, solution casting, or even polymerizing directly on Li metal surfaces. Its thickness can also be controlled by the concentration or reaction time of the polymer solution used in the coating process. Thinner coatings can improve the ionic conductivity of polymer films, while thicker coatings can improve film toughness and selectivity for Li⁺ conduction. However, polymer coatings exhibit swelling behavior in liquid electrolytes, and the resulting ionic conductivity and selectivity to Li ions should be investigated in details. Based on this, a polymer-inorganic hybrid (PTMEG-Li/Sn) was prepared [177] by combining the advantages of polymer and inorganic materials. This polymer-inorganic hybrid exhibits not only excellent moisture/water stability but also fast Li⁺ conductivity and good electrochemical cycling stability. Moreover, an inorganic composite protective layer composed of amorphous germanium (Ge, GeOₓ) and lithium compounds (LiₓCOₓ, LiOH, Li₂O, and LiCl) was prepared by steam treatment. The electronically insulating lithium compound suppresses electrolyte decomposition and lixiviation of Ge/GeOₓ, while the germanium composition has great potential to prevent dendrite penetration/H₂O attack, and allows fast Li-ion transport/less interfacial resistance due to the formation of Li-Ge alloys. Although surface reactions with pure gases can form highly uniform inorganic layers, the reactions are rather time-consuming. In conclusion, the formed protective layer is generally a composite coating of one or more inorganic substances/polymer, which is favorable to improve the moisture/water stability and electrochemical performance of LMA. However, in situ surface passivation is versatile and uncertain, and exploring the formation and evolution mechanisms of coatings through in situ characterization techniques is crucial for the controllable preparation of future interfacial protective layers.

5. Air/Water-Stable Protective Layers in ASSBs

Sulfide ASSBs are regarded to be one of the most promising energy storage technologies due to their higher safety and ionic conductivity [180–184] However, the poor air/water stability of Ni-rich cathode, sulfide SE, and LMA in sulfide ASSBs system makes them extremely costly and complicated in production, storage, transportation, and battery assembly processes, which seriously hinders the practical production and application of high specific energy sulfide all-solid-state batteries [14, 15, 28, 185–187]. Therefore, solving the air/water instability of Ni-rich cathode, sulfide SE, and
<table>
<thead>
<tr>
<th>Protective layer</th>
<th>Agent</th>
<th>Layer thickness</th>
<th>Air/water stability</th>
<th>Electrolyte</th>
<th>CE or symmetric cell performance</th>
<th>Reference</th>
</tr>
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<tr>
<td>Li,SiSy</td>
<td>Li$_2$S$_8$+SiCl$_4$/THF</td>
<td>150 nm</td>
<td>24 h (dry air); 5 h (30% RH)</td>
<td>Li$_3$PS$_4$</td>
<td>0.1 mA cm$^{-2}$/0.5 mAh cm$^{-2}$/2000 h</td>
<td>[164]</td>
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<tr>
<td>Li–PEO–Upy</td>
<td>PEO–UPy/THF</td>
<td>70 nm</td>
<td>30 min</td>
<td>LiTFSI/DME-DOL+2%LiNO$_3$</td>
<td>20 mA cm$^{-2}$/1 mAh cm$^{-2}$/400 h;</td>
<td>[175]</td>
</tr>
<tr>
<td>PTMEG/Sn hybrid</td>
<td>SnCl$_2$/THF</td>
<td>10 μm</td>
<td>24 h (25% RH)</td>
<td>LiTFSI/DME-DOL+1%LiNO$_3$</td>
<td>1 mA cm$^{-2}$/1 mAh cm$^{-2}$/1000 h;</td>
<td>[177]</td>
</tr>
<tr>
<td>LiF</td>
<td>Feron gas</td>
<td>40 nm</td>
<td>15 min</td>
<td>LiPF$_6$/EC-DEC</td>
<td>1 mA cm$^{-2}$/1 mAh cm$^{-2}$/450 h</td>
<td>[178]</td>
</tr>
<tr>
<td>Ge, GeO$_x$, Li$_2$CO$_3$, LiOH, LiCl, and Li$_2$O</td>
<td>GeCl$_2$/THF steam</td>
<td>1.5 μm</td>
<td>1 h (moist electrolyte)</td>
<td>LiTFSI/TEGDME</td>
<td>3 mA cm$^{-2}$/1 mAh cm$^{-2}$/350 h</td>
<td>[162]</td>
</tr>
<tr>
<td>OPA-Li-CNT</td>
<td>Octadecyl phosphonic acid (OPA)/THF</td>
<td>—</td>
<td>1 h (dry air)</td>
<td>LiTFSI/DME-DOL</td>
<td>1 mA cm$^{-2}$/0.5 mAh cm$^{-2}$/200 h;</td>
<td>[179]</td>
</tr>
</tbody>
</table>
LMA is crucial for the development of sulfide ASSBs. Currently, the most promising and effective approach is to significantly improve their air/water stability and electrochemical performance of the battery by constructing air/water-stable and good ion-conducting protective layers that isolate them from air or moisture without impeding the conduction of Li ions. As mentioned above, Xu et al. [15] successfully constructed an air/water-stable and ion-conductive superhydrophobic protective layer on the surface of the sulfide SE \( \text{Li}_{x}\text{Si}_{y}\text{Cl} \) membrane. Compared with the pristine \( \text{Li}_{x}\text{Si}_{y}\text{Cl} \) membrane, the ASSBs assembled using the F-POS@LATP protected \( \text{Li}_{x}\text{Si}_{y}\text{Cl} \) membrane as the SE exhibited almost the same cycling performance and rate capability. More surprisingly, the electrochemical properties of the ASSBs were almost unchanged before and after exposure of F-POS@LATP-coated \( \text{Li}_{x}\text{Si}_{y}\text{Cl} \) membrane to extreme conditions of water jetting (RH~70%). This simple spray method can effectively improve the performance of air/water-sensitive sulfide membranes under extreme conditions, paving the way for the large-scale production of large-area sulfide-based SE membranes. Notably, this modification strategy is a postprocessing method, which can also be extended to other air/water unstable materials such as Ni-rich cathodes and LMAs, in addition to sulfide-based SEs. Moreover, Liang et al. [164] reported that an moisture/water-stable \( \text{Li}_x\text{Si}_y \) protective layer was used as the \( \text{Li}_x\text{PS}_y/\text{Li} \) interface layer in ASSBs, which effectively prevented Li from reducing sulfur-based SEs. The symmetric cell of \( \text{Li}_x\text{Si}_y/\text{Li}_x\text{PS}_y \) protected LMA with \( \text{Li}_x\text{PS}_y \) as electrolyte shows stable cycling for 2000 h. Furthermore, the \( \text{LiCoO}_x/\text{Li}_x\text{PS}_y/\text{Li}_x\text{Si}_y \)-Li ASSB showed a capacity retention rate of 87.3% over 100 cycles, while only 4 cycles use pure Li metal as the anode. It can be seen that the application of the moisture/water-stable protective layer on LMA can improve the stability of ASSBs to a certain extent. However, this method of forming a moisture/water-stable protective layer using liquids to passivate highly reactive Li metal is not suitable for application on sulfide SEs. It is difficult to build a surface protective layer by in situ reactions similar to the above-mentioned Ni-rich cathodes or LMAs for sulfide SEs, because of its strong reactivity with air, moisture, and polar solvents. Even if ex situ coating method is adopted, the choice of solvent should be fully considered, which is limited to several nonpolar or low polar solvents such as toluene, n-heptane, xylene, and anisole. Therefore, the chemical vapor deposition method (such as CVD, ALD, MLD, and PVD) is selected as a more efficient approach to deposit air/water stable and ion-conductive substances (e.g., \( \text{Al}_2\text{O}_3 \) [118, 120], LiF [130], and Li_3PO_4 [134–136]) on sulfide SE membranes as a protective layer. Last but not least, the methods used to construct air/water stable protective layers on Ni-rich cathodes, sulfide SEs and LMAs are diverse and similar in some aspects to be mutually applicable to each other.

6. Conclusions and Perspectives

In this work, the research status on air/water stability of SEs, cathodes, and anodes is systematically reviewed. The underlying mechanisms are also discussed in details. To solve their air/water instability problems, numerous strategies have been proposed, among which the construction of surface protective layers is one of the most effective strategies. The air/water-stable protective layers enable the production, storage, transportation, processing, and application of SEs, cathodes, and anodes under less demanding environmental conditions. Therefore, the air/water-stable protective layers are of great significance for the mass production and storage of battery materials, as well as the practical application of high-energy-density ASSBs. Although some progress has been made in the construction of these air/water-stable protective layers, the construction methods for different materials such as SEs, cathodes, and anodes still require further investigation.

First, with regard to the air stability of sulfide SEs, two main modification strategies have been proposed: element/metal oxide doping and construction of surface protective layers. According to the HSAB theory, the use of elemental/metal oxide doping modification to improve the air stability of sulfide SEs is the most fundamental strategy. Although these modification strategies have been effective, the range of humidity they can withstand is limited to dry environments of less than 3% RH, which fails to meet the requirements of practical production, storage, and transportation. Constructing air/water stable protective layers through surface modification can completely prevent the direct contact of air and water with sulfide SEs, enabling large-scale production of sulfide SEs for ASSBs. The strategy of constructing composite SE membranes by coating oxide SEs on sulfide membranes is the most effective for improving the air/water stability of sulfide SEs. Notably, this modification strategy is a postprocessing method, which can also be extended to other air/water unstable materials such as Ni-rich cathodes and LMAs, in addition to sulfide-based SEs. Furthermore, by embedding the sulfide SEs into the polymer matrix, the sulfide SEs can be well protected from air/water, but the consequent negative effect may be a significant reduction in ionic conductivity. Therefore, developing SEs with both ionic conductivity and air/water stability at the same time is the main research direction in the future.

Secondly, both elemental doping and the construction of surface protective layers can effectively improve the air/water stability of cathode, especially Ni-rich cathode materials. However, elemental doping strategy can only retard the degradation process of Ni-rich cathode materials exposed to humid air and cannot fundamentally solve the occurrence of interfacial side reactions, let alone effectively improve the electrochemical performance of the battery. The gas release will cause the battery to swell and lead to safety hazards. Although both ex situ constructed metal oxides and in situ constructed phosphate protective layers can effectively suppress the formation of residual lithium compounds on the surface of Ni-rich cathode materials, they may increase the interfacial resistance, thereby degrading the kinetic performance of the battery. In addition, the organic hydrophobic protective layer constructed in situ only improves the storage performance of Ni-rich cathode materials in humid air but fails to improve their electrochemical performance. This is because the hydrophobic protective
layer may dissolve into the organic electrolyte during cycling and may be oxidized under high pressure, thereby impairing the electrochemical performance of the battery. It is worth mentioning that polymers with high electrical conductivity and fast ionic conductivities are highly desirable as the protective layer of Ni-rich cathode materials. Despite the above advantages, problems such as the uniformity of the protective layer, high-temperature resistance, and process difficulty still require further research.

Last but not least, two protection strategies for anode materials are proposed, taking the highly reactive LMA as an example. The moisture/water stability of LMA is significantly improved by constructing a protective layer on LMA via ex situ coating or in situ reaction to passivate its surface. The ex situ or in situ formed protective layer not only keeps the LMA stable when exposed to air or even water but also resists the growth of Li dendrites during cycling, which provides inspiration for the low-cost large-scale fabrication of moisture/water stable and interfacially stable LMAs. Ex situ coating methods (including vapor deposition and liquid coating processes) can produce thin films with well-defined composition and high reproducibility. On the one hand, ultrathin protective layers with precisely tunable properties can be fabricated by vapor deposition methods (such as CVD, ALD, MLD, and PVD), which can significantly improve the moisture/water stability and electrochemical performance of LMAs. However, the vapor deposition process is time-consuming and requires high vacuum, making it difficult to be implemented on a large scale. On the other hand, although the liquid coating process has the advantages of simple operation, low cost, and wide selection of coating materials, the resulting protective layer is relatively thick (micrometer-scale), which may reduce the ionic conductivity and energy density. Liquid coating methods such as dip/spray/spin coating, which can be easily integrated into existing battery fabrication processes, hold great promise for large-scale production of moisture/water stable and safe LMAs. Therefore, uniform regulation of liquid-coating thickness and creation of ion transport pathways are crucial to simultaneously improve the moisture/water stability and electrochemical performance of LMAs. The in situ formed protective layer will bind more tightly to lithium metal than the ex situ formed protective layer because of the stronger chemical bonding. Surface conditioning with solutions or their vapors is convenient, timely, and easy to carry out and transferrable to industrial scale. The formed protective layer is generally a composite coating of one or more inorganic substances/polymers, which is propitious to improve the moisture/water stability and electrochemical performance of LMA. However, in situ surface passivation is versatile and uncertain, and exploring the formation/evolution mechanisms of coatings through in situ characterization techniques is crucial for the controllable preparation of interfacial protective layers in the future.

Conflicts of Interest

The authors declare no competing financial interests.

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