Strategies towards inhibition of aluminum current collector corrosion in lithium batteries

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Received: 11 Jul 2023 First Decision: 10 Aug 2023 Revised: 30 Aug 2023 Accepted: 13 Sep 2023 Published: 8 Nov 2023

Abstract

Aluminum (Al) foil, serving as the predominant current collector for cathode materials in lithium batteries, is still unsatisfactory in meeting the increasing energy density demand of rechargeable energy storage systems due to its severe corrosion under high voltages. Such Al corrosion may cause delamination of cathodes, increase of internal resistance, and catalysis of electrolyte decomposition, thus leading to premature failure of batteries. Hence, a systematic understanding of the corrosion mechanisms and effective anticorrosion strategies are necessary to enhance overall performance of lithium batteries. In this review, the corrosive mechanisms related to Al current collectors are systematically summarized and clarified. In addition, an overview on recent progress and advancement of strategies toward inhibiting Al corrosion is presented. In the end, we also provide a perspective with motivation to stimulate new ideas and research directions to further inhibit Al corrosion to achieve high energy density, long cycle life, and high safety of lithium batteries.

Keywords: Al corrosion, corrosive mechanisms, inhibition strategies, lithium batteries
INTRODUCTION
Lithium-ion batteries (LIBs) with high energy density and long cycle life have become the dominative energy storage systems for 3C electronics, electric vehicles (EVs), and grid storages\cite{1}. However, the energy density of state-of-the-art LIBs comprising conventional capacity-limited graphite anodes (372 mAh g\(^{-1}\)) has approached their energy density ceiling of 350 Wh kg\(^{-1}\), which cannot meet the ever-increasing demand for energy storage devices\cite{2}. In addition to employing lithium anode with ultra-high theoretical capacity (3,860 mAh g\(^{-1}\))\cite{3,4}, considerable efforts have been devoted to elevating battery operation voltage (e.g., > 4.5 V vs. Li/Li\(^+\)) to further increase energy density by exploring high-voltage cathodes composed of Ni-riched layered oxide Li\([\text{Ni}_{x}\text{Co}_{y}\text{Mn}_{1-x-y}]\text{O}_2\) or spinel Li\([\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4\)\cite{5-8}. Although elevating cell operation voltage can effectively improve the energy density of LIBs, this may pose particular stringent requirements on the electrochemical stability of active and/or inactive cell components\cite{9}. Nevertheless, researchers are mainly focusing on the deactivation and failure of cathodic active materials, and extensive efforts have been made to improve the electrochemical stability and cycle stability of those high-voltage cathode materials\cite{10-12}. In fact, the failures of auxiliary materials under high operating voltages may also play an important role in dictating the overall performance of LIBs\cite{13-15}. As an indispensable component of LIBs, metallic aluminum (Al) foil is chosen as the most dominating current collector for cathode materials among various metallic foils due to its high electronic conductivity, outstanding chemical stability, low density, and low cost\cite{14,16,17}. However, the anodic Al corrosion during the long-term operation may cause the loss of adhesion of active materials to Al current collectors, partial delamination, and even detachment of active materials from Al current collector, thus destroying structural stability of cathodes and batteries\cite{18}. Besides, the parasitic products formed by the Al corrosion may hinder lithium-ion transportation, increase internal resistance, and decrease electronic conductivity, resulting in rapid capacity loss and inferior battery power density\cite{19}. In addition, the Al\(^{3+}\) species formed on the Al current collector during the corrosion process may dissolve and deposit on the anode surface, which could catalyze severe electrolyte decomposition and potentially result in notorious lithium dendrite growth and even short-circuit of cells, leading to catastrophic battery failure and severe safety concerns\cite{17,19}. Consequently, it is indispensably urgent and important to understand the Al corrosion mechanism and circumvent this problem under high voltages to further improve the energy density and overall performance of lithium batteries.

Considering the aforementioned points and the urgency of improving Al corrosion resistance, herein, in this review, the corrosive mechanisms related to Al current collectors are fully summarized and clarified in sufficient detail. In addition, an overview on recent progress and advancement of strategies toward inhibiting Al corrosion is presented, which mainly focuses on the optimization of electrolytes and modification of Al current collectors [Figure 1]. Finally, we include a perspective in this review to stimulate new ideas and research directions to further understand and tailor the Al corrosion, eventually enabling the development and advancement of the long-term cycling life of lithium batteries with high energy density.

MECHANISM OF AL CORROSION IN LITHIUM BATTERIES
Corrosion, in general, is commonly defined as the deterioration of a metal material and/or its properties because of reactions with its environment, which can take place at corrosion potential or at an open circuit\cite{20}. Corrosion also occurs independently of external current\cite{21}. Since the materials applied to lithium batteries are normally in a thermodynamically non-equilibrium state, corrosion-related processes with the presence of electrolytes are highly relevant for such systems, including Al corrosion, formation of solid electrolyte interphase (SEI) and cathode electrolyte interface (CEI), and galvanic corrosion\cite{22}. In this review, we are mainly focusing on discussing Al corrosion in lithium batteries.
As mentioned above, the Al foil has been widely employed as a cathode current collector since the commercialization of LIBs in 1991 because of its high electronic conductivity and cost-effective advantage\cite{14}. Yet, it is worth noting that the standard electrode potential of Al/Al\textsuperscript{3+} (1.38 V vs. Li/Li\textsuperscript{+})\cite{23} is far below the operating voltage of commonly used cathode materials for lithium batteries. Hence, it is anticipated that the Al corrosion is inevitable during the long-term operation and calendar processes of lithium batteries. Thanks to the natural Al\textsubscript{2}O\textsubscript{3} passivation layer formed on the Al surface, which could extend the oxidized potential to > 3.5 V vs. Li/Li\textsuperscript{+} and prevent Al corrosion to some extent, Al foil is still used as the predominant cathodic current collector for lithium batteries\cite{24}. On the basis of published literature, the Al corrosion mechanism comprising consecutive elementary steps can be understood and summarized as follows. Firstly, when an external voltage is applied to the lithium cell, the naturally formed Al\textsubscript{2}O\textsubscript{3} is not stable under anodic polarization and tends to initially release Al\textsuperscript{3+}, and then the exposed Al metal is prone to be oxidized to generate Al\textsuperscript{3+} (Equations 1 and 2). Subsequently, the generated Al\textsuperscript{3+} is a strong Lewis acid and tends to be coordinated or solvated with the anions and solvents in electrolytes to form complicated and easily soluble complexes (Equation 3). After that, the formed complexes dissolve and diffuse into the bulk electrolyte, leaving corrosion on Al current collectors (Equation 4; note that the subscripts ad and sol represent adsorbed and dissolved species, respectively)\cite{25-29}.

\[
\begin{align*}
\text{Al}_2\text{O}_3 & \rightarrow 2\text{Al}^{3+}_\text{ad} + \frac{3}{2} \text{O}_2 + 6\text{e}^- \quad (1) \\
\text{Al} & \rightarrow \text{Al}^{3+}_\text{ad} + 3\text{e}^- \quad (2) \\
\text{Al}^{3+}_\text{ad} + \text{anion/solvent} & \rightarrow \text{Al} - \text{complexes}_{\text{ad}} \quad (3) \\
\text{Al} - \text{complexes}_{\text{ad}} & \rightarrow \text{Al} - \text{complexes}_{\text{sol}} \quad (4)
\end{align*}
\]
Considering the corrosion mechanism described above, the Al corrosion processes are dominated by complicated factors, including the applied voltage and current, the cell operation temperature, the recipes and compositions of electrolytes, the purity of Al current collectors, the thickness, uniformity, and integrity of Al$_2$O$_3$, etc. [25,26]. It should also be noted that the corrosion reaction of the Al foil is a coupled electrochemical-chemical reaction [30]; these two reactions can occur simultaneously during cell operation, and it is difficult to separate and distinguish between them in reality [22]. In addition, the Al corrosion is not an issue that happens in any type of lithium-ion cells; however, it is an important parameter when searching for and evaluating a new electrolyte.

An electrolyte, an indispensable component for lithium batteries, is the environment that metal Al reacts with when Al corrosion happens [20], which not only facilitates the migration of ionic species but also plays a crucial role in affecting Al corrosion behaviors [31]. Nowadays, LiPF$_6$-based electrolytes are still the most common choice for lithium batteries due to their well-balanced properties, including ionic conductivity, electrochemical stability, etc. [32,33]. In addition, these electrolytes show superior combability toward Al current collectors and are capable of preventing Al corrosion under high voltages [34]. This is because the HF generated from the thermal decomposition of LiPF$_6$, oxidative decomposition of carbonate solvents, and/or the hydrolysis of LiPF$_6$ with the trace of H$_2$O tends to react with the natural Al$_2$O$_3$ and form a protective AlF$_3$ layer on the top of Al$_2$O$_3$ (Equations 5-9), which contributes to the Al corrosion resistance in lithium batteries [30-35,42]. It should be noted that the thickness of the passivating AlF$_3$ layer formed in LiPF$_6$-based electrolytes has been assessed around 1-2 nm [43,44], and pit corrosion is subjected to occur under extreme cycling conditions [45]. Nevertheless, the trade-off properties and the excellent SEI formation ability of LiPF$_6$ enable the successful implementation of LiPF$_6$-based electrolytes in current lithium batteries, and Al corrosion is not a severe issue in LiPF$_6$-based electrolytes.

\[
\begin{align*}
\text{LiPF}_6 & \leftrightarrow \text{LiF} + \text{PF}_5 \\
\text{PF}_5 + \text{ROH} & \rightarrow \text{POF}_3 + \text{RF} + \text{HF} \\
\text{PF}_5 + \text{H}_2\text{O} & \rightarrow \text{POF}_3 + 2\text{HF} \\
\text{PF}_6^+ + \text{R} - \text{H} & \rightarrow \text{PF}_5 + \text{HF} + \text{R}^+ \\
\text{Al}_2\text{O}_3 + 6\text{HF} & \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}
\end{align*}
\]

Actually, HF, formed in LiPF$_6$-based electrolytes, is a double-edged sword because the HF also aggressively attacks the cathode materials and causes the dissolution of transition metal oxides at the cathode side, leading to the deterioration and inferior cyclability of the cathode, which is detrimental to long-term cycling of lithium batteries [46-48]. Furthermore, the chemical and thermal instability of LiPF$_6$ at elevated temperatures (e.g., 60 °C) and its moisture sensitivity are key challenges that limit its large-scale application [14,23,31]. Hence, imide-based electrolytes such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) with excellent physical and chemical stabilities and strong resistance to water are suggested to tackle the drawback of LiPF$_6$-based electrolytes to improve the tolerance of electrolyte toward temperature/moisture and reduces the formation of acidic species and the destruction of the cathode material. LiTFSI was first scrutinized as lithium salt for highly conducting polymer electrolytes (PEs) by Armand in 1989 owing to its highly delocalized negative charge and high flexibility of TFSI anion [49]. Yet, the LiTFSI-based electrolytes turn out to be aggressively corrosive toward Al current collectors with a much lower corrosion potential of around 3.8 V vs. Li/Li$^+$ [19]. Compared to the LiPF$_6$-based electrolytes, there should be less amount of HF present in the LiTFSI-based electrolytes due to the high stability of C-F bonds [50], so no efficiently passivating AlF$_3$ layer could form to protect Al current collectors. In fact, the corrosive behavior of LiTFSI-based electrolytes is
Figure 2. Schematic illustration of Al corrosion caused by LiTFSI-based electrolytes.

induced by the formation and dissolution of the stable Al(TFSI)₃ compound. The Al(TFSI)₃, formed during the initially anodic polarization at high potentials is prone to be solvated and dissolved by carbonate solvents, thereby resulting in the continuous exposure of a fresh Al surface that can be subsequently oxidized and dissolved, causing severe Al corrosion [Figure 2].

As an analog of LiTFSI, lithium bis(fluorosulfonyl)imide (LiFSI) has been widely studied for lithium batteries owing to its super ability to provide high ionic conductivity for electrolytes and forming excellent interphases with both anode and cathode materials; however, the LiFSI-based electrolytes also suffer from the Al corrosion dilemma though the corrosion potential is larger than that of the LiTFSI-based one (i.e., 4.3 V vs. Li/Li⁺ of LiFSI vs. 3.8 V vs. Li/Li⁺ of LiTFSI). The slightly higher Al corrosion potential of LiFSI compared to LiTFSI is probably because the easier cleavage of S-F in LiFSI might be beneficial for passivating Al current collector. It is reasonable to conclude that the Al corrosion caused by LiFSI is ascribed to the formation and dissolution of Al(FSI)₃, considering that the LiFSI has a similar anionic structure to LiTFSI. Other studies indicate that the residual impurity of Cl⁻ from the preparation of LiFSI salt might be responsible for inducing Al⁺ ions to be dissolved in electrolyte solutions. Until now, the corrosion mechanism of LiFSI-based electrolytes is controversial and under debate. Further investigation is highly needed to confirm the corrosion mechanism when using LiFSI as the electrolyte salt. Considering the severe Al corrosion caused by LiTFSI- and LiFSI-based electrolytes, in this contribution, we will mainly talk about the corresponding inhibition strategies with regard to these two electrolytes.

STRATEGIES TOWARD INHIBITING OF AL CORROSION

In consideration of the problem caused by Al corrosion in lithium batteries, many strategies have been proposed and developed to prevent Al current collectors from corrosion in the hope of enabling lithium cells to be cycled under high voltages with long-term cyclability and high energy density. In this part, the progress and advancement of strategies toward inhibiting Al corrosion are summarized. Figure 3 shows a brief timeline of all the novel findings in this field.
Figure 3. A brief timeline summarizing the progress of strategies toward inhibiting aluminum corrosion.

Optimization of electrolytes
Electrolytes have been regarded as the “blood” of lithium batteries, which play a significant role in dictating overall performance of these batteries. According to the corrosion mechanisms discussed above, tuning and tailoring conventional liquid electrolyte compositions, including lithium salts, solvents, concentration, etc., and utilization of other types of liquid electrolytes, such as ionic liquids (ILs) and PEs, might be beneficial for inhibiting the formation and dissolution of Al(TFSI)₃, thus preventing the Al current collector from serious corrosion. The chemical structures of the representative lithium salts, solvents, additives, ILs, and polymer matrices published for the inhibition of Al corrosion are summarized in Scheme 1. The advanced strategies of optimization of electrolytes to increase the Al corrosion resistance are discussed in detail in the following sections.
Scheme 1. The chemical structures of the representative lithium salts, solvents, additives, ionic liquids, and polymer matrices.

Optimization of lithium salt

Lithium salts not only provide lithium sources for ionic transportation but are also capable of facilitating the formation of robust and highly conductive interphases with both anodes and cathodes, which are the “crowns” for lithium batteries. By virtue of decreasing the low solubility of aluminum salts with highly fluorinated bulky anions, extending the length of the perfluorinated alkyl chains in sulfonimides demonstrates a feasible way to tackle the aggressive Al corrosion behaviors of LiTFSI-based electrolytes. Hence, newly synthesized lithium sulfonimides show higher Al corrosion potentials, e.g., 4.8 V vs. Li/Li$^+$ of lithium (trifluoromethanesulfonyl)(nonafluorobutanesulfonyl)imide (Li(C$_4$F$_9$SO$_2$)(CF$_3$SO$_2$)N; LiTNFSI; Scheme 1), thus improving the electrochemical compatibility of imide-based salts with the Al current collectors. Noteworthily, the remarkably enhanced compatibility of the new lithium sulfonimide with the Al current collector is generally achieved at the cost of decreased ionic conductivity, wettability, and interphase-forming ability. Importantly, Qiao et al. have recently reported a non-corrosive sulfonimide salt, lithium (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide (LiDFTFSI), for 4-V-class rechargeable lithium metal batteries without sacrificing ionic conductivity (e.g., 3.7 mS cm$^{-1}$ at 20 °C). Different from the typical LiTFSI-based electrolyte, the LiDFTFSI-based electrolyte remarkably suppresses Al corrosion under a higher potential of 4.2 V vs. Li/Li$^+$ [Figure 4A]. This is attributed to the chemical instability of
Al(DFTFSI)$_3$ in carbonate solvents, which readily decomposes to form a stable passivation layer containing AlF$_3$ and LiF species that could completely cover the surface of the Al current collector and thereby prevent its further anodic dissolution [Figure 4B]. In sharp contrast, the Al(TFSI)$_3$, formed in the LiTFSI-based electrolyte, is stable, tends to dissolve into the electrolyte solution, and then diffuse and deposit on the surface of lithium metal anodes, causing inferior cell performance [Figure 4C]. In addition, the LiDFTSI salt results in the growth of advantageous interfacial layers on both lithium metal anodes and cathodes [Figure 4D], enabling a NMC111||Li cell with superior cycling stability and capacity retention (87% at cycle 200; Figure 4E), demonstrating the decisive role of the salt anion in determining the electrochemical performance of lithium batteries. From a viewpoint of practical application, the LiDFTFSI-based electrolyte is suggested to be evaluated in cells using graphite or graphite@nano Si/SiO$_2$ as anodes and high voltage LiCoO$_2$, Ni-rich layered materials or LiNi$_{x}$Mn$_{1-x}$O$_2$ as cathodes (typical industry level is $>3.5$ mA h cm$^{-2}$) with lean electrolyte [typical industry level for an electrolyte to capacity (E/C) ratio is $\sim 2$-5 g (Ah)$^{-1}$] to prove its practical feasibility [72-75].
In addition to lithium sulfonimides, lithium borates have been widely used as high-performance lithium salts in lithium batteries owing to their unique properties such as excellent thermal stability and superior compatibility with Al current collectors\cite{61,76-80}. The chemical structures of representative lithium borates with inhibition abilities against Al are shown in Scheme 1. Lithium tetrafluoroborate (LiBF$_4$)\cite{61} is favored for low-temperature applications due to its smaller anionic size, faster anionic mobility, and smaller charge transfer resistance relative to LiPF$_6$\cite{80,82}. Besides, LiBF$_4$-based electrolytes could efficiently passivate Al due to the formation of a protective passivation layer on the Al surface because of the reaction of electrolyte with Al and the decomposition of organic solvents under high voltages\cite{81}. X-ray photoelectron spectroscopy (XPS) study reveals that this passivation layer consists of Al-F compounds (e.g., AlF$_3$\cite{82,83}), B-F compounds (Al(BF$_4$)$_3$), and organic species (e.g., Al(CH$_2$CO$_2$)$_3$)\cite{85}. However, the low ionic conductivity and inferior SEI-forming properties of LiBF$_4$ have been the major obstacles that limit its extensive application\cite{16,31,61}.

Lithium bis(oxalato)borate (LiBOB)\cite{65}, comprising two oxalate-coordination groups, has a unique tetrahedron structure wherein no fluorine and hydrogen are present. Probably owing to the fact that the BOB anion contains no labile fluorine and LiBOB is thermally stable up to 302 °C, it enables stable cell cycling performance even at 60 °C, whereas LiPF$_6$-based cells would usually fail. In contrast to LiBF$_4$, LiBOB shows better compatibility with graphite anodes and satisfactory stability toward charged cathode surfaces\cite{61,44,45,66}. Importantly, LiBOB can stabilize Al current collectors to more positive potentials (> 4.0 V vs. Li/Li$^+$) due to the formation of a passivating layer containing AlBO$_3$, BO$_3$, and Li$_2$CO$_3$, generated from the decomposition of LiBOB under high anodically polarized potentials, demonstrating the superior inhibition ability against Al corrosion\cite{41,87-89}. Here, again, similar to LiBF$_4$, LiBOB-based electrolytes also suffer from low ionic conductivity because of the low solubility of LiBOB in carbonate solvents [e.g., 0.7-0.8 M in ethylene carbonate/dimethyl carbonate (EC/DMC)]\cite{19,63}, expelling its utilization as a main salt in lithium batteries. Even though LiBOB shows undesirable ionic conductivity, it has been widely employed as a functional additive to enhance overall performance of lithium batteries, considering its outstanding properties mentioned above, which will be discussed in the following section\cite{60-66}.

To circumvent the drawbacks of LiBF$_4$ and LiBOB without sacrificing their respective properties, lithium difluoro(oxalato)borate (LiDFOB) with single oxalato- and two fluoro-substituting groups was synthesized by Zhang in 2006\cite{82}. Since LiDFOB comprises both structural moieties of LiBF$_4$ and LiBOB, the LiDFOB-based electrolytes present the combined advantages of those two salts. Different from LiBF$_4$, LiDFOB is highly capable of stabilizing SEI on the surface of graphite anodes, enabling lithium cells to be operated stably during long-term cycling performance. Compared to LiBOB, LiDFOB is more soluble in linear carbonates and the obtained electrolyte solution is less viscous, which is beneficial for enhancing ionic conductivity and high-rate performance\cite{84}. Meanwhile, benefiting from the Al inhibition property of both LiBF$_4$ and LiBOB, the LiDFOB-based electrolytes exhibit the best performance in passivating Al because a much thicker protective layer containing Al-F species in addition to Al in lithium batteries owing to their unique properties such as excellent thermal stability and superior compatibility with Al current collectors\cite{61,76-80}. The chemical structures of representative lithium borates with inhibition abilities against Al are shown in Scheme 1. Lithium tetrafluoroborate (LiBF$_4$)\cite{61} is favored for low-temperature applications due to its smaller anionic size, faster anionic mobility, and smaller charge transfer resistance relative to LiPF$_6$\cite{80,82}. Besides, LiBF$_4$-based electrolytes could efficiently passivate Al due to the formation of a protective passivation layer on the Al surface because of the reaction of electrolyte with Al and the decomposition of organic solvents under high voltages\cite{81}. X-ray photoelectron spectroscopy (XPS) study reveals that this passivation layer consists of Al-F compounds (e.g., AlF$_3$\cite{82,83}), B-F compounds (Al(BF$_4$)$_3$), and organic species (e.g., Al(CH$_2$CO$_2$)$_3$)\cite{85}. However, the low ionic conductivity and inferior SEI-forming properties of LiBF$_4$ have been the major obstacles that limit its extensive application\cite{16,31,61}.

Inspired by the advantages of the fluoroalkoxy group in enhancing ionic conductivity and oxidation stability improvement, a promising bulky anion-based lithium borate salt, lithium trifluoro(perfluoro-tert-butyloxy)borate (LiTFPFB), was synthesized by our group for lithium metal batteries\cite{96}. The LiTFPFB-based electrolyte not only showed significantly enhanced ionic conductivity but also passivated Al current collector from corrosion even at a high voltage of 4.5 V vs. Li/Li$^+$ [Figure 4F and G]. In another work, we reported a highly oxidative-resistant cyanophenyl-functionalized lithium borate salt, namely lithium difluoro(1,2-dihydroxyethane-1,1,2,2-tetracarbonitrile) borate (LiDFTCB; see in Scheme 1), also showing excellent oxidative stability toward Al current collectors [Figure 4H]\cite{97}. Recently, Roy et al. demonstrated that the
lithium 1,1,1,3,3,3-(tetrakis)hexafluoroisopropoxy borate (LiBHfip)-based electrolyte presented an outstanding stability of an Al substrate at an ultrahigh potential up to 5.8 V vs. Li/Li’. XPS analysis of the Al surface after chronoamperometry test revealed the AlF and Al2O3 species probably appearing from the breakdown of the BHFip anion at high potentials contributed to the inhibition of Al corrosion[98]. In short conclusion, lithium borates are prone to form passivating layers comprising Al-F, B-O, B-F, and similar compounds on the surface of Al substrate, and these layers are more stable than Al2O3; thus, they can maintain their stability at high potentials to avoid direct contact between Al current collectors and electrolytes, thereby preventing corrosion from occurring and facilitating improving cycling performance at high voltages, although the ionic conductivity of lithium borates is highly needed to be improved.

Motivated by the efficient impact of lithium salts on improving electrolyte compatibility toward Al substrate, new types of lithium salts, such as Al-centered[99], carbon-centered[71], and “Hückel” type salts[100-102] [e.g., lithium 2-trifluoromethyl-4,5-dicyanoimidazolide (LiTDI); Scheme 1], are designed for high-voltage lithium batteries. Although the passivation of Al by those salts prevents Al current collector dissolution to high potentials (e.g., 4.5 V vs. Li/Li’), the mechanisms for those beneficial actions require further elucidation and demonstration. Except for using a single salt as the main salt, blended-salt electrolytes with synergistic effects have been formulated by simply mixing two or more lithium salts in an electrolyte. The functionalities of formulating blended-salt electrolytes for lithium batteries include not only inhibition of Al corrosion but also improvement of thermal/electrochemical stability, enhancement of performance over a wide temperature range, and formation of favorable interfacial layers on both electrodes, which have been comprehensively discussed in our previous review[65]. Hence, in this contribution, we are mainly talking about the electrolytes with a single main lithium salt and only discussing a few research works related to blended-salt electrolytes.

Optimization of solvent
Non-aqueous organic solvents are critical media to dissolve and dissociate lithium salts and simultaneously facilitate the rapid migration of active charges in the bulk electrolytes under an electric field. Hence, the intrinsic properties of non-aqueous solvents, including thermal transitions (melting and boiling points), density, viscosity, dipole moment, dielectric constant, and donor number, are important parameters for identifying suitable electrolyte solvents for rechargeable lithium batteries[23]. According to Equation 4 in Section 2, those solvents with low dielectric constant and donor number could be good solvent choices for electrolytes to inhibit anodic Al dissolution. Besides, the solvents whose decomposition products could passivate Al efficiently are also good candidates for lithium batteries. The structures of the representative solvents are shown in Scheme 1.

Standard solvents for commercial lithium batteries are mostly composed of cyclic and linear carbonates, such as propylene carbonate (PC), EC, and DMC, whose mixtures with well-balanced properties are beneficial to obtain sufficient ionic conductivities. Nevertheless, the organic carbonates with high dielectric constant and donor number are easy to coordinate and dissolve the Al-containing species [e.g., Al(TFSI)4], accelerating Al corrosion behaviors. Fluorination of certain organic carbonates can efficiently protect Al current collectors by facilitating the formation of insoluble coordination polymers[103] or a protective Al fluoride surface layer[104-106], thus preventing continuous and severe anodic Al dissolution.

Ethers are the other promising electrolyte solvents for lithium batteries because of their unique compatibility with anodes (e.g., lithium metal anode)[107]. In comparison, the donor number of ethers is relatively higher than that of carbonates, but their relative dielectric constant is much lower. Recently, Park et al. introduced a new low-dielectric solvent, 1,2-dimethoxypropane (DMP), as an electrolyte
solvent[108]. The enhanced oxidative dissolution of the Al current collector (4.5 V vs. Li/Li⁺) is associated with the different dielectric constants of 1,2-dimethoxyethane (DME) and DMP (i.e., 6.9 for DME and 5.5 for DMP). The DMP with a lower dielectric constant decreases the dissolution of Al corrosion byproducts and thus enables effective prevention of the Al corrosion. However, it should be noted that ethers can chelate Al³⁺ cations by virtue of the structural flexibility of their C-O moieties when there are multiple sites, endowing ethers with strong solvating ability[23]. More seriously, the inferior anodic stability of ethers may pose challenges to be used in high-voltage lithium batteries[109].

Apart from the commonly used carbonate and ether solvents, phosphates[110,111], sulfonamide[112], sulfones[113-116], and nitriles[117-124] were also evaluated as promising solvents to suppress the anodic Al dissolution. In 2020, Zheng et al. synthesized a fluorinated cyclic phosphate solvent, 2-(2,2,2-trifluoroethoxy)-1,3,2-dioxaphospholane 2-oxide (TFEP) [Figure 5A], for use in LIBs[110]. The decomposition of TFEP formed a synergistic layer consisting of organic fluorophosphate and AlF₃[Figure 5B] that may decrease the direct contact between Al and electrolytes, thereby suppressing Al corrosion. Very recently, Wu et al. found that the AlF₃ species generated from the preferential decomposition of N,N-dimethyl fluorosulfonamide contributed to effectively protecting fresh Al from physical contact, which inhibited continuous exposure of Al surface to electrolytes and alleviated Al corrosion [Figure 5C][112].

Additives for the inhibition of Al corrosion

An electrolyte additive is another important part of lithium batteries, which makes the realistic energy density toward the theoretical value and enhances the battery lifespan. Introducing functional additives into electrolytes is a facile but effective way to improve the comprehensive performance of lithium batteries[6,125]. As a benchmark salt for lithium batteries, LiPF₆ can also be used as an additive to protect Al current collectors in a dual salt system [Figure 6A][34,126-128]. Al corrosion can be completely suppressed in the presence of a trace of the LiPF₆ additive (e.g., 0.05 M), as demonstrated by the absence of an Al signal in the energy dispersive X-ray spectrum of the Li metal anode recovered from LiTFSI-LiBOB dual-salt electrolytes after 500 cycles [Figure 6B][129]. Thanks to the passivating layer formed through the decomposition of lithium borates, namely LiBF₄, LiBOB, and LiDFOB, they are widely used as additives for Al protection[34,75,81,83,95,126,129], and among them, LiDFOB exhibits the most effective inhibition, as it inherits the merits of both LiBF₄ and LiBOB [Figure 6C][95].

Inorganic additives have a significant effect on the protection of Al current collectors as well. In order to inhibit Al corrosion, a small amount of HF was added to the LiTFSI-based electrolyte. The suppression of Al corrosion due to the addition of HF can be understood by the surface film change from Al₂O₃ to AlF₃-Al₂O₃[66]. However, the corrosion of Al is still observed under high voltages, and HF may have an adverse effect on the electrochemical cycling performance of lithium batteries. The Al corrosion can also be attenuated in the presence of another inorganic additive, i.e., fumed silica nanoparticles. It is reasonable to assume that fumed silica nanoparticles could cover the defect site of the film formed on the surface of Al; thus, pitting corrosion may be inhibited[130]. Besides, the addition of silica particles contributes to forming physical crosslinking among the silica particles to produce a gel state, which hinders the dissolution of corrosion products[131]. In addition, the added fumed silica nanoparticles are able to scavenge impurities (e.g., H₂O) in the electrolytes and thus improve the electrochemical stability of Al because those impurities could substantially exacerbate the corrosion behavior of Al[132]. In a word, screening and customizing ideal functional additives to inhibit Al corrosion is one of the most competitive and promising routes to achieve high energy density of lithium batteries with improved cycling performance.
Figure 5. (A) Design of the fluorinated cyclic phosphate solvent. (B) High-resolution XPS spectra of the Al foil after the chronoamperometry tests carried out in the three electrolytes: Al 2p (left column), F 1s (middle column), and P 2p (right column). (A and B) Reproduced from Ref. [110] with permission. Copyright 2020, Springer Nature. (C) Features of DMFSA as an electrolyte solvent. Reproduced from Ref. [112] with permission. Copyright 2022, Springer Nature.

High-concentration electrolytes

To achieve relatively high ionic conductivity and low viscosity, the concentration of lithium salts in the range of ca. 0.8-1.2 mol L\(^{-1}\) is utilized for most of the representative lithium electrolytes\(^{[23]}\). In recent years, increasing salt concentration to prepare highly concentrated electrolytes (the concentration of lithium salt usually > 3 mol L\(^{-1}\))\(^{[132-134]}\) has aroused intensive attention, considering their intrinsically outstanding interfacial compatibility with anodes owing to the formation of robust anion-derived SEI layers\(^{[135,136]}\), high selectivity of lithium ions transportation, and suppressed Al corrosion\(^{[23,137]}\). In addition, higher concentration significantly limits the number of free solvent molecules, which, in turn, suppresses the dissolution of transition metals cations from the cathode and widens the operating temperature of electrolytes\(^{[138]}\), thereby enabling high-voltage operation of lithium batteries with high safety. Yamada \textit{et al.} systematically studied the corrosion inhibition mechanism of Al in highly concentrated LiFSI/acetonitrile (ACN) electrolytes (e.g., 5 mol L\(^{-1}\))\(^{[29,139]}\). In a dilute LiFSI/ACN electrolyte, a large number of free ACN solvents exist in the electrolyte. The Al\(^{3+}\), formed at high voltages, is solvated by free ACN solvents and could easily diffuse from the Al surface to bulk electrolytes, leading to the continuous corrosion of Al [Figure 6D]. In sharp contrast, Al corrosion is significantly suppressed owing to the lack of free ACN solvents and reduced dissolution and diffusivity of Al(FSI), complex in the highly viscous concentrated electrolyte [Figure 6D]. Benefiting from this advantage, the oxidative corrosion of Al is effectively improved up to 4.5 V (\textit{vs.} Li/Li\(^+\)) when the salt concentration is increased to 5 mol L\(^{-1}\).

Matsumoto \textit{et al.} reported that the Al corrosion could be suppressed in a moderate concentration, e.g., 1.8 mol L\(^{-1}\) LiTFSI in EC/diethyl carbonate (DEC)\(^{[140]}\). They attributed this suppression mechanism to the shortened distance between the TFSI\(^-\) anion and the Li\(^{+}\) cation, which facilitates the forming of a stable LiF-rich protective layer on the Al surface [Figure 6E]\(^{[140,141]}\). Yet, McOwen \textit{et al.} suggested that C-F bonds in the TFSI\(^-\) anions are strong and do not easily oxidize to form F\(^-\) anions\(^{[142]}\). They supposed that the solubility
of Al-TFSI complexes would be much lower because the solvent molecules and anions are already extensively coordinated with Li$^+$ cations. In addition, the high concentration of TFSI$^-$ anions at the Al-electrolyte interface will also serve as a barrier that hinders the access of solvent molecules to the Al surface and thus suppresses the anodic dissolution of Al. However, these properties mentioned above are achieved at the cost of the loss of ionic conductivity. Compared with the solution concentration of 1 mol L$^{-1}$, the viscosity of the highly concentrated electrolytes is greatly increased, so the ionic conductivity of the solution is usually lower than that of the solution concentration of 1 mol L$^{-1}$. In addition, the high cost of lithium salts is another challenging concern that may hinder their application.

Ionic liquid electrolytes

ILs comprising only ionic species are of particular interest for lithium batteries owing to their extremely low volatility and good electrochemical and chemical stability. The representative chemical structures of those ILs with good Al corrosion inhibition ability are shown in Scheme 1. Peng et al. demonstrated that the suppression of Al corrosion in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide-based IL is achieved by the formation of a passivation layer on the Al surface$^{[14]a}$. Further work revealed that components of the passivation layer are highly associated with the anionic structures in ILs, and the boron-based anions tend to passivate Al substrates efficiently. For example, the ILs with BF$_{4}^-$ anion seem to form a compact and dense passive layer composed of AlF$_3$ and Al$_2$O$_3$.$^{[14]b}$ In another work, the
1-alkyl-3-methylpyrrolidinium difluoro(oxalato)borate (PY1RDFOB) IL is evidently able to passivate the Al working electrode and prevent corrosion by the decomposition of the DFOB anion to form AlF$_3$, or the formation of an Al(DFOB)$_3$ complex$^{[144,145]}$. Indeed, the high viscosity and the lack of coordination sites endow ILs with low solubility of Al(TFSI)$_3$, and the low solubility of this compound also contributes to the formation of a stable and protective layer on the Al surface, which, in turn, eliminates the corrosion process$^{[146,147]}$.

Nevertheless, the higher viscosity of ILs compared with traditional carbonate-based liquid electrolytes normally causes poor wettability and inferior contact toward polyolefin separators and porous electrodes. Moreover, the high viscosity may also result in decent bulk ionic conductivity and poor cell performance. In addition, although the decomposition of the representative ILs could form desirable passivating layers on Al, the cations and anions of ILs generally undergo parasitic reactions at both anodes and cathodes, respectively, leading to premature failure of batteries$^{[21]}$. Hence, a careful evaluation of the comprehensive performance of IL-based lithium batteries is urgently required to boost their practical applications.

**Polymer electrolytes**

PEs have been considered as one of the most promising alternatives to state-of-the-art LIBs owing to their excellent flexibility and processability and good physical contact with the electrodes$^{[148-151]}$. Their development can be traced back to the 1970s when Armand first proposed the utilization of conductive polymers as safe electrolytes for rechargeable batteries$^{[151,152]}$. After that, tremendous efforts have been devoted to designing and preparing novel polymer matrices and conductive lithium salts with the motivation of improving overall performance of PE-based lithium batteries$^{[50,150,153-176]}$. The successful implementation of poly(ethylene oxide) (PEO)-based lithium batteries in commercial electric vehicles (i.e., Bluecars) has clearly demonstrated the practical feasibility of utilizing PEs in high-performing solid-state batteries$^{[49]}$.

Compared with liquid electrolytes, solid-state PEs (SPEs) comprising typical PEO and LiTFSI salts are supposed to exhibit intrinsic weaker solubility of Al$^{3+}$ species, showing resistance to Al corrosion$^{[177]}$. The incorporation of functional lithium salts as additives is of significance to further inhibit Al corrosion behaviors in PE-based electrolytes$^{[127,178-180]}$. Geng et al. introduced small amounts of LiPF$_6$ into the in-situ polymerized poly(1,3-dioxolane) (poly-DOL) electrolyte$^{[180]}$. The LiPF$_6$ plays an important role in prevention of Al corrosion and acceleration of in-situ polymerization of DOL solvent inside the lithium cell. Following the same methodology, AlF$_3$ additives were added into the poly-DOL electrolytes by Zhao et al., which were thought to create a solution saturated with Al$^{3+}$ and immobilize TFSI$^-$, thus inhibiting Al anodic dissolution [Figure 7A]$^{[178]}$.

Among various polymer matrices, PEO, with a superior solvation ability, low cost, and facile processability, has been the dominant matrix for PE-based lithium batteries. However, the PEO-based electrolytes suffer from low ionic conductivities (e.g., $10^{-6}$–$10^{-7}$ S cm$^{-1}$) at room temperature owing to the semi-crystalline nature of the PEO. Hence, replacing PEO with other alternatively representative polymer matrices, such as perfluoropolyether$^{[181]}$, polycarbonates$^{[182-186]}$, and polyesters$^{[187]}$, is another feasible method to enhance the ionic conductivity and simultaneously improve the Al stability$^{[180]}$. For example, Cong et al. reported a multifunctional perfluoropolyether-based PE [Figure 7B] for lithium metal batteries, the polyether chains of perfluoropolyether coordinate with the TFSI anions [Figure 7C], which reduces the free TFSI$^-$ anionic concentration and thus prohibits the corrosion of Al foil$^{[181]}$. Our group also demonstrated that there are no Al corrosion phenomena in the poly(propylene carbonate)-based lithium metal batteries even after 100 cycles [Figure 7D]$^{[182]}$. In addition to tuning the structure polymer matrices, the concentration of lithium
salts for PEs may also affect the Al corrosion inhibition ability. The anodic Al dissolution is efficiently suppressed, and the electrochemical performance of cells is greatly elevated by increasing LiTFSI concentration in PE-based lithium batteries\textsuperscript{185,189,190}. However, the notion of suppression of Al corrosion by increasing salt concentration in PE-based cells has recently been under debate\textsuperscript{191}.

In short, the implementation of PEs in lithium batteries seems to be more effective in prohibiting Al corrosion due to the intrinsic properties of PEs. However, more attention should be paid to clarifying the inhibition mechanisms, as this is critical for realizing high-performing SPE-based lithium batteries.

**Treatment of Al current collector**

Generally, the Al corrosion in lithium batteries results from the contact between electrolytes and Al current collectors\textsuperscript{18}. Apart from the optimization of advanced electrolytes, the surface treatments of Al to improve the electrochemical stability of Al toward electrolytes have been extensively investigated as well. So far, researchers have focused on the fabrication and preparation of artificial passivating films directly on the Al surface to suppress Al corrosion, including the formation of thicker Al\textsubscript{2}O\textsubscript{3} passivation films by thermal treatment\textsuperscript{41} and protective AlF\textsubscript{3} species by functional additives and surface coating. Among them, the technologies of surface coating have attracted a lot of attention. According to the nature of materials, the versatile materials for the Al coating could be generally divided into three categories: carbon-derived materials, conversion materials, and other materials (e.g., MXene-based materials, AlPO\textsubscript{4}\textsuperscript{40}, and polymeric materials), as detailed below.
Carbon-derived materials for Al coating

In recent decades, the carbon-coated Al foils have been widely used as current collectors for commercial cathode materials\cite{192,193}. The conductive carbon-coated layer not only increases the contact area between Al substrates and cathode materials but also serves as a buffer layer to strengthen their adhesion, which is beneficial to decreasing the interface resistance and maintaining chemical stability and structural integrity during cell operation\cite{194,195}. Furthermore, it also plays a role in suppressing the Al corrosion and facilitating improving cell performance\cite{196-198}. The mainstream carbon materials for the coating mentioned above are normally carbon black and graphite. Yet, these coated layers normally reach a thickness of 1-5 μm, which occupies too much volume of electrodes and thus sacrifices a lot of volumetric and specific energy density. In addition, previous reports also demonstrated that the carbon-coated Al decreased the corrosion issue occurring upon charge-discharge processes; however, such a non-dense carbon coating with essentially island-like surface coverage is unevenly distributed, whose structure with high specific area might easily be submerged by electrolytes and does not totally prevent the corrosion of the Al current collector\cite{197,199}.

Graphene with two-dimensional features has extraordinary mechanical properties (~130 GPa of tensile strength), extremely high electric conductivity (~$10^8$ S m$^{-1}$), and notable flexibility\cite{200}. When graphene-coated Al foils are used as current collectors, their thinner thickness, superior adhesion, higher electronic conductivity, and Al corrosion inhibiting property synergistically improve overall performance of lithium batteries\cite{201}. Recently, Li et al. demonstrated a novel graphene-coated Al for lithium batteries, and the graphene-coated layer acted as a corrosion inhibitor that protected the Al foil from corrosion [Figure 8A], showing an increased capacity by over 100 mAh g$^{-1}$ after 450 cycles compared to the bare foil\cite{202}. Kim et al. found that the LiCoO$_2$ cell using the three-layered graphene-coated Al exhibited better cycling and rate performance than that of common Al [Figure 8B and C] due to their corrosion resistance and high electronic conductivity\cite{203}. Strikingly, a graphene-armored Al current collector was prepared by Wang et al. via a plasma-enhanced chemical vapor deposition method to serve as an extraordinary conductive shield that could efficiently eliminate the attacks of the anions/other coordinating species to Al$^{3+}$\cite{25}. Consequently, the Al foil armored with conductive graphene sheath presented significantly reinforced resistance against the anodic Al corrosion [Figure 8D]. Nevertheless, this kind of technology excessively relies on the equipment, and there still exist several intractable technical problems in large-scale production and uniformity of the coating as well. In this regard, graphene oxide or reduced graphene oxide instead of graphene may be a more suitable candidate for the coating due to its facilely established technologies after decades of research\cite{24,194,204,205}.

Conversion materials for Al coating

The use of conversion materials to improve the corrosion resistance of Al foils has been widely applied in electronics, aerospace, and batteries\cite{206,207}. The chromate conversion coating (CCC) on the surface of the Al current collector was pretreated by Piao et al. to suppress Al corrosion in the LiTFSI-based electrolyte\cite{27}. In contrast to the uncoated Al current, where the soluble Al(TFSI)$^3$ continuously produced corrosion, the protective chromate conversion layer on the surface of Al can prevent TFSI$^-$ from accessing Al$^{3+}$. Furthermore, the insoluble Cr$^{3+}$ species reduced by the soluble Cr$^{4+}$ species may migrate to cracks or defective parts of the passivation film, thereby contributing to increasing the corrosion resistance of CCC-Al foil [Figure 8E]. Considering the low working limit voltage and the toxicity of Cr$^{4+}$ ions, a molybdate conversion coating was fabricated to circumvent the dilemma and simultaneously enhance the anticorrosion property of Al current collectors\cite{210}. The NMC111||Li cell with coated Al current collector worked well at 4.5 V vs. Li/Li$^+$ and presented better cycling performance than that of the control cell owing to the anticorrosion property of the protective film. Although the conversion materials can effectively enhance the corrosion resistance of the Al current collector, there are only a few studies on conversion materials, and the inhibition mechanisms need to be further explored.
Other materials for Al coating

MXene nanosheets with high conductivity, abundantly adjustable functional groups, and excellent anticorrosion properties have been widely used as active materials or conductive substrates to construct advanced electrodes\(^\text{[211-213]}\). For the first time, a homogeneous and ultrathin (< 100 nm) MXene-armored layer was fabricated on pure Al current collectors (MXene-Al) via a simple self-assembly procedure by Yang et al. Li||Al cells based on the MXene-Al could operate under a broad electrochemical window of 2-5.5 V vs. Li/Li\(^+\) owing to its outstanding anticorrosion (e.g., high strength, chemical stability, and conductivity)\(^\text{[199]}\).

Polymetric materials have reportedly been used as corrosion protection layers for various metals\(^\text{[214-218]}\). Among them, polyaniline (PANI) has gained widespread attention in protecting the metal against corrosion in recent years due to its reasonable anticorrosion performance, high conductivity, and eco-friendly and facile coating preparation\(^\text{[219-222]}\). It is reported that incorporation of Ni(II)tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)-phenoxy)]phthalocyanine (Ni-Pc) into the PANI polymer matrix can further improve the anticorrosion property. This is because the incorporation of Ni-Pc nanoparticles can reduce the porosity and deformation and increase the tortuosity of the PANI matrix\(^\text{[223]}\). In a brief summary, it seems that the treatment of Al current collectors could effectively protect Al from corrosion; however, most of these processes are carried out under mild laboratory conditions, and more attention is suggested to be paid to preparing the treated Al under relevant practical conditions. In addition, the cost of treating Al on a large scale is another concern.
CONCLUSION AND PERSPECTIVES

Al foils with high electronic conductivity, outstanding chemical stability, and good cost-effectiveness have been considered as dominative current collectors for cathode materials in lithium batteries. Yet, the corrosion and anodic dissolution of Al current collectors normally lead to delamination of cathodes, increasement of internal resistance, and catalysis of electrolyte decomposition, thus causing premature failure of lithium batteries. In addition, if the Al corrosion occurs at a low voltage (e.g., 3.8 V of LiTFSI-based electrolytes), it will significantly comprise energy density of lithium batteries. As summarized in this review, although tremendous efforts have been devoted to the optimization of electrolytes and treatment of Al current collectors to enhance their stability, substantial room remains for the improvement of the cycle life and safety of batteries and the reduction of the overall cost in the viewpoint of practical applications.

(1) Electrolytes, as the direct contact and environment of Al current collectors, have a significant impact on performance of lithium batteries. Therefore, tuning and designing novel electrolytes could be a facile way to alleviate Al corrosion. The nature of liquid electrolyte solutions is mainly determined by two factors: Li salts and solvents. This implies that the search for electrolytes to inhibit Al corrosion requires fundamental innovation in the case of novel lithium salts and electrolyte solvents. Based on a careful review of the literature results in this work and our understanding of electrolytes, we tentatively suggest that the key principles of designing novel salts and solvents to inhibit corrosion lie in that the newly proposed salts and solvents could either form passivation layers on Al current collectors or inhibit $\text{Al}^{3+}$ dissolution. In addition, to improve the safety of liquid electrolyte-based lithium batteries, the development of solid PEs is certainly of supreme importance; however, much more attention should be paid to building highly conductive electrolytes with high ionic conductivity and excellent Al passivating properties.

(2) Advanced characterizations, including \textit{in situ} and \textit{ex situ} techniques, are highly desirable for an in-depth study and to further clarify the corrosion mechanisms of Al corrosion. These kinds of characterizations can be carried out in combination with multi-scale modeling simulations to provide atomistic insights.

(3) From the viewpoint of practical applications, the evaluation of the Al corrosion strategies is suggested to be undertaken in practical scenarios rather than in mild laboratory conditions since external temperature and mechanical stress are important aspects in practical applications.

DECLARATIONS

Authors’ contributions
Conceptualization, methodology, writing - original draft: Qiao L
Writing - review and editing, figures set up: Han C
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Supervision, writing - review and editing: Cui G

Availability of data and materials
Not applicable.

Financial support and sponsorship
This work was supported by the National Natural Science Foundation of China (Grants 22102206, 21901248, and U22A20440), Natural Science Foundation of Shandong Province (Grants ZR2021QB030 and 2023HWYQ-104), the Strategic Priority Research Program of Chinese Academy of Sciences (Grant XDA22010600), Key-Area Research and Development Program of Guangdong Province (Grant 2020B090919005), and the Taishan Scholars Program. L. Q. gratefully acknowledges further support from
Shandong Energy Institute (Grant E2553F01) and the Natural Science Foundation of Qingdao City (Grant 23-2-1-22-zyyd-jch).

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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