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Review

Alkali-Metal Anodes: From Lab to Market

Jingwei Xiang,[1,6] Luyi Yang,[2,6] Lixia Yuan,[1,*] Kai Yuan,[1] Yao Zhang,[3] Youyuan Huang,[4] Jian Lin,[5] Feng Pan,[2,*] and Yunhui Huang[1,*]

Alkali-metal batteries (AMBs) are one of the most promising candidates for next-generation high-energy battery systems. However, dendrite growth and serious safety implications limit the commercialization of AMBs. After years of development, the process of bringing alkali-metal anodes from lab to market is still full of tremendous challenges in terms of safety and cycle life. In this review, we divide the commercialization process of alkali-metal anodes into three stages: the first stage is fundamental researches on alkali-metal anodes, the second stage is the application of alkali-metal anodes in high-energy-density battery systems, and the third stage is satisfying the needs of industrialization. We mainly focus on the second and third stages and attempt to establish a relationship between academia and industry in this field. Finally, we give several perspectives on opportunities and challenges in the future development of AMBs for practical applications.

Context & Scale

With an ever-increasing demand for advanced energy storage, the traditional lithium-ion batteries (LIBs), due to their limited energy density, cannot satisfy the key market, especially for the expanding market of electric vehicles. Therefore, it is imperative to discover new advanced materials with high-energy-density battery system. Among all the possible anode materials for rechargeable batteries, alkali-metal batteries (AMBs) are regarded as the most promising candidates due to their high specific capacity and low redox potential. However, poor cycling performance and serious safety implications caused by dendrite growth have limited the commercialization of AMBs. In this review, recent progress in fundamental researches on alkali-metal anodes is highlighted. We attempt to explore the application of AMBs in specific battery systems and connect academia with industry in this field. Finally, we present perspectives on current challenges and future opportunities for the commercial development of AMBs.

Introduction

With an ever-increasing demand for advanced energy storage, lithium-ion batteries (LIBs), which are used to occupy an important place in this area during the past decades, could not satisfy the key market needs even when fully developed (theoretical energy density *390 Wh kg^{-1}), especially for the rapidly expanding market of electric vehicles.[1–3] Now, the mainstream electric vehicles loaded with LIBs can only be driven less than 500 km with a single charge, which is closely related to the limited capacity of commercial LIBs (*250 Wh kg^{-1}). Therefore, it is imperative to discover new advanced materials with high-energy-density battery system. Due to the high energy densities (Li: 3,860 mAh g^{-1}; Na: 1,166 mAh g^{-1}; K: 685 mAh g^{-1}) and low redox potentials (Li: -3.04 V, Na: -2.71 V, K: -2.93 V versus normal hydrogen electrode), alkali metals (Li, Na, K) have stood out as the anode materials from the competition.[3,4] Among various possible options, alkali-metal-sulfur (AM-S) batteries and alkali-metal-oxygen (AM-O_2) batteries, which are two alkali-metal-based energy storage systems, have been widely accepted as the promising next-generation batteries to replace LIBs, as they have the potential of achieving an energy density of 500 Wh kg^{-1}.[5,6]

However, the road to commercialization of rechargeable batteries based on alkali-metal anodes is full of tremendous challenges in terms of safety and cycle life. Since Whittingham pioneered the first viable Li secondary batteries at Exxon, several companies have tried to commercialize rechargeable Li-metal batteries.[7–9] Unfortunately, after a few commercial trials by Moli Energy and Mitsui, the safety issues of Li-metal batteries remained unresolved, resulting in the halt of the commercialization of Li-metal batteries.[1,10] Similar to the Li-metal anode, Na- and K-metal anodes also face the major challenges of poor safety and cyclability. There are three main obstacles for the application of alkali-metal anodes: (1) the naturally non-uniform deposition of alkali-metal ions that leads to uncontrollable dendritic growth. During repeated deposition and dissolution processes, the dendrites will continue to grow and eventually penetrate through the separator, resulting in battery short circuit and

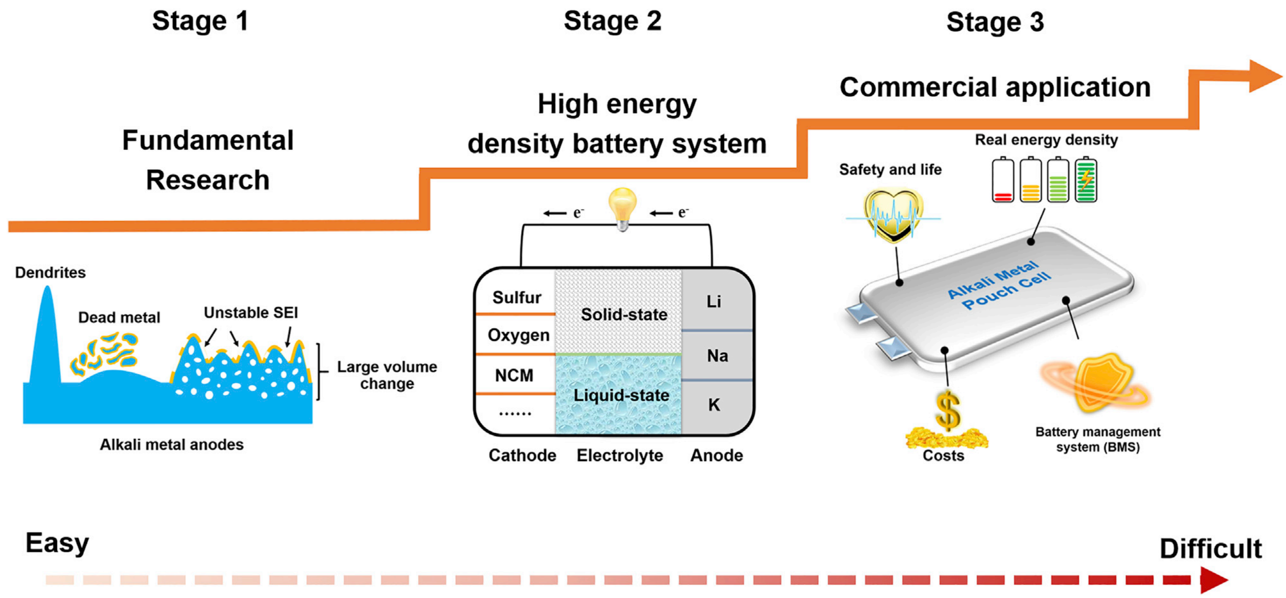

Figure 1. The Trilogy of Alkali-Metal Anodes: From Lab to Market

thermal runaway, which impose a risk of explosion; (2) low Coulombic efficiency (CE) caused by the continuous consumption of alkali metal and electrolyte. Due to the high reactivity between alkali metals and conventional electrolytes, once the alkali metal is in contact with organic electrolytes, irreversible reactions occur and a thin layer of solid electrolyte interphase (SEI) will be generated on the alkali-metal surface. However, the formed passivation film is generally not robust enough to withstand the morphology change during the alkali-metal-ion plating and stripping processes. Therefore, the alkali metal and the electrolyte will be consumed continuously during cycling, leading to capacity fading and low CE. Even worse, some large dendrites could easily fracture and detach from the current collector. These electrochemically inactive dendrites called "dead alkali metal" further decrease the CE; (3) large volume expansion of alkali-metal anodes during repeated deposition and dissolution, especially under high capacity utilization and high current densities, which would cause more serious corrosion of the bulk alkali-metal anodes or even anode pulverization.[11,12] In recent years, many researches have been carried out to seek breakthroughs in this field. Strategies such as electrolyte modification, anode structuring, and buffer layer and current manipulation have greatly improved the rechargeability of the alkali-metal anodes under lab conditions.[13,14] However, owing to different working and testing conditions, more efforts are still needed in extending such successful experience in protecting alkali-metal anodes from labs to commercial applications.

In this review, we divide the commercialization process of alkali-metal anodes into three stages (schematized in Figure 1): the first stage is fundamental researches on alkali-metal anodes; the second stage is the application of alkali-metal anodes in specific battery systems such as AM-S, AM-O_2, and solid-state electrolytes (SSEs); the third stage is to satisfy the needs of industrialization such as the requirements for safety, costs, and real energy density. Since the first stage has already been discussed in detail by some excellent reviews in recent years,[12,14] this review mainly focuses on the second and third stages. Based on the overview of recent progress on alkali metals, we attempt to explore the application of alkali-metal

[1] State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

[2] School of Advanced Materials, Peking University, Shenzhen Graduate School, Shenzhen 518055, China

[3] Sunwoda Electric Vehicle Battery Co., Ltd., Shenzhen 518106, China

[4] BTR New Energy Materials Inc., Shenzhen 518107, China

[5] R&D Institute, Shenzhen BAK Power Battery Co., Ltd., Shenzhen 518119, China

[6] These authors contributed equally

*Correspondence: yuanlixia@hust.edu.cn (L.Y.), panfeng@pkusz.edu.cn (F.P.), huangyh@hust.edu.cn (Y.H.)

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anodes in specific battery systems and connect academia with industry in this field, hoping to provide suggestions for future development in alkali-metal anodes.

Fundamental Researches on Alkali-Metal Anodes

Dendritic growth is a critical issue for safe rechargeable alkali-metal batteries (AMBs). Since the Li dendritic growth was first directly observed in the 1980s, great efforts have been made in trying to realize the dendrite-free alkali-metal anodes. However, influenced by many factors, dendritic growth is a very complicated process. Although some models have been gradually put forward and related theories proposed, the mechanism of nucleation and growth of dendrites is still not fully understood. In addition, low CE, unstable SEI, and large volume expansion of alkali-metal anodes during cycling have also limited their commercial development. Fortunately, aiming at resolving these issues, an increasing number of scientists have been concentrating on the protection of alkali-metal anodes and intensive progress has been achieved in this field. As shown in Figure 2, the corresponding strategies can be divided into four types:

Electrolyte Optimization

The chemical nature of the electrolyte has great influence on the dendrite growth and the stability of alkali-metal anodes. For non-aqueous liquid electrolytes, adopting electrolyte additives is an effective way of realizing dendrite-free deposition (Figure 2A).[15] Additives such as fluoroethylene carbonate (FEC),[23] vinylene carbonate (VC),[24] lithium bis(oxalate)borate (LiBOB),[25] $LiNO_3$,[26] and potassium bis(fluorosulfonyl)imide (KFSI)[27] can greatly improve the stability of alkali-metal anode by promoting the formation of a compact and stable SEI film. In addition, it is also found that a higher content of certain inorganic species (e.g., LiF and NaF) in the SEI layer can greatly improve the stability of SEI.[23,28] Recently, the high-concentrated electrolyte (usually >3 M) as an effective strategy to improve the stability of alkali-metal anodes has also been reported by many researchers.[13] The origin of the improved performance of highly concentrated electrolytes can be traced to reductive decomposition reactions that predominantly occur in the anions, leading to better stability of the solvent (Figure 2B).[16] Consequently, anion-derived SEI layers are formed on the surface of metal anodes, which are found to be denser and more stable than solvent-derived ones. In addition, for Li metal, the less free solvent content could not only reduce the dissolution of SEI compositions, resulting in a more stable SEI, but also shift the equilibrium potential of Li/Li^+ upward by around 0.2–0.3 V according to the Nernst equation.[29] Compared with conventional liquid electrolytes, SSEs are also demonstrated as a potential solution for alkali-metal anodes due to their chemical stability and safety features. More details on SSEs will be discussed in Application in Next-Generation Batteries.

Constructing a Stable Interface

The formation of an ideal SEI layer plays a vital role in improving the stability and CE of alkali-metal anodes. Recently, many strategies of creating an artificial SEI layer have been proposed to improve the interfacial stability between alkali-metal anodes and the electrolyte. Among them, polymer coating is a commonly studied approach for its high flexibility. Polymer materials such as poly(dimethylsiloxane) (PDMS),[30] polyacrylic acid (PAA),[31] etc., are proven to be beneficial in regulating the protective layer of alkali-metal anodes. Apart from adopting polymer coating, a wide range of inorganic coating techniques, such as an artificial LiF layer (Figure 2C),[17] a double-layer film of nanodiamond,[32] a layer of carbon fibers,[33] a thin layer of Al_2O_3 via atomic layer deposition (ALD),[34] and a layer of NaBr (Figure 2D),[18] have also been demonstrated as efficient methods to construct a stable interface for their superior

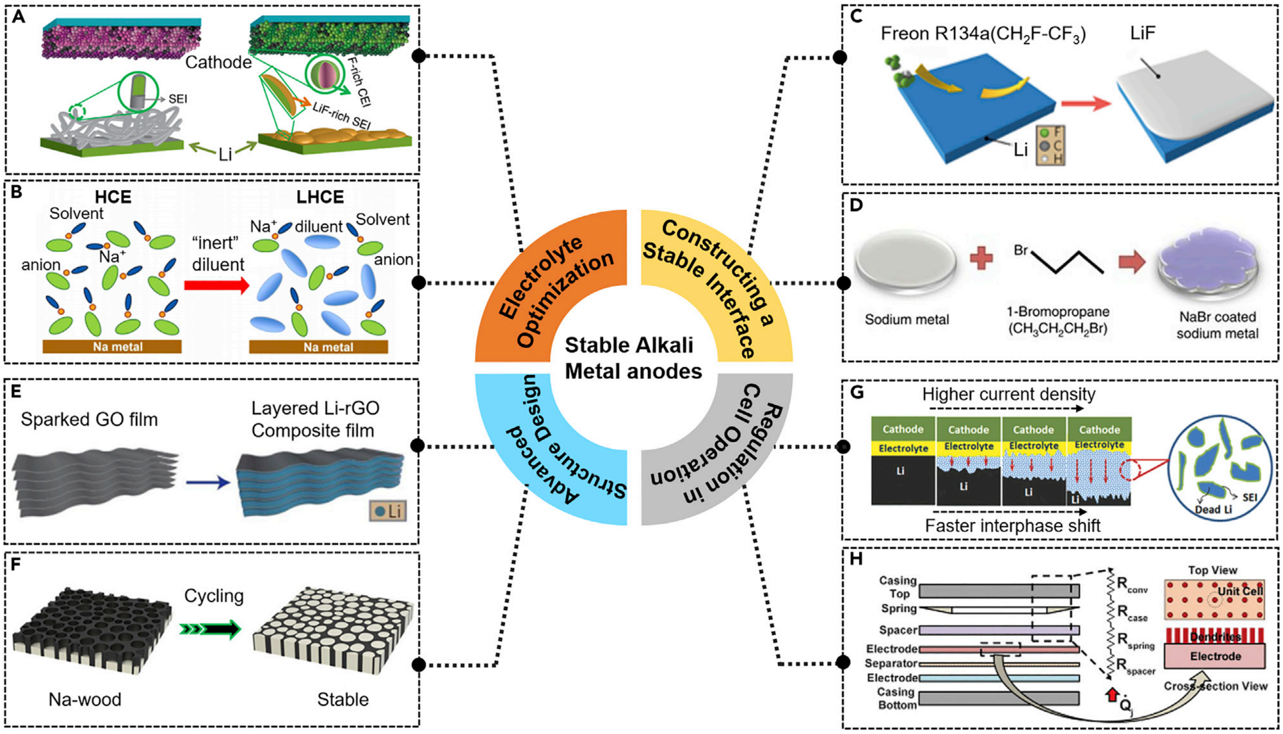

Figure 2. Strategies for Stable Alkali-Metal Anodes

(A) Schematic diagrams of SEI and cathode electrolyte interphase (CEI) formed in traditional carbonate and all-fluorinated electrolytes. Reprinted from Fan et al.,[15] with permission. Copyright 2018, Nature Publishing Group.

(B) Schematic of dilution from a high-concentration electrolyte (HCE) to a localized high-concentration electrolyte (LHCE). Reprinted from Zheng et al.,[16] with permission. Copyright 2018, American Chemical Society.

(C) Schematic diagrams of surface LiF coating and major chemical reactions. Reprinted from Lin et al.,[17] with permission. Copyright 2017, American Chemical Society.

(D) Schematic of the procedure of surface NaBr coating on Na metal. Reprinted from Choudhury and co-workers,[18] with permission. Copyright 2017, Nature Publishing Group.

(E) The synthetic procedure from a GO film to a layered Li-rGO composite. Reprinted from Lin et al.,[19] with permission. Copyright 2016, Nature Publishing Group.

(F) Schematic of encapsulating metallic Na in carbonized wood. Reprinted from Luo et al.,[20] with permission. Copyright 2017, American Chemical Society.

(G) Schematic of the failure mechanism of Li metal at high current densities proposed in the present work. Reprinted from Lu et al.,[21] with permission. Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(H) Illustration of the cross section of a coin cell and the thermal modeling of a single dendrite. According to the resistance diagram, the heat generated can be transferred to the substrate or the surrounding electrolyte. Reprinted from Li et al.,[22] with permission. Copyright 2018, the American Association for the Advancement of Science.

stability and negligible solubility in commonly used electrolytes. It can be learned that in order to improve the performance of alkali-metal anodes, the artificial SEI should be chemically and electrochemically stable, ionic conductive, pinhole free, and mechanically robust. Similar to the coating layer strategy, separator modification such as polydopamine modification[35] and Janus separators[36] has the same effect in suppressing dendritic growth and stabilizing the interface.

Advanced Structure Design

As a "hostless" electrode, there is a significant percent volume change during alkali-metal ions deposition and dissolution, which aggravates the inhomogeneous alkali-metal ion stripping and deposition and results in the pulverization of alkali-metal anode. Therefore, adopting a proper matrix for alkali-metal ions deposition and dissolution has become a very promising strategy for pursuing homogeneous electrochemical stripping and deposition on alkali-metal anodes and suppressing dendrite growth. For instance, employing a 3D conductive framework such as 3D Cu foil,[37] graphene-based material,[38] and carbon nanofibers[39,40] as the host not only effectively decreases current density but also buffers volume change. Compared to a conductive matrix, matrices with surface functional modification have also been developed to realize a dendrite-free morphology by distributing the alkali-metal ions on the surface of the anodes. Similar strategies such as rGo-based material (Figure 2E),[19] 3D glass fiber cloths with functional groups[41] and functional carbon matrices (Figure 2F)[20,42,43] are employed to regulate the nucleation sites of alkali-metal deposition and uniform ion deposition by chemical interactions. Although many outstanding results in dendrite suppression have been demonstrated, the major drawback of this method needs to be eliminated: higher surface area means more degradation reaction sites, indicating a faster consumption of the electrolyte. Therefore, in the future, more attention should be paid to improving the CE and developing facile and effective methods for mass production of these matrices.

Regulation in Cell Operating Conditions

Except the strategies mentioned above, it is widely accepted that the cell operation patterns also play a vital role in the alkali-metal ion depositing behavior such as the current densities, depth of discharge (DOD) of AMBs and intermittent plating. For example, it has been demonstrated that the Li nucleation size, shape, and areal density are dependent on the current density, which is consistent with classical nucleation and growth theory.[44] Under limited current densities or DOD of AMBs, no obvious Li dendrite growth can be observed and a satisfactory cycling performance can be achieved (Figure 2G).[21,45] Recently, a self-heating-induced healing mechanism of Li dendrite has also been proposed (Figure 2H).[22] The current research in this field mainly focuses on the Li-metal anode, and this idea can be extended to the protection of Na and K anodes in the future. Moreover, this strategy is economically attractive since it does not require complicated material design and synthesis. Nonetheless, these strategies may not be suitable for certain application scenarios such as fast-charging and high-load systems, which require high power output. Therefore, great improvements are required before these protocols can practically meet the demands of charging and discharging of real batteries.

Application in Next-Generation Batteries

Alkali-metal anodes are perceived as ideal candidates for the next-generation batteries as they are a perfect match for the high specific capacity of S and O_2 cathodes. In addition, the good safety properties of solid-state batteries (SSBs) also bring new opportunities for the application of alkali-metal anodes.

Solid-State Li-, Na-, and K-Metal Batteries

In recent years, SSBs have attracted broad attention. Compared with conventional liquid electrolytes, SSEs are generally non-flammable, demonstrating excellent safety features. Moreover, many SSEs exhibit high shear moduli, which physically prevents the propagation of metal dendrite. Therefore, they have been widely studied as electrolyte candidates for metal-anode batteries.

Challenges for Solid-State Li-Metal Batteries. It is believed that the "Achilles' heel" for the practical application of solid-state SSLIBs is not obtaining SSEs with high ionic conductivity but rather is the facilitation of a stable electrolyte/electrode interface.[46] In order to achieve a stable Li/SSE interface, two urgent issues need to be addressed: chemical instability and poor interfacial contact.

Unstable SEI between SSE and Li Metal. In terms of composition, SSEs can be classified into solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs), and composite solid electrolytes (CSEs). Similar to liquid electrolytes, SSEs tend to be reduced by Li, forming an SEI layer. Peled and co-workers[46] and Brandell and co-workers[47] studied the SEI layer formed between Li and SPEs and found that the species produced at the interface are similar to those in liquid electrolytes, indicative of similar reaction routes for SEI formation. Interestingly, as the most commonly investigated SPE, polyethylene oxide (PEO) has a molecular structure that resembles those of ether-based liquid electrolytes (e.g., dimethoxy ethane [DME], diglyme [DEGDME], and tetraglyme [TEGDME]). As mentioned above, ether-based liquid electrolytes exhibit higher stability with Li metal, which might explain why SPEs commonly exhibit even better compatibility with Li metal than conventional liquid electrolytes after long-term Li plating and stripping processes.[48,49]

However, the use of SPEs is limited by their low upper electrochemical window, low room-temperature (RT) conductivity, and low shear moduli. Therefore, solid-state ceramic or glass electrolytes have been widely investigated in recent years as alternatives to polymer electrolytes.[50] Despite the commonly accepted conclusion from potential sweep experiments that some ISEs maintain outstanding stability with Li metal, decomposition reactions have been observed.[51,52] As shown in Figure 3A, Mo and co-workers performed a computational study on the interface stability between ISEs and Li metal, and the results show that the apparent good stability of ISEs is only the result of sluggish decomposition kinetics.[53] In addition, the decomposition products depend on the type of solid electrolytes used, some of which might significantly increase the interfacial resistance. For instance, ISEs such as NASICON-type LATP ($Li_{1+x}Al_xTi_{2-x}P_3O_{12}$), LAGP ($Li_{1+x}Al_xGe_{2-x}P_3O_{12}$), and perovskite LLTO ($Li_{3x}La_{2/3-x}TiO_3$) result in high interfacial resistance during cycling. This is due to the fact that cation dopants such as Ti^{4+} and Ge^{4+} are very likely to be reduced by Li metal.[54] Despite exhibiting high ionic conductivity, sulfide ISEs are also reported to be thermodynamically unstable with Li, generating decomposition products such as Li_2S and Li_xP_y and hence creating high interfacial resistance.[55] Compared to SEI layers formed in liquid electrolytes, such SEI layers exhibit much lower ion conductivity,[56] and we believe this type of interfacial deterioration in solid materials can considerably obstruct the Li-ion pathways. Among all oxide ISEs, Garnet-type SSEs like $Li_7La_3Zr_2O_{12}$ (LLZO) exhibit the lowest reduction potential (0.05 V versus Li/Li^+), indicating superior chemical compatibility with Li compared to other candidates.[53] However, despite having a higher shear modulus, garnet-type ISEs generally suffer from more severe short-circuiting issues than liquid electrolytes. Manthiram's team claimed that this could be caused by two reasons: (1) a much larger dendrite curvature due to the confined space and (2) less dendrite consumption by side reactions.[57] In contrast, the chemically unstable interface between LATP and metallic Li leads to a continuously growing SEI that suppresses short-circuiting despite a higher voltage polarization. Recent studies have shown that the electronic conductivity of garnet-type electrolyte is the main cause for the short circuit.[58] Pan and co-workers[59] proposed that by applying an electronic insulating coating layer ($LiAlO_2$) on the grain boundaries of electrolyte particles, the short circuit can be significantly suppressed.

Poor Contact Li/SSE Interface. Due to the nature of solid-solid interfaces, there is poor contact between Li metal and SSEs, especially for ISEs. The lack of contacting sites not only leads to high areal specific resistance (ASR), but also causes inhomogeneous ion flux, which further contributes to protuberance formation on Li metal.[65] Therefore, another important task is to pursue a well-contacted Li/SSE interface.

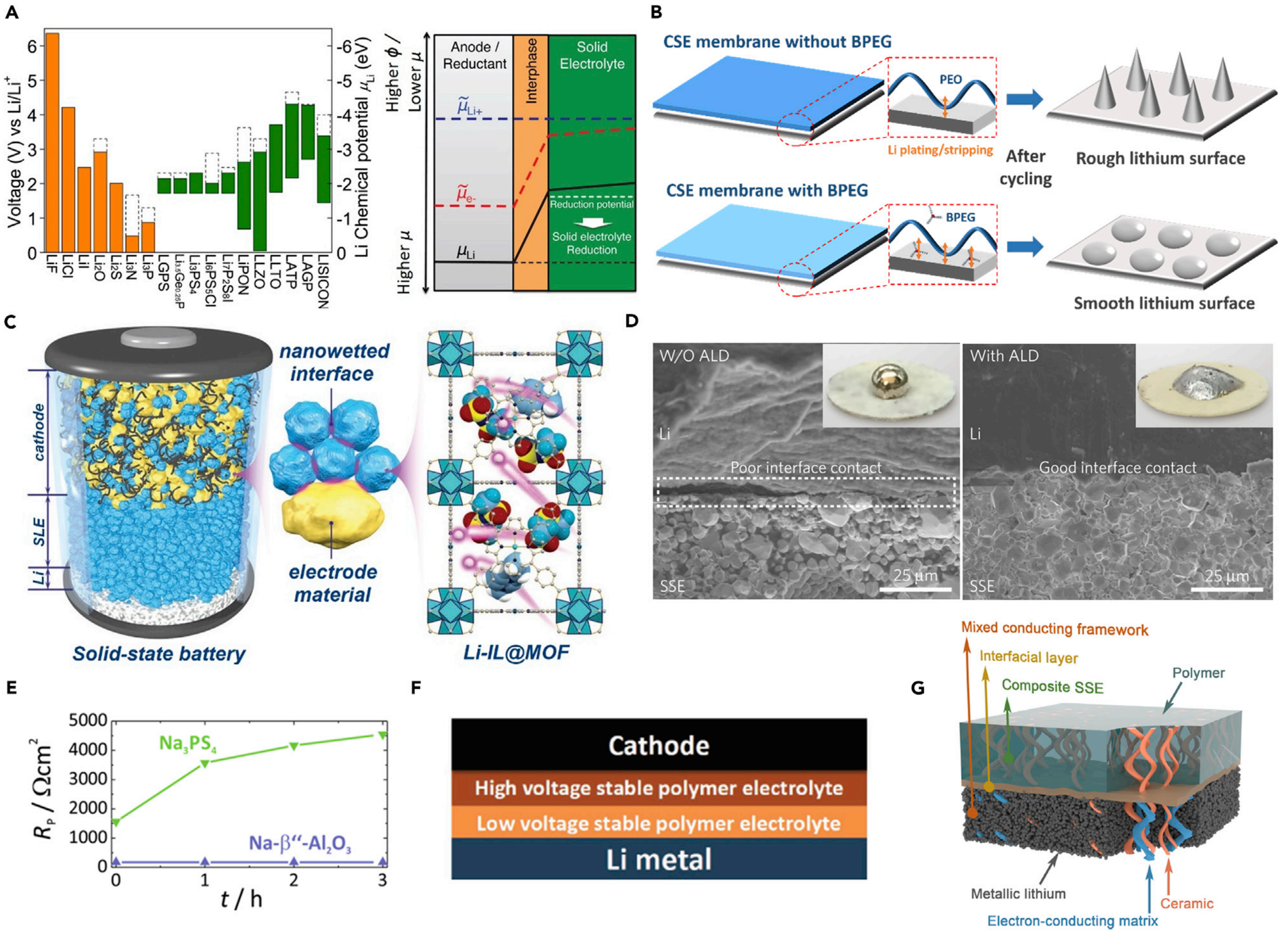

Figure 3. Typical Strategies and Theoretical Illustrations for the Interfacial Engineering in Solid-State Batteries

(A) Electrochemical window of solid electrolyte and other materials. Reprinted from Zhu et al.,[53] with permission. Copyright 2015, American Chemical Society.

(B) Proposed Li plating and stripping processes when Li metal is in contact with different CSE membranes. Reprinted from Yang et al.,[60] with permission. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(C) Schematic illustration for the architecture and nanowetted interfacial mechanism. Reprinted from Wang et al.,[61] with permission. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(D) Scanning electron microscopy (SEM) images of the garnet solid-state electrolyte/Li metal interface. Insets are photos of melted Li metal on top of the garnet surface. Reprinted from Han et al.,[34] with permission. Copyright 2017, Nature Publishing Group.

(E) Obtained changes in the polarization resistance at the Na/SE interface with time. Reprinted from Wenzel et al.,[62] with permission. Copyright 2016, American Chemical Society.

(F) Stacking model of double-layer SPE in an all-solid-state cell. Reprinted from Zhou et al.,[63] with permission. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(G) A solid-state Li-metal anode with the mixed ion- and electron-conducting framework in the electrode materials. Reprinted from Cheng et al.,[64] with permission. Copyright 2018, Elsevier.

Since SPEs generally work at temperatures above their melting point, their contact with Li is comparable with liquid electrolytes in the melted state.[48] In this case, the ASR is low.

For ISEs, their contact with Li anodes is generally very poor without wetting agents or proper treatments. Only mechanically pressing ISEs together with Li anodes will result in high ASR values (usually as high as 10^4 Ω cm^2). It was demonstrated that by increasing adhesive strength at the Li/LLZO interface, the ASR can be significantly reduced.[66] One feasible approach is to apply an annealing process, in which the cell is heated above the melting point of metallic Li (180.5°C). Consequently, the melted lithium can achieve a better wetting effect on the ISE. However, for some ISEs (e.g., LAGP), a high annealing temperature (200°C) could lead to pulverization and thermal runaway.[67] In addition, for LLZO, its microstructures[68] as well as the impurities (e.g., Li_2CO_3) formed on the sample surface could also greatly affect the wettability of Li metal.[69]

Surface Engineering for Solid-State Li Metal Batteries. To address the issues above, various surface engineering techniques can be tailored for different purposes. We will discuss these techniques in terms of the following categories.

In previous discussions, it has been mentioned that electrolyte additives (e.g., FEC) in liquid electrolytes could facilitate a more stable SEI layer on Li-metal anode. Therefore, similar results can be expected for SSEs, especially for SPEs. The use of lithium azide (LiN_3) as an electrolyte additive in PEO has been found to achieve more stable Li plating and stripping behavior than the widely used $LiNO_3$.[70] The effect of anions on lithium salt has also been investigated. It has been found that the addition of FSI^- anions in PEO solid electrolyte can improve Li plating and stripping performance,[71] which is consistent with the results obtained using liquid electrolytes. Therefore, it can be predicted that the additives or other strategies that work well in liquid electrolyte systems can be also applicable to solid-state Li metal batteries.

As mentioned above, SPEs are able to form stable SEI layers with Li metal. Therefore, they are often chosen as artificial buffers at the interface between Li and ISEs. As a result, the rigid contact between Li and SSEs also becomes "softer."[72,73] Goodenough and co-workers used a cross-linked polymer (CPMEA) Li-ion conductor[74] and cross-linked PEO (CPEO)[75] as buffers. The addition of the polymer layer not only improves interfacial contact, but also provides good electrochemical stability against Li. Alternatively, ISEs can also be incorporated into the domain of SPEs. Pan and co-workers investigated CSE-consisting LATP, PEO, and boronized PEG (BPEG).[60] Figure 3B shows that BPEG oligomers not only increase the ionic conductivity of the electrolyte but also facilitate a "soft contacting" interface, which enables homogeneous Li plating and stripping on the Li-metal anode. Compared with solid/solid interfaces, liquid interfaces are more likely to promote homogeneous Li-ion transport. As shown in Figure 3C, a solid-like electrolyte is prepared by impregnating metal-organic frameworks (MOFs) with ionic liquid,[61] creating "nanowetted interfaces" that enable Li symmetric cells to run stably for 1,000 cycles.

Despite their high stability with Li metal, garnet-type electrolytes are generally considered to be "lithiophobic." Therefore, another common approach in surface engineering is to apply a lithiophilic interface between Li-metal anodes and SSEs. Sputtering a thin Au layer on the surface of Ta-substituted LLZO can effectively reduce interfacial resistance and enable stable Li plating and stripping without dendrite formation.[76] It is believed that Li-Au alloying can improve lithiophilic properties and hence enhance surface contact. By coating a thin layer of Al_2O_3 onto a garnet solid electrolyte via ALD technique, Hu's group successfully reduced the interfacial impedance from 1,710 to 1 Ω cm^2.[34] As shown in Figure 3D, improved wettability of Li metal can be observed on the modified electrolyte due to the formation of a Li-Al-O interlayer, indicative of a good contact between Li and the solid electrolyte. Besides Al_2O_3, they also experimented with different lithiophilic coating layers such as Al[77] and Si[78] to obtain good contact between metallic Li and garnet electrolytes. However, the methods above have only been used in garnet-type electrolytes, so their suitability in other SSE systems needs to be tested. Aside from lithiophilic properties, internal pressure can also play a critical part in interfacial resistance. It has been reported that a pressurized interface can lead to a dramatic drop in R_{int} between Li and LLZO solid electrolytes.[66] Recently, Janek and co-workers reported that vacancy accumulation near the interface leads to contact loss between Li and LLZO when cycled at relatively high current densities. Applying a high pressure causes the Li anode to undergo plastic deformation, thereby suppressing pore formation.[79]

Solid-State Na- and K-Metal Batteries. As discussed before, one fatal issue for Na- and K-metal anodes is the instability of the SEI films formed in liquid electrolytes. Moreover, Na- and K-metal anodes exhibit even higher chemical reactivity toward electrolytes. Therefore, SSEs' immobility, which prevents continues electrolyte consumption, could provide a potential solution for creating practical Na- and K-metal anodes. However, due to the much larger ion radii of Na^+ (1.02 Å) and K^+ (1.38 Å) than Li^+ (0.76 Å), the quest to find high-performance solid-state ion conductors for them is still an important task for the moment.

Solid-State Na-Metal Batteries. In recent years, an increasing number of ambient-temperature SSEs have been employed in ambient-temperature solid-state sodium-ion batteries (SSSIBs), such as SPEs,[80] NASICON-type electrolytes,[81] and sulfide electrolytes.[82] As in Li-metal anodes, metallic Na can also be wetted effectively by SPEs, resulting in low ASR values as well as stable Na plating and stripping performance over 1,000 h at a current density of 0.1 mA cm^{-2}.[83] With high ionic conductivity,[84] NASICON-type electrolytes have been reported to be able to suppress Na dendrite growth due to a thin but stable SEI layer.[85] However, their poor contact with electrode materials requires additional wetting agents or proper treatment.[86] In comparison, sulfide electrolytes are mechanically more adaptable, enabling good interfacial contact with electrode materials and hence yielding better cycling performance.[82] However, similar to Li-ion-based ones, the continuous decomposition of Na-ion-based sulfides at the Na/SSE interface leads to increasing interfacial resistance.[87] Liang and co-workers proposed a Sb^{5+}-doped superionic conductor (Na_3SbS_4) with excellent stability in air as well as good compatibility with Na metal. The improved performance was attributed to the fact that Sb^{5+} is a soft acid that can combine strongly with the soft base S^{2-}.[88] Aside from these commonly studied solid electrolytes, the stability between Na anode and complex hydride electrolytes has also been investigated recently.[89] Despite its low oxidation potential (3 V versus Na/Na^+), $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$ exhibits excellent Na plating and stripping stability. In addition, as a pioneer SSE for Na batteries, Na-β″-alumina has been successfully used in high-temperature Na-S batteries.[87] Despite low ionic conductivity at RT, Na-β″-alumina shows excellent interfacial stability with Na metal (shown in Figure 3E).[62] Therefore, it can be used as a buffer layer between SSEs and Na anodes.

Based on the above findings, interfacial engineering for solid-state Na-metal batteries should also focus on forming a stable SEI film and building a well-contacted Na/SSE interface. For SPEs, the electrolyte additives that work well in SSLIBs could be also applicable in SSSIBs. However, the higher reactivity of metallic Na than Li should be taken into account. The simulation of the interfacial reactions between Na metal and ISEs using first-principles calculations demonstrates that some binary oxide buffer materials like HfO_2 exhibit higher chemical stability with Na than the commonly used Al_2O_3.[90] These simulations could be further employed to predict the SSEs that have higher interfacial capability with metal anodes. Alternatively, as a simple solution, SSEs with better interfacial stability can be used as buffer layers to modify unstable Na/SSE interfaces.

Solid-State K-Metal Batteries. The investigation of solid-state K-ion batteries (SSPIBs) is still an uncharted area due to the lack of suitable K-ion conductors. However, the quest for solid-state ionic conductors for K ions is much more complicated than Li and Na. The low melting point of K metal does not allow the use of SPEs such as PEO, which has a melting point even higher than that of K metal. In addition, the ion radius of K^+ is even higher than that of Na^+, leading to a large diffusion energy barrier in crystalline structures. Feng and co-workers proposed a SSPIB operating at RT using poly (propylene carbonate) (PPC) as the solid electrolyte, which demonstrated an ionic conductivity of 1.36×10^{-5} S cm^{-1} at 20°C. Yuan et al. reported a SSPIB with high-rate capability using a K-ion superionic conductor ($K_2Fe_4O_7$) with large ion channels.[91] However, the inadequate electrochemical stability of $K_2Fe_4O_7$ leads to severe capacity fading. Recently, a honeycomb-layered tellurate ($K_2Mg_2TeO_6$) was reported as a fast K-ion conductor. However, its electrochemical properties are yet to be investigated.[92] Since most K-ion conductors are ternary or quaternary K and oxygen containing compounds, Eremin et al. carried out a high-throughput search for potential K solid electrolytes.[93] As a result, they have narrowed 374 potential compounds down to fewer than 10 promising compounds and their approach could be further applied to predict ion conductivity in crystalline solids. Although the interface between K metal and SSEs has not been extensively studied yet, some predictions can still be made. For instance, the contact between K metal and SSEs should be better than that of Li or Na since K metal has a lower melting point and rigidity. In addition, owing to the large ionic size of K^+, the ion conducting capability of the SEI formed between SSE and K metal may also become a limiting factor.

In summary, owing to their high chemical stability and safety features, SSEs are considered as a possible solution for AMBs, especially for Na and K metals, which usually deliver unsatisfactory cycling stability and CE in liquid electrolytes. As the most widely studied system, SSLIBs are faced with two major challenges: developing a stable SEI layer and facilitating a well-contacted interface. Despite having a lower oxidation voltage, SPEs generally exhibit much better wetting ability and more stable SEI than ISEs. Recently, a double-layer SPE was applied in a high-voltage SSB and it was found that one side of the SPE could withstand a high oxidation voltage while the other side was stable with a Li-metal anode, as demonstrated in Figure 3F.[63] This strategy can provide useful information for the modification of SSEs. Therefore, using SPEs as a buffer layer between Li and ISE could be a simple but effective method. Alternatively, Zhang and co-workers proposed an SSB with a mixed ion- and electron-conducting framework in the Li-metal anode, as well as dense, flexible electrolyte and interfacial layer (shown in Figure 3G).[64] Compared to SSLIBs and SSSIBs, very little research has been carried out on SSPIBs due to the lack of appropriate solid ion conductors.

Metal Anodes in Alkali-Metal-O_2 Batteries

Li-Metal Anode in Li-O_2 Batteries

With the highest theoretical specific energy among Li battery systems, non-aqueous Li-O_2 batteries or Li-air batteries have received increasing attention in recent years. In a typical Li-O_2 battery, the overall reaction is:

$$2Li + O_2 \leftrightarrow Li_2O_2 \qquad \text{(Equation 1)}$$

The theoretical energy density is as high as 3,450 Wh kg^{-1}.[94,95] Only when coupled with Li-metal anode, can the high energy density of the system be fully realized. Apart from the common issues discussed in previous sections, Li anode in Li-O_2

batteries faces several additional challenges, a major one of which is the choice of the electrolytes. The electrolytes in ether-based solvents like DME, DEGDME, and TEGDME have been extensively studied in Li-O_2 batteries. And other solvents with high donor numbers (DNs) such as DMSO and N, N-dimethylacetamide (DMA) can stabilize $[Li^+(solvent)_n\text{-}O_2^-]$ and enable solution phase reactions, contributing to improving the cycle stability.[96,97] However, those solvents are very unstable toward metallic Li. In addition, contaminants like H_2O and O_2 are easily introduced to the electrolyte during the gas intake process, which may lead to complicated reactions on the Li-metal anode.[98] Therefore, the anode protection is especially needed in such a complicated system.

A simple way of solving these complications is to employ a Li-ion conducting solid-state electrolyte to physically separate the Li electrode and the O_2 electrode.[99] Figure 4A demonstrates an asymmetric cell configuration based on SSEs. The chemical environment at the cathode side can be separated from the anode, downsizing the protection of the Li metal significantly to the interface between Li and SSEs. As for the choice of SSEs, NASICON-type ceramic SSEs such as LATP and LAGP show excellent protection ability for Li anode due to their resistance toward moisture and O_2^- radicals from O_2 reduction.[100,101] However, such designs may lead to complications in manufacturing as well as cause a high cost. Moreover, since high charging overpotentials have greatly limited the application of Li-O_2 batteries, the addition of such blocking layers may further increase the overpotentials. Modified separators also work in a similar way with SSEs. According to the work completed by Choi's group, the Li-metal degradation is effectively retarded by applying a moisture and O_2 impermeable separator (shown in Figure 4B) in the Li-O_2 battery system to inhibit the permeation of unwanted contaminants from the cathode side to the anode.[102]

One unique challenge for Li protection in Li-O_2 batteries is the use of certain unconventional solvents that exhibit even poorer stability with metallic Li. The use of highly concentrated LiTFSI-DMSO electrolyte can greatly improve the stability of metallic Li against DMSO.[106] Similar to other solvents, a larger amount of free DMSO solvent molecules lead to a less stable Li metal. To improve the stability of amide-based electrolytes with Li, Bryantsev et al.[103] and Zhou and co-workers[107] tried to use fluorinated amides as potential alternatives to DMA. As shown in Figure 4C, N, N-dimethyltrifluoroacetamide (DMTFA) demonstrates the best stability with Li anode because of the formation of LiF-rich SEI layer. An artificial SEI layer can also be used to facilitate a stable Li interface. Kim et al. explored the performance of Li_3P as a coating layer on Li metal, and obtained stable Li plating and stripping process at 3 mA cm^{-2}.[108] In addition, the modified Li metal exhibits excellent stability in DMA electrolyte.

For non-aqueous electrolytes, dissolved O_2 contributes to forming stable SEI layers on Li metal.[109] Through proper designs, the ambient chemical environment for Li anodes in Li-O_2 batteries can also be positively utilized. For example, an additive-free Li-O_2 battery is proposed by increasing the concentration of dissolved O_2 to boost the formation of stable SEI layer that mainly consists of Li_2O, Li_2O_2 and LiOH.[110] As a widely investigated additive that can only dissolve in ether-based electrolytes, $LiNO_3$ plays an important role in shielding Li-metal anode in both Li-O_2 batteries and Li-S batteries. The synergistic effect of O_2 and $LiNO_3$ can create a high-quality SEI that enables stable Li plating and stripping with a high CE.[111,112] It is further explained that this synergistic effect is ascribed to the fact that $LiNO_3$ is reduced to $LiNO_2$ by Li first, and then oxidized back to $LiNO_3$ by O_2 to regenerate $LiNO_3$.[113]

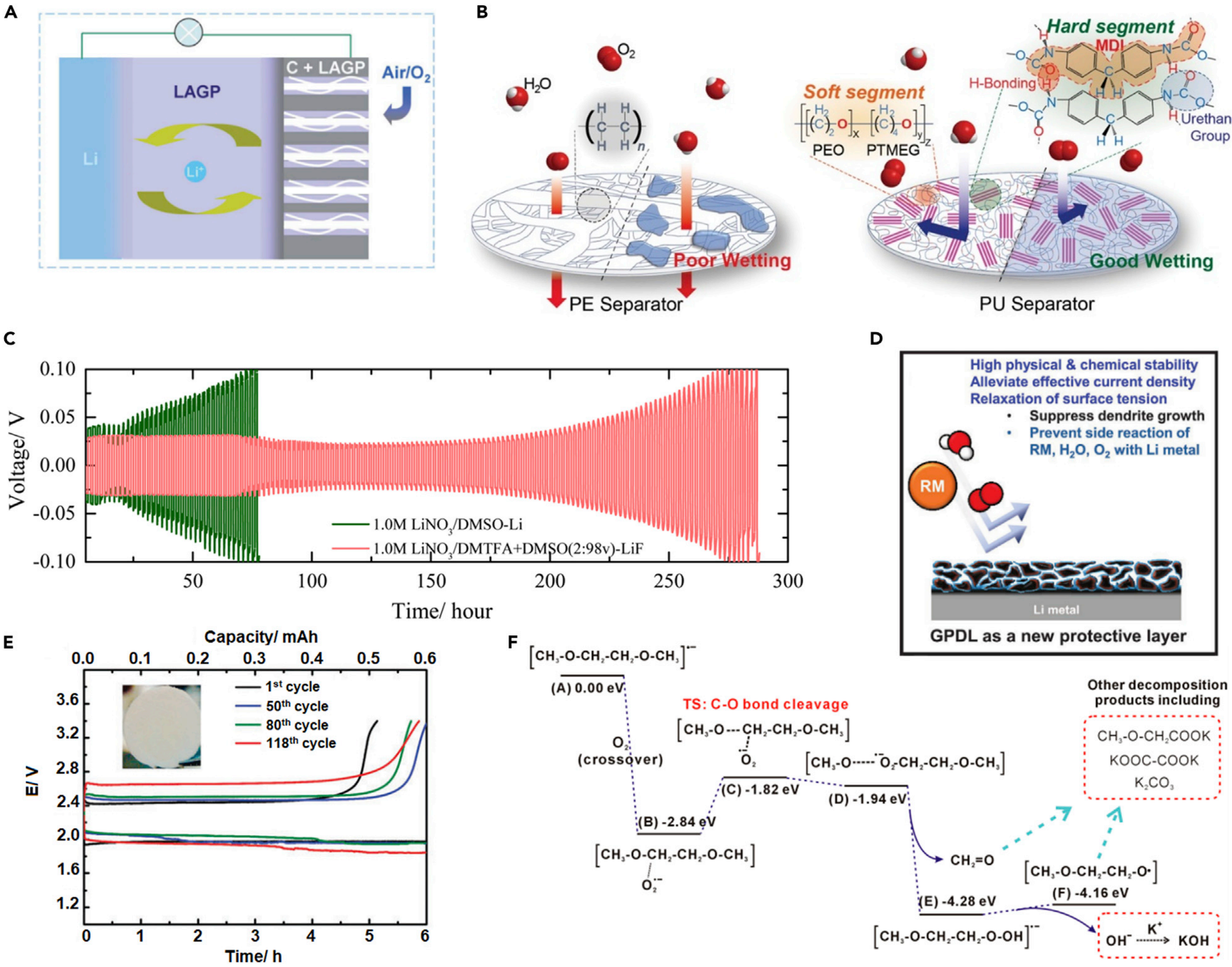

Figure 4. Typical Strategies and Theoretical Illustrations for the Metal Anode Protection in Alkali-Metal-O_2 Batteries

(A) Configuration of an integrated solid-state Li–air battery. Reprinted from Li et al.,[99] with permission. Copyright 2013, the Royal Society of Chemistry.

(B) Schematic illustration on the separator effect on electrolyte wetting and gas and water permeation. Reprinted from Kim et al.,[102] with permission. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(C) Voltage-time plots of Li/Li cell with different electrolytes. Reprinted from Bryantsev et al.,[103] with permission. Copyright 2013, American Chemical Society.

(D) Schematic illustration of the effect of GPDL. Reprinted from Kwak et al.,[35] with permission. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(E) Discharge and charge profiles of Na-O_2 batteries with Nafion-Na^+ membrane. The inset shows the glass fiber separators after cycling. Reprinted from Bi et al.,[104] with permission. Copyright 2015, the Royal Society of Chemistry.

(F) Proposed mechanism of DME decomposition on the anode side with oxygen crossover. Reprinted from Ren et al.,[105] with permission. Copyright 2014, American Chemical Society.

Other than O_2, a small amount of moisture is easily introduced into Li-O_2 batteries. To minimize this, a "water-defendable" protecting layer is desirable on the Li anode, which can be formed by pretreatment with $GeCl_4$.[114] The protected Li exhibits excellent stability in the presence of 10,000 ppm of H_2O.

Another challenge for Li anodes in Li-O_2 batteries lies in the irreversible decomposition of redox mediators (especially for oxygen evolution reaction [OER] mediators) on the surface of metallic Li, which may result in a gradual increase in overpotential.[115] To solve the problem, one effective approach is to coat a protective layer on Li metal to separate Li from the redox mediator. It was demonstrated that a composite protective layer (CPL) comprising Al_2O_3 and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) could enhance the cyclability of Li metal in a Li-O_2 battery.[116] They further tested the chemical stability of 2, 2, 6, 6-tetramethylpiperidinyl-1-oxyl (TEMPO), a redox mediator (RM) for OER.[117] Consequently, the use of CPL-coated Li can significantly improve the reversibility of TEMPO. Sun et al. applied graphene-polydopamine composite layer (GPDL) as a protective film on Li and found that it could also prevent side reaction between RM and Li metal effectively, as demonstrated in Figure 4D.[35]

Na-Metal Anode in Na-O_2 Batteries

In Li-O_2 batteries, each O_2 molecule follows a two-electron reduction to form Li_2O_2. However, in Na-O_2 batteries, the single electron (1 e^-/O_2) process occurs as follows:

$$Na + O_2 \leftrightarrow NaO_2, \qquad \text{(Equation 2)}$$

which results in a theoretical energy density of approximately 1,100 Wh kg^{-1}. Since the main ORR product is NaO_2 despite that the formation potential of Na_2O_2 is very close to that of NaO_2,[118] Na-O_2 batteries are more rechargeable than LIBs that have a much lower overpotential.[119] In most studies for Na-O_2 batteries, researchers generally choose ether electrolytes (e.g., DEGDME and TEGDME) that exhibit relatively higher stability with the Na metal as well as O_2^- species.[120] It has been pointed out by Tarascon and co-workers that the cycling stability of Na-O_2 batteries depend to a large extent on the choice of Na salt anions, different from those using special solvents with a high DNs that exhibit low stability with metal anodes.[121] They also found that PF_6^- anion could form the most stable SEI on Na in DME. Consequently, many approaches discussed in Fundamental Researches on Alkali-Metal Anodes, such as employing polymer-based interlayer,[122] artificial SEI,[123] and TiO_2 sandwiched separator, are expected to suppress dendrite formation or improve the CE in Na-O_2 batteries.[124]

It is noteworthy that the parasitic reactions between the anode and O_2 (or even H_2O) are also expected to be more severe in Na-O_2 batteries due to the high reactivity of metallic Na. As the reduction product of O_2, the crossover of O_2^- to Na anode could lead to low CE.[125] Therefore, additional steps should be taken to minimize such an implication. For instance, the use of solid-state Na-ion conductor is a feasible solution to protect the Na anode from soluble species at the cathode side. Alternatively, an ion-selective membrane (Nafion-Na) is also an option. As previously reported, the Na dendrite as well as the O_2 crossover could be successfully suppressed for improved cyclability due to the formation of a Na salt-derived SEI film (see Figure 4E).[104]

K-Metal Anode in K-O_2 Batteries

Owing to the steric repulsion between cations in the crystal packing structure (i.e., K_2O_2),[126] non-aqueous K-O_2 batteries show a one-electron reduction of oxygen, resulting in a theoretical energy density of approximately 935 Wh kg^{-1}.

$$K + O_2 \leftrightarrow KO_2 \qquad \text{(Equation 3)}$$

This pair of redox reaction exhibits an overpotential as low as 50 mV due to the low oxidation energy barrier from KO_2 to O_2, indicating that no extra catalyst or RM is required for this battery system. Therefore, the limiting factor for K-O_2 batteries lies in the stability of K-metal anodes.

The ethereal electrolytes are extensively investigated in K-O_2 batteries for their high stability toward superoxide radical species. However, the pure DME can dissolve K metal to form a blue solution.[127] Therefore, an impermeable SEI layer is necessary to prevent the corrosion. As mentioned above, the degradation reaction between ether-based solvent and K metal can be mitigated by adding KTFSI to form a stable SEI on K anode.[128] However, according to the density functional theory (DFT) calculation results, O_2/O_2^- crossover could promote the parasitic reactions on metallic K (Figure 4F).[105] Therefore, by using a polymeric K-ion selective membrane (Nafion-K^+) as the separator, the battery's cycle life will be improved significantly. Since the investigation on K-ion SSEs is still at an early stage, no successful prototype has been reported for an asymmetric K-O_2 battery where the K-metal anode can be completely separated from the catholyte.

In addition, according to previous discussions, FSI^- anion is considered an ideal anion for AMBs because it enables highly reversible, dendrite-free plating as well as the formation of stable MF-rich (M = Li, Na, and K) SEI layers on the anode. However, in a metal-O_2 battery, its weak S-F bond makes it susceptible to the attack of superoxide radicals. Wu and co-workers first cycled K metal in KFSI-DME electrolyte to build an artificial SEI on it. Then they assembled the modified anode in a K-O_2 cell with KTFSI salt to attain improved cycling performance.[27]

In summary, owing to the complexity of the electrochemistry (electrolytes, soluble catalysts, and O_2/O_2^- species), the application of metal anode in non-aqueous metal-O_2 batteries is more challenging. For Li-O_2 batteries, the direct contact between the catholyte and Li can be realized through various means of Li anode protection. However, since the O_2 electrode is still questionable for Li-O_2 batteries, a rational chemical and electrochemical engineering for Li anodes should be "tailor-made" for the prototype that can actually work. In contrast, Na-O_2 and K-O_2 batteries exhibit much lower overpotentials, making them promising alternatives to Li-O_2 batteries despite their much lower theoretical energy densities. Unlike in Li-O_2 batteries, the crossover of soluble O_2/O_2^- species in Na-O_2 and K-O_2 batteries may lead to severe corrosion on the metal anode because of the high reactivity of metallic Na and K. This calls for a physical barrier that is not only impermeable for those species but also conductive to Na/K ions. Such barriers can be either a solid-state ion conductor or a dense SEI layer. However, as discussed in Fundamental Researches on Alkali-Metal Anodes, both approaches require extensive investigations in the future.

Metal Anodes in Alkali-Metal-S Batteries

AM-S batteries generally consist of alkali-metal anodes (Li, Na, and K) and sulfur cathodes. Due to the high theoretical energy density, they have attracted worldwide attention for its capability of becoming the next-generation electrochemical devices to meet the long-term requirement for applications such as in the extended-range electric vehicles. However, its mass commercialization is severely restricted because of its poor cathode rechargeability, fast capacity fading, and unstable alkali-metal anode during the long-term cycling. Different from the good many reviews with a focus on sulfur cathode,[129,130] we concentrate on the progress of the alkali-metal anodes in AM-S batteries.

Li-Metal Anode in Li-S Batteries

Among these AM-S batteries, Li-S batteries have been most researched owing to high theoretical energy density of 2,600 Wh kg^{-1}.[4] Compared to conventional Li-ion batteries, the failure mechanism of Li-metal anode in Li-S batteries is much more complicated. In particular, the soluble polysulfide intermediates generated during the cathode process will shuttle to the Li anode where they can be reduced to short-chain polysulfides and stay in the electrolyte or become solid products to participate in the formation of the SEI on the anode. This "shuttle" phenomenon not only leads to fast fading of the cathode capacity but also affects the composition and structure of the SEI and therefore reduces the stability of Li-metal anode. It is found that with highly concentrated (0.5 M) polysulfide species, the Li metal surface will be gradually etched.[131] Thus, in the Li-S batteries, to protect the Li-metal anode, the influence of the sulfur cathode must be taken into consideration, and the electrolyte plays a more important role in Li-metal anode protection.

As previous mentioned, $LiNO_3$ is also the most widely used additive to suppress the Li dendrite and the side reactions in Li-S batteries. The strong oxidizing $LiNO_3$ participates in the reactions between electrolyte and Li metal by being reduced or oxidizing polysulfides to form protective Li_xSO_y/Li_xNO_y species,[132] thus largely remitting the ''shuttle'' effect and boosting a more stable and smoother SEI layer. Furthermore, $LiNO_3$ can increase the ionic conductivity of the electrolyte, enhancing the rate capability of the Li-S battery.[133] It was found that Li metal was better protected, and high CE (99.5%) was achieved by increasing the concentration of $LiNO_3$ to 3 M.[134] And $CsNO_3$, rather than $LiNO_3$, could effectively inhibit the dendrite growth as well owing to the electrostatic repulsion force from Cs^+.[135] Other additives such as LiI,[136] InI_3,[137] and lithium oxalydifluoroborate (LiODFB)[138] have also been used as electrolyte additives for Li-S batteries.

On the other hand, as reduction products of sulfur in Li-S batteries, Li polysulfide species can help to form a relatively stable SEI layer on metallic Li that contains Li_2S_2 and Li_2S composites. Cui's group studied the synergic effect of $LiNO_3$ and Li_2S_8 on forming a uniform SEI layer on Li anode.[139] According to X-ray photoelectron spectroscopy (XPS) studies, it is speculated that $LiNO_3$ first reacts with Li to form a passivation layer. Then Li_2S_2/Li_2S layer can be formed in the upper layer in the SEI, acting as a protective layer (Figure 5A). Zhang's group found that by adding 0.02 M Li_2S_5 and 5 wt % $LiNO_3$ into the electrolyte, a LiF-Li_2S_x rich SEI could be formed, producting a CE of 95% after 233 cycles.[131] However, when the concentration of polysulfide increased to 0.5 M, the *in-situ*-developed SEI no longer remained stable. Furthermore, they demonstrated that an artificial protective layer formed through this method could enable dendrite-free Li plating and stripping (Figure 5B).[140] The modified Li metal can be implanted to both Li-S and Li-ion batteries. The effect of P_2S_5 additive is also investigated in Li-S batteries.[141] It was found that P_2S_5 could enhance the capacity retention by solubilizing the insoluble Li_2S and forming a stable and dense SEI layer on the Li anode. The SEI contains Li_3PS_4, which is a highly conductive Li-ion conductor. In addition, the stable and safe highly concentrated electrolytes have also been proposed for Li-S batteries. It has been demonstrated that a robust LiF-rich SEI film formed in highly concentrated electrolyte can not only block the polysulfides migration but also effectively suppress the dendrite growth.[142]

As mentioned above, one promising strategy to block the polysulfides migration and suppress the Li dendrite growth is the use of solid-state or pseudo-SSEs. So far, polymer electrolytes, especially the gel polymer electrolytes (GPEs) such as pentaerythritol tetraacrylate (PETEA)-based GPE,[144] PVDF-based GPEs,[145] and sandwich-structured GPE[146] have shown their cycling capability in Li-S batteries. In the meantime, solid-state PEO-based polymer electrolytes have also been investigated.[147] Li-S cells with good cycling stability and Li-metal compatibility that use sulfide-based Li-ion conductors including $75Li_2S$-$24P_2S_5$-P_2O_5[148] and Li_6PS_5Cl[149] have also been verified. Other commonly used methods, such as modification with artificial SEI films (e.g., Al_2O_3,[150] Poly(3,4-ethylenedioxythiophene) (PEDOT)-co-PEG,[151] and Li_3N[152]) and electrochemical conditioning,[153] have also shown their compatibility in Li-S system as well as their impacts on the protection of Li-metal anode by forming more stable interfaces between Li and electrolytes.

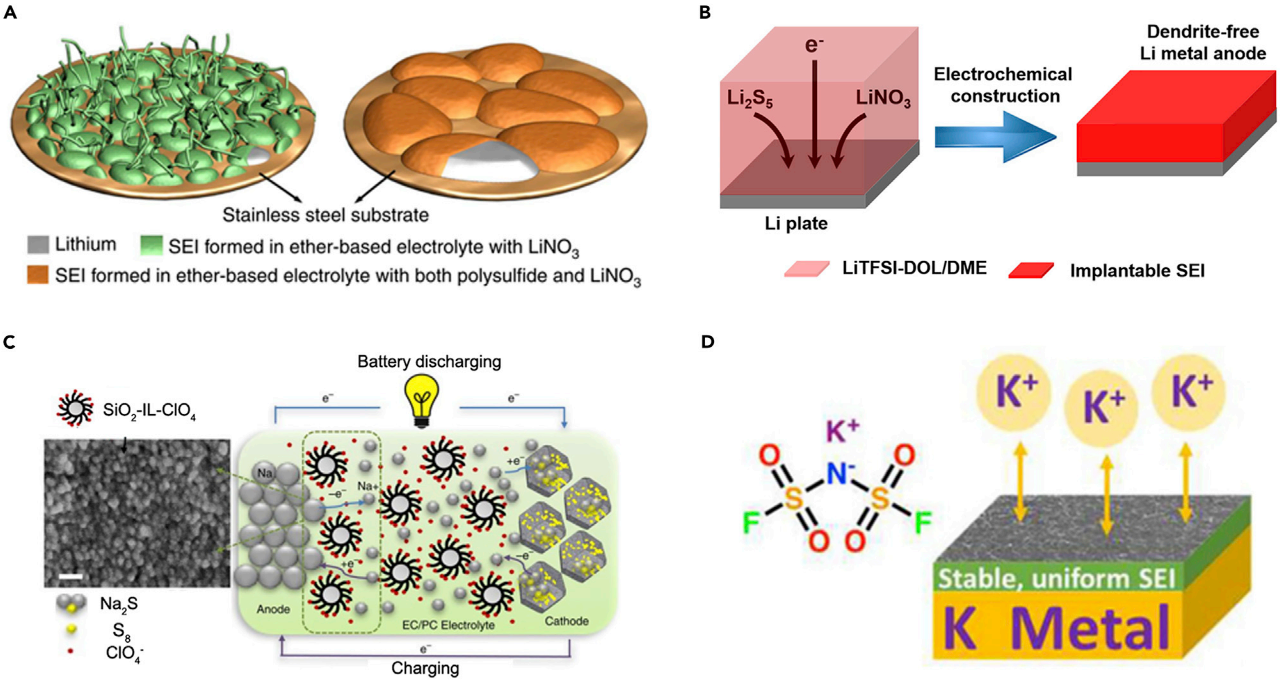

Figure 5. Typical Strategies for Anode Protection in Alkali-Metal-S Batteries

(A) Schematic of the morphologies of Li deposited on the substrate in different electrolytes. Reprinted from Li et al.,[139] with permission. Copyright 2015, Nature Publishing Group.

(B) Schematic of the implantable SEI formed on the Li-metal anode with 0.02 M Li_2S_5 and 5.0 wt % $LiNO_3$ as hybrid additives. Reprinted from Cheng et al.,[140] with permission. Copyright 2017, Elsevier.

(C) Schematic of the Na/S battery using SiO_2-IL-ClO_4 as additives in a carbonate-based electrolyte and the SEM image of Na anode after cycling. Reprinted from Wei et al.,[143] with permission. Copyright 2016, Nature Publishing Group.

(D) Schematic of a robust and uniform SEI film formed in high concentrated KFSI-DME electrolyte. Reprinted from Xiao et al.,[27] with permission. Copyright 2017, American Chemical Society.

Na-Metal Anode in Na-S Batteries

Although investigations on Li-S batteries with high energy density have been going on for years and have achieved remarkable progress, the limited availability of Li on a global scale makes it difficult to meet the long-term demand for the next-generation energy storage. Therefore, in terms of economic and sustainable development, Na-S batteries are regarded as a good candidate for the next-generation electrochemical devices. However, Na-S batteries face similar major challenges with Li-S batteries. The issue of high reactivity of Na metal is even more obvious than Li metal.

Usually working at >300°C, high-temperature (HT) Na-S batteries have been commercially viable for supporting large-scale energy storage.[154] However, the high operating temperature, the potential safety, reliability, and maintenance issues limit the widespread application of HT Na-S systems, such as the mobile and discrete applications. Therefore, researches have been more focused on RT Na-S batteries in recent years to address these issues. However, especially for the Na-metal anode, the operation of RT Na-S batteries also faces many challenges. The polysulfides generated from cathode will shuttle to the reactive Na anode, resulting in drastic differences in SEI composition and serious corrosion. In addition, compared to Li metal, Na with higher instability will lead to dendrite growth and more side reactions between Na and organic electrolyte. Therefore, a more suitable electrolyte is necessary to protect Na-metal anode.

Robust SEI films are also desirable for Na metal protection in Na-S batteries. By adopting a simple electrolyte, $NaPF_6$ in glymes (mono-, di-, and tetraglyme), a uniform inorganic SEI film consisting of Na_2O and NaF is formed on the surface of Na metal.[28] Surprisingly, the SEI thus formed is highly impermeable to electrolyte solvent and can effectively suppress the polysulfides migration and Na dendrite growth, which results in a high reversibility. In addition, ionic liquids have also been used for the Na metal protection in Na-S batteries. Archer et al. chose 1-methyl-3-propylimidazoliumchlorate ionic-liquid-tethered (SiO_2-IL-ClO_4) as an additive in a carbonate-based electrolyte (Figure 5C).[143] The results indicate that the ionic liquids contribute to the formation of a stable and robust SEI film on the Na metal surface, which greatly improves the stability of the interface between Na anode and electrolyte. It is noteworthy that NO_3^- as an effective additive facilitates a stable SEI layer on Li-S batteries. However, the addition of NO_3^- leads to deterioration of Na metal in Na-S batteries.[155] Compared to other traditional strategies, the use of SSEs, which not only blocks the polysulfides migration but also suppresses the Na dendrite growth, prove to be one promising way for RT Na-S batteries to surmount the challenges mentioned above.[156] However, the limited choices for Na-ion SSEs have restricted the development of solid-state Na-S batteries. Therefore, there is still a long way to go for their practical application.

K-Metal Anode in K-S Batteries

As mentioned above, in sulfur-based electrochemistry, K-metal anode also faces similar issues with Li and Na, such as high reactivity, dendrite formation, and the corrosion caused by polysulfide migration. In addition, compared to Li- and Na-metal anodes, K-metal anode is much more reactive toward electrolytes and the SEI formed on K anode is more unstable.[157] Therefore, constructing an ideal SEI film on K-metal anode plays a vital role in the operation of K-S batteries.

However, unlike the extensively studied Li-S or Na-S batteries, only a few researches in K-S batteries have been conducted. The main reason lies in that K-metal anode can only give a capacity of 685 mAh g^{-1}, which is about one-sixth of that of Li.[158] What is worse, the larger K ion limits the formation of K_2S in the cathode, resulting in only partial utilization of its theoretical capacity and the limited cycle life of the cell. Compared to Na-S battery in theoretical voltage though, K-S battery is no match for Na-S or Li-S battery in energy density. Based on the current researches, the interest in K-S battery tends to be more academic, and its advantages in energy storage application over other AM-S systems remain uncertain.

So far, researches have been mainly focusing on the cathode modification of K-S batteries to solve the low utilization of sulfur, and those in K anode are still in infancy. It is well known that K-metal anode is highly overactive toward electrolyte components, leading to its poor stability. Inspired by the previous work,[27] it might be an effective route to employ a highly concentrated electrolyte for improving the stability of K-metal anode by forming a robust and uniform SEI film, contributing to the reversible K-ion deposition and dissolution and suppressing the corrosion caused by polysulfide (Figure 5D). In addition, it is also important to choose suitable solvents and K-salts, which might contribute to the passivation of K-metal anode and thus inhibit the side reactions. Compared to traditional liquid electrolytes, employing SSEs might be a better alternative and much attention should be paid to this area in the future. Admittedly, the stable and dendrite-free K-metal anode is of vital importance for the safe operation of K-S batteries.

In conclusion, due to the low cost and high theoretical capacities, alkali-metal-sulfur batteries as the next-generation energy storage devices have attracted increasing attention. However, the alkali-metal anode protection in sulfur electrochemistry is complicated due to the dissolved LPs, which can be a double-edged sword in the formation of stable SEI films: on the one hand, polysulfides react with metal anode, leading to low CE; on the other hand, this reaction is also found to form a stable SEI films on metal anode. Therefore, seeking for a uniform and robust SEI layer by taking advantages of the "shuttle effect" can be an effective solution to this issue. Alternatively, similar to AM-O_2 batteries, the complicated chemical environment in the liquid electrolyte can be circumvented by Na-SSEs, which have drawn much more attention in recent years. It is worth noting that issues in both metal/SSE and sulfur/SSE interfaces also need to be solved urgently. Though the path for commercialization of AM-S batteries may not be easy, we are convinced that the problems will be solved in a near future.

Commercial Application

To this date, some energy storage systems based on alkali metals (e.g., HT Na-S batteries, ZEBRA batteries, and thin-film Li batteries) have been commercialized in some specific areas. For instance, NGK Insulators, LTD has large installation of MWh sized electric energy storage stations in more than 200 locations worldwide with NAS batteries (HT Na-S batteries), which has achieved an energy storage capacity over 500 MW. Nevertheless, the strict operating conditions, such as high operating temperatures (300°C–350°C), have limited the applications of Na-S batteries in other fields. In addition, thin-film Li batteries with Li-metal anodes have also been commercialized in the fields of wearable devices and micro-electro-mechanical systems for their high energy densities and long cycling lifetime. However, the low capacity (<10 mAh) hinders their large-scale applications. In order to meet the growing market demands as power batteries especially for electric vehicles, it is crucial to develop high-energy AMBs that could work at ambient temperatures. Compared with Na- and K-metal anodes, Li-metal batteries (LMBs) are most likely to be the starting point of the commercialization of AMBs owing to the success of traditional LIBs. In order to achieve this goal, it is of great importance to listen to the voices beyond the academic community. Herein, we have consulted some experts in the Li-ion battery industry for their perspectives and concerns on AMBs.

Practical Evaluation of Battery Performance

Alkali-metal anodes have received increasing attention due to their high specific capacity. Although significant progresses have been made in fundamental researches, the testing conditions reported in most studies are not practical for real batteries. These issues are also mentioned in several researches[159–162] and Liu and co-workers recently developed a prototypical 300 Wh kg^{-1} Li metal pouch cell, which can undergo 200 cycles with 86% capacity retention.[163] As shown in Figure 6, performances of real batteries are greatly affected by factors such as excessive metal anode and electrolyte, low electrode loading, and low charge-discharge rate.

Large Excess of Li and Low Cathode Loading. Currently, most research results are obtained using coin cells. In such cell configurations, a Li foil of 500 μm thick is commonly used, which is equivalent to an areal capacity of 100 mA cm^{-2}. However, the charge and discharge depths in these studies are normally lower than 3% (3 mAh cm^{-2}) per cycle. Under shallow anode plating and stripping processes, the real impact of Li dendrite, Li loss, volume change, and electrolyte consumption cannot be properly examined. In addition, energy density of the battery will be compromised in the presence of large excess Li. Therefore, in order to reflect the energy density and cycle life in practical use, it is recommended that the amount of metal anode should not only be provided, but also carefully controlled to approach

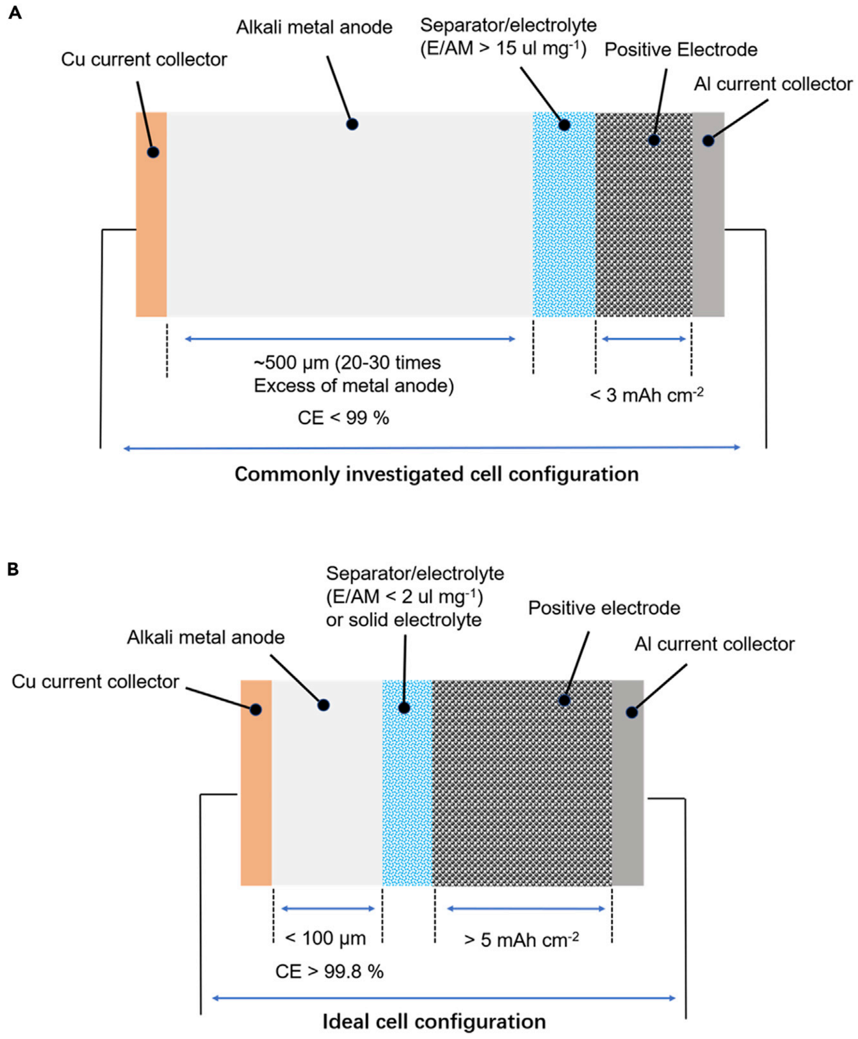

Figure 6. Brief Cell Designs
Commonly investigated (A) and ideal (B) cell configurations.

100% of cathode capacity in order to avoid the compromise in energy density. In this case, a high areal loading of the cathode material (e.g., >20 mg cm^{-2} for $LiCoO_2$) is also required for full-cell studies.

Large Excess of Electrolyte. The use of liquid electrolyte in LMBs remains extremely challenging since the depletion of liquid electrolyte can accelerate dendrite formation and anode pulverization, causing battery failure and even safety hazards. However, similar to Li metal, excessive or even unspecified amounts of electrolyte are widely reported in academic researches, which offers little guidance for other researchers. For instance, the electrolyte to active material (E/AM) ratios in most Li-S battery studies are above 15 µL mg^{-1}, whereas this value in commercial LIBs is approximately 0.3 µL mg^{-1}. Such a large excess of electrolyte not only severely affects the energy density of Li-S batteries but also leads to overestimation of their cycling stability. Therefore, it is strongly recommended the E/AM ratio should be controlled within a reasonable range (e.g., 2 µL mg^{-1}). In addition, electrolyte consumption and overpotential are more severe under lean electrolyte conditions, leading to lower cycle life and capacity fading. Overall, the fair judgment of

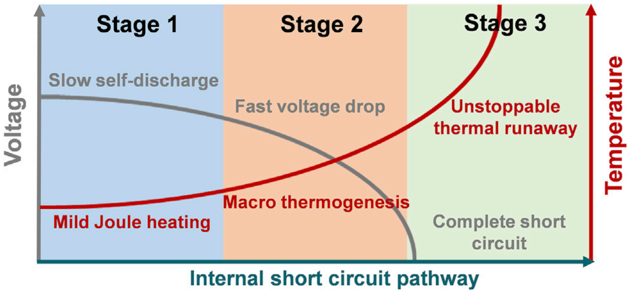

Figure 7. Three Stages of the Internal Short Circuit

LMBs depends on the amount of electrolyte in a large extent, which should be properly controlled and recorded in future researches.

Short Cycle Life. As mentioned above, assuming that 100% of excess Li is used, the CE should reach 99.8% to achieve 500 stable cycles. ($2 \times 0.998^{500} = 0.735$) Despite the great efforts made in improving the low CE in LMBs, a gap still exists between the reported values (generally below 99.5%) and the demands for practical use. Thereafter, future works regarding further improvements of CEs are still required. In this case, solid electrolytes are more promising candidates due to the slow kinetics of side reactions.

High Current Density Performance. The capability of fast charging is an important criterion for electric vehicles (EVs). However, for the time being, it is very difficult for EVs to compete with gasoline automobiles, which only require less than 2 min to refuel (equivalent to charging in 30 C). Therefore, the more practical goal is to reduce the charging time to less than 30 min (2 C). For instance, to achieve 80% of charge, Tesla Model S 85 kWh and BYD e5 450 needs 40 min at most, whereas Geely Emgrand needs only 30 min. Moreover, the new V3 Supercharger that is to be launched by Tesla may further shorten the time needed to 15 min. To achieve fast charging within 30 min, the battery should enable a charging current of 120–240 A, which is very demanding for Li-metal anodes. Therefore, the electrochemical performance of Li-metal anode under high current densities should be included in future researches. This also requires testing the full-cell with a higher areal loading of active materials in the positive electrode.

Safety Concerns

In commercial LIBs, thermal runaway must be prevented under extreme application conditions. Abuse behavior of commercial LIBs is mainly evaluated by mechanical abuse (e.g., pressure and puncture), electrical abuse (e.g., over-charge and internal short circuit), and thermal abuse (e.g., heat impact). Thermal runaway reactions generally undergo the following steps: (1) between 50°C and 90°C, the internal temperature increases and the capacity gradually decreases; (2) between 90°C and 120°C, SEI films start to decompose, releasing gases and heat; (3) between 120°C and 140°C, separators start to shut down, leading to high internal resistance; (4) as temperature continue to increase, separators start to melt and shrink while electrolytes react violently with both electrodes; and (5) separators collapse when the temperature reaches 170°C (this value can be made higher by coating layers), leading to massive internal short circuits and generating immense heat.[164] Under this mechanism, as shown in Figure 7, the process of thermo-induced internal short circuit consists of three stages: (1) self-discharge occurs with slow heat release; (2) macro thermogenesis and accelerated voltage drop can be observed; and (3)

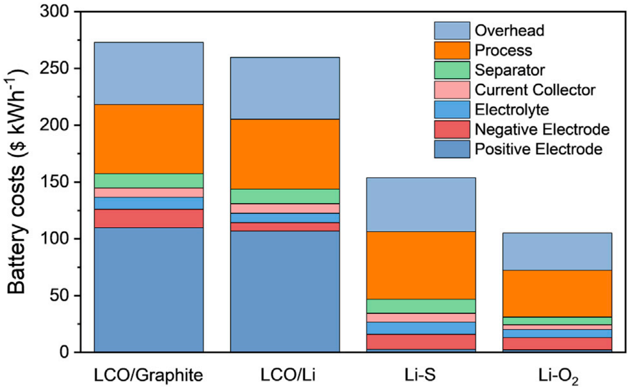

Figure 8. Estimated Cost Breakdown for Different Battery Systems

large-scale short circuit occurs due to separator collapse, followed by unstoppable thermal runaway. By replacing traditional anode materials with alkali-metal anodes, thermal runaways could become more severe due to the high reactivity and dendrite formation. As a cautionary tale, the unsuccessful attempt from Moli Energy in the 1980s has cast a shadow over the public confidence in the safety of LMBs. Therefore, tremendous precautions have to be taken into account before introducing LMBs to the market again. Apart from methods of stabilizing Li-metal anodes as discussed in previous sections, the stability of the electrolyte and the separator are equally important.

Separator Stability. By employing a ceramic (e.g., Al_2O_3 and SiO_2) coating layer, the collapse temperature of polymer-based separators can be effectively improved to 200°C–260°C. In addition, this coating layer is also found to suppress dendrite growth and increase wettability by liquid electrolytes. Ideally, the thickness of the coating layer should also be kept between 2–6 μm and the porosity should be controlled between 40%–50%. Alternatively, employing polymers with higher thermal stability is another approach to mitigate thermal runaway. For instance, with a high decomposition temperature above 600°C, polyimide (PI) separator can remain stable even under 350°C.

Electrolyte Stability. The electrolyte solvents employed in commercial LIBs are carbonates with high flammability (e.g., EC, PC, dimethyl carbonate (DMC), and DEC), which may be another safety hazard. Hence, developing fire-retardant electrolyte solvents is also considered an effective method of improving safety of LMBs. Fire retardants such as phosphorous-based carbonates including trimethyl phosphate (TMP), triethyl phosphate (TEP), and dimethyl methylphosphonate (DMMP) will release P-based radicals upon heat, which can capture flammable radicals (e.g., H· and HO·) and consequently shut off the combustion chain reactions. Alternatively, considering the potential hazards of using liquid electrolytes, we believe that SSEs are more suitable for LMBs in terms of safety.

Cost Control

Other than performance and safety, the overall cost also plays a critical role in the commercialization of LMBs. In recent years, the cost of LIBs has been greatly reduced from 600–900 \$ kWh^{-1} (2010) to below 200 \$ kWh^{-1}. For instance, the cost of 21,700 cylindrical cells has been reduced to 111 \$ kWh^{-1}, which is below the critical point (150 \$ kWh^{-1}) of cost-competitiveness of EVs compared with gasoline vehicles. As shown in Figure 8, Li-metal anode has a lower cost (*36 \$ kAh^{-1}) in

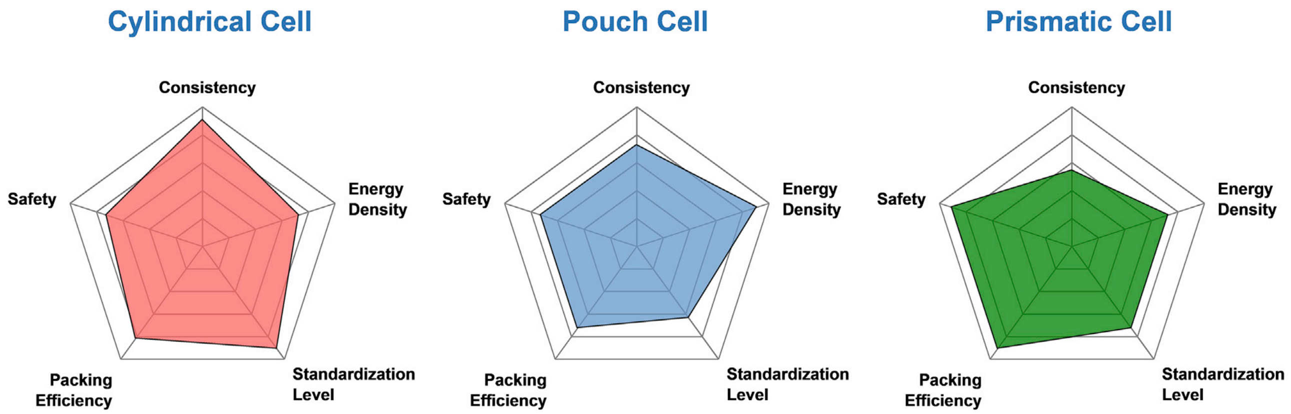

Figure 9. Features of Different Cell Configurations

theory than traditional anode materials (e.g., *70 \$ kAh^{-1} for graphite), which also require additional binder and conductive materials. Therefore, by replacing graphite with Li metal in batteries using transition metal oxides as positive electrode materials, the total cost can be slightly reduced as shown in Figure 8. However, due to the relatively low proportion of negative electrode cost in the total cost, such a small saving might be insufficient for commercialization. Alternatively, the Li metal anode is the perfect candidate for the next-generation battery systems such as Li-S and $Li-O_2$ batteries, which use much cheaper positive electrode materials. Consequently, the commercialization of these battery systems is more economically attractive, as shown in Figure 8.

In addition, in order to address the current issues for Li metal anodes, various modification methods have been reported in academic periodicals. However, most of them are currently impractical for commercialization owing to high costs and the difficulty in scaling up. For instance, garnet-type ceramic solid electrolytes cost as high as *2,000 \$/kg, making them unsuitable for civil uses. Its cost reduction can still be achieved by choosing less expensive materials or ramping up production capability. Herein, we strongly recommend that as an important criterion for evaluating newly developed materials or methods, the commercial feasibility should be briefly stated in research articles.

Other than the material cost, the manufacturing cost should also be taken into account. As will be discussed below, the handling of alkali metals will bring some complications, thus requiring other safety measures. In addition, production lines need also be updated.

Processing Feasibility

In addition, owing to the large volume changes of metallic Li during cycling, the assembling design also becomes more complicated, which may require an update of the production line. There are also trade-offs in the choice of battery configurations, as presented in Figure 9. As a classical cell configuration, cylindrical battery exhibits excellent production efficiency and consistency. Moreover, the robust packaging can withstand large volume changes. Nevertheless, for safety concerns, cylindrical cells also suffer from limited single-cell capacity. Prismatic batteries with aluminum and stainless-steel packaging have been widely adopted in power batteries due to their high packing efficiency. However, such cell configuration has relatively low energy density, which limits its applications in high-performance batteries.

Compared with prismatic batteries with the same volumes, pouch cells with Al-polymer packaging are 10% to 20% lighter. Therefore, pouch cells are desirable for maximizing energy densities. However, their relatively poor consistency and weatherability should be addressed in future studies. For power batteries, another critical factor that should be considered is the packing efficiency. For instance, despite the highest energy density for single cells, the packing efficiency of pouch cells is approximately 60%–65%, lower than cylindrical cells (65%–70%) and prismatic cells (75%–80%). Therefore, pouch cells with energy density of 500 Wh kg^{-1} are required to manufacture a battery pack with energy density of 300 Wh kg^{-1}.

Excess Li metal is required during battery assembly for the process of alkali-metal anodes. It is far more complicated to handle such reactive materials (not to mention Na and K) than traditional graphite anode, which can be directly processed in a dry room. Therefore, it is also a challenge to prepare a thin, dense, and smooth Li-metal anode within an acceptable cost budget. All these factors may also require an entirely new processing protocol and a workspace filled with inert atmosphere since extra safety precautions need to be taken. In addition, stacking and rolling techniques have their strengths: on the one hand, the rolling technique shows better consistency and simplicity; on the other hand, the stack technique promises higher energy density and lower internal resistance.

In summary, although a great deal of exciting news has been reported in recent years regarding the potential commercialization of LMBs, where high energy densities (400–500 Wh kg^{-1}) have been achieved. Concerns about cycle life, safety, and cost are not fully addressed. In reality, there are still many unsolved issues regarding the use of liquid electrolyte in LMBs. Therefore, we claim that from the view of cycle life and safety, the use of solid electrolytes is a more feasible approach to eventually realize LMBs. However, cost reduction and battery engineering for SSBs are much more challenging, which may require novel approaches. In the long term, researchers should continue to develop new solid electrolytes with desirable properties (e.g., high ionic conductivity, chemical/electrochemical stability, low costs, and ease of processing). Meanwhile, more feasible approaches (e.g., the use of suitable quasi-solid electrolytes) should be also considered as reasonable trade-offs.

Conclusion and Outlook

The investigation of alkali-metal anodes (Li, Na, and K) is being extensively carried out owing to their high energy density. The process of realizing AMBs consists of three steps: fundamental researches, applications in high-energy-density battery systems, and commercialization. Herein, first by revisiting fundamental researches on Li-, Na-, and K-metal anodes, we hope to extend our knowledge frontier to practical systems (AM-O_2, AM-S, and SSBs) and eventually toward the commercialization of AMBs. The challenges and perspectives of each step have been summarized as below:

General Protection Strategies for Alkali-Metal Anodes

Fundamental researches on alkali-metal anodes can be categorized according to their different purposes as following: (1) stable electrolyte/electrode interfaces have been designed to achieve high CE and cycle stability (e.g., electrolyte additives, localized super-concentrated electrolytes, and artificial SEI layer). In the future, the reliability of these strategies should be further investigated under high current densities (5 mA cm^{-2}) and prolonged cycles. (2) Structured (e.g., 3D) anode frameworks have been employed as hosts, which not only increase surface area for metal plating and stripping, but also buffer volume change. Although many excellent results on dendrite suppression have been demonstrated, the major drawback of this method needs to be improved since higher surface area means more degradation reaction sites, suggesting a faster consumption of the electrolyte. (3) It is widely accepted that the cell operation pattern also plays a vital role in the alkali-metal ion depositing behavior such as current densities, DOD of AMBs, and intermittent plating. Moreover, this strategy is economically attractive since it does not require complicated material design and synthesis. Nonetheless, these strategies may not be suitable for certain application situations that require high power output, such as fast-charging and high-load systems.

Metal Anodes in SSBs

SSEs have shown potential in AMBs due to their excellent chemical stability and safety. For ISEs, their poor interfacial properties lead to very low operating current density (1 mA cm^{-2}). Therefore, tremendous efforts have been made in facilitating a well-contacted interface with a stable SEI. However, their electrochemical performance at high current is still unsatisfactory. In addition, the cost of ISEs does not make commercialization possible. These factors have limited their practical applications and should be addressed in future studies. Although SPEs generally exhibit low upper decomposition voltage and low shear moduli, they can perfectly wet the metal anode to form a very stable SEI. One promising approach is to design CSEs, which may ideally inherit the advantages of ISEs and SPEs. Though an ideal system has not yet been developed, various cell designs based on composite electrodes and electrolytes have been proposed recently, where a major challenge emerges: how to integrate the cell into a compact and efficient system in both chemistry and engineering?

Oxygen and Sulfur Batteries

Alkali-metal anodes match perfectly with O_2 and S based cathodes in terms of capacities. Apart from the universal methods mentioned above, additional strategies can be adopted for protecting metal anodes for next-generation battery systems such as AM-O_2 and AM-S batteries. In AM-O_2 batteries, the unusual solvents for electrolytes (like DMSO and DMA) and the crossover of soluble O_2-related species should be taken into consideration. It is crucial to either physically separate the anode and the cathode (e.g., using SSEs) or to create a buffer layer for the anode protection, especially for the highly reactive Na- and K-metal anodes that are severely affected by electrolyte contaminates. As for sulfur batteries, it has been widely reported that the shuttling of PS species plays a critical role in SEI formation on Li-metal anode. Despite capacity fading at the cathode side, such shuttle effect can be rationally utilized to form a robust SEI layer on the metal anode, which leads to improved cycling stability for the anode.

Application of New Probing Techniques

As discussed above, great progresses have been made in the protection of alkali-metal anodes, especially for Li. Nevertheless, these existing methods cannot meet the demand of practical use. For instance, the current densities applied are normally too low (<5 mA cm^{-2}) to reflect the real testing conditions. In addition, as a critical aspect in the dendrite formation, the elaborate mechanisms of nucleation and deposition of alkali metal in various chemical environments are yet to be clarified. Therefore, future studies should focus on both technical and fundamental issues. By far, several advanced characterization techniques such as *in situ* TEM, synchrotron X-ray microtomography, and cryoelectron microscopy have been used to understand the fundamental aspects of Li-metal anode. However, powerful electrochemical characterization tools are yet to be applied. For instance, by *in operational* combining atomic force microscopy (AFM) to probe microstructure, electrochemical quartz crystal microbalance (EQCM) to weigh atoms or molecule and differential electrochemical mass spectrometry (DEMS) to test the released gas-compositions against different potentials. Pan and co-workers have depicted the formation process of SEI film on graphite anode.[165] It is believed that by applying appropriate electrochemical characterization techniques in relevant studies, new development for Li-metal anode can be explored. Apart from experimental results, computational simulations can also provide useful guidance in the rational design of metal anode protection.

Roadmap of Commercialization

To commercialize AMBs, the following critical points should be also considered: (1) A standard testing protocol should be established for fair comparison between different approaches as inconsistent or even contradictory results can be found between different research articles. For instance, the amounts of electrolyte and metal anode are believed to play important roles in the cycling life of AMBs. Therefore, they should be carefully controlled and stated in detail; (2) More severe thermal runaway is expected due to the high reactivity of metal anodes. Therefore, more stable separators and electrolytes should be investigated. For instance, the applications of solid electrolytes or fire-retardant liquid electrolytes are two promising strategies. Furthermore, safety monitoring and control should also be updated for AMBs; (3) The cost, as a critical factor for commercialization, has been neglected in most research articles. Therefore, in order to practically evaluate a method for protecting alkali-metal anode, the economic aspects should be taken into serious consideration; (4) It is of great importance to choose a more feasible technical route for the scaling up process. For instance, various cell configurations can be chosen depending on the specific requirement.

In the past decade, alkali-metal anodes as the "holy grail" have been re-summoned in response to the growing demand for high-energy batteries. Although extensive progress has been achieved in the protection of alkali-metal anodes in both traditional Li-ion batteries and the next-generation batteries (e.g., AM-O_2, AM-S, and SSBs), alkali-metal anodes are still in their infancy stage toward practical commercial applications because of their potential safety issues, relatively low CE, and lack of cost-effective scalable manufacturing. With continuous efforts from the academia and the industry to address these challenges, we believe that it is only a matter of time before AMBs can truly "rise from ashes."

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AUTHOR CONTRIBUTIONS

Yunhui Huang, L. Yuan, and F.P. proposed the topic and organized the manuscript. J.X. and L. Yang conducted the literature search and wrote the manuscript. J.X., L. Yang, K.Y., L. Yuan, F.P., and Y.H. discussed and revised the manuscript. Y.Z., Youyuan Huang, and J.L. assisted in the editing of the manuscript and provided input for discussions. J. X. and L.Yang contributed equally to this work.

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