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Engineering Triple-Phase Interfaces of the Anode towards Practical Alkali Metal-Air Batteries

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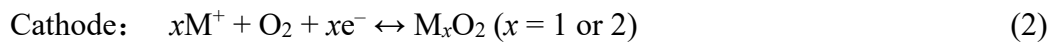
ABSTRACT: Alkali metal–air batteries (AMABs) promise ultrahigh gravimetric energy densities, while the inherent poor cycle stability hinders their practical application. To address this challenge, most previous efforts were devoted to advancing the air cathodes with high electrocatalytic activity. Recent studies have underlined the significance of improving the stability of solid–liquid–gas triple-phase interface around the anode. Besides the bottlenecks of uncontrollable dendrite growth and gas evolution in conventional alkali metal batteries, the corrosive atmospheric gases, intermediate oxygen species, and redox mediators in AMABs cause more severe anode corrosion and structural collapse, posing greater challenges to the stabilization of the anode triple-phase interface. This work aims to provide a timely perspective on the anode interface engineering for durable AMABs. Taking the Li–air battery as a typical example, we have a critical review of the latest developed anode stabilization strategies, including formulating novel electrolytes to build protective interphases and alleviate corrosive attacks, fabricating advanced anodes to improve their anti-corrosion capability, and designing functional separator to shield the corrosive species. Finally, we highlight the remaining scientific and technical issues from the prospects of anode interface engineering, particularly materials system engineering, for the practical use of AMABs.

Keywords: alkali metal–air batteries, triple-phase interfaces, electrolyte formulation, anode engineering, functional separator

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have dominated the global energy storage market, including portable electronics, electrified transportation, and large-scale grid storage.^[1-3] Since their first successful commercialization, the theoretical energy density limit based on Li-intercalation chemistry has been approached after 30 years of development.^[4] The growing demand to further increase energy density has accelerated the investigation of new energy storage technologies beyond Li-ion batteries.^[5-7] Non-aqueous alkali metal-air batteries (AMABs) have emerged as one of the most promising alternatives to traditional LIBs for next-generation energy storage. Unlike LIBs utilizing intercalation compounds of heavy equivalent weight as electrode materials, an AMAB typically comprises an alkali metal anode and a porous air cathode.^[8-11] For instance, Li-air battery (LAB) delivers an ultrahigh potential energy density of ≈ 3500 Wh kg⁻¹ based on the reaction of $2\text{Li}^+ + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ ($E^0 = 2.96$ V vs. Li⁺/Li), which is comparable to that of gasoline (**Figure 1a**).^[12-14]

In AMABs, the metal anode and air cathode are separated by a separator soaked with electrolytes.^[6, 15-17] The electrochemical reactions at two electrodes are shown below:



In the initial discharge process, alkali metal (M) is oxidized to M⁺ at the anode side. At the same time, multi-step reduction of O₂ occurs at the cathode side, first to thermodynamically unstable superoxide (O₂⁻) and then to more stable peroxide

(O_2^{2-}).^[18, 19] The as-generated O_2^{2-} combines with M^+ to form insoluble M_xO_2 deposits.^[20, 21] Upon charging, M_xO_2 are expected to be reversely oxidized to release O_2 and M^+ . The charge transfer processes are mediated by the reactive oxygen, including O_2^- , O_2^{2-} , and singlet oxygen ($^1\text{O}_2$),^[22] which unfortunately tend to decelerate the reaction kinetics.^[23] Moreover, these oxygen species are corrosive, which may continuously degrade the electrolyte and metal anode, causing unsatisfactory cycling durability and poor round-trip efficiency of AMABs.^[24-26]

To address the above issues, a significant amount of studies have been conducted to boost the reversibility and kinetics of oxygen reduction at the air cathode in the past decades.^[27-30] A broad and in-depth understanding of the cathode chemistry in AMABs has been built, and (electro)chemically stable and high-surface-area air cathodes with excellent electrocatalytic activities toward oxygen reduction/oxidation have been developed.^[27, 31-35] However, many recent studies revealed that the poor interfacial stability of the alkali metal anode is another bottleneck restricting the practical applications of AMABs.^[36, 37] In particular, the open environment containing mixing gas species of O_2 , CO_2 , and H_2O in the AMAB electrolyte results in complex electrochemical reactions.^[38] The alkali metal anode is confronted with a complex solid (metal anode)–liquid (the electrolyte)–gas (ambient air) triple-phase interface.^[39] The crossover of $\text{O}_2/\text{CO}_2/\text{N}_2$, trace H_2O , and redox mediators (RMs) from the cathode to the anode causes severe parasitic reactions with the metal anode and, thus performance deterioration of AMABs.^[40-42] The reactive oxygen intermediates like the highly nucleophilic O_2^- , O_2^{2-} , and $^1\text{O}_2$ may interfere with the O_2 electrochemistry.^[43, 44] Besides,

the uncontrollable dendrite growth derived from uneven metal deposition and inhomogeneous SEI deteriorates at the complex triple-phase anodic interface and easier structural collapse of anodes.^[45, 46]

Stabilizing the anode interface of AMABs is thus quite challenging. In recent years, numerous strategies have been developed to address these challenges,^[17, 47, 48] such as the utilization of alternative anode chemistry with lower reactivity,^[49, 50] novel electrolyte formulation for building protective interphases and reducing corrosive attacks,^[51-53] and fabrication of ion-selective membranes/scaffolds to shield the corrosive species.^[54-57] Unfortunately, still no review or perspective covers recent advancements in this promising research direction. To fill this void, recent progress on stabilizing the anode interfaces is reviewed comprehensively in this work to provide easy and timely access for readers to follow the latest developments in the anodic interface area. In this critical review, we first overview the alkali metal anode electrochemistry for AMABs and the current challenges by examining lithium–air batteries (LABs) as a typical example. We then discuss the recent progress in stabilizing the solid–liquid–gas interface of alkali metal anodes by various strategies, such as electrolyte formulation, advanced metal anode construction, and separator modification (Figure 1b). We also highlight recent advances in constructing high-performance Na/K–air batteries. Finally, we shed light on the current limitations and the future scope for stabilizing anode interfaces, aiming to inspire the construction of stable anodic interfaces for next-generation AMABs.

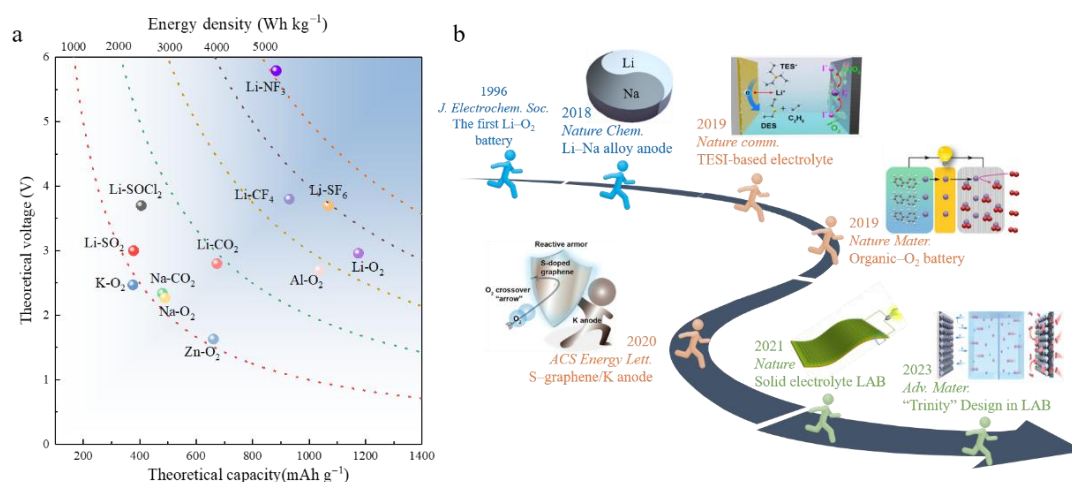


Figure 1. Advanced AMABs for next-generation high-density energy storage. (a) Energy density comparison among various high-energy battery technologies.^[58-69] (b) The main progress in the anode stabilization of AMABs.^[50, 70-75]

2. Challenges for stabilizing the triple-phase interfaces around the anodes in AMABs

Compared to the two-phase interface at the anode in conventional alkali metal batteries, the complex triple-phase reactions at the anode interface cause more uncontrollable growth of “dead” alkali metal and dendrites, easier cracking and continuous generation of passivating SEI, and more severe structural collapse of the metal anode (**Figure 2**). Among various AMAB technologies, LABs have been the most widely studied. Therefore, the following discussion focuses on the challenges toward stabilized anode interfaces in LABs, including electrolyte degradation, cross-contamination of atmospheric gases, corrosion of alkali metal anodes by reactive species, and structural collapse of metal anodes.

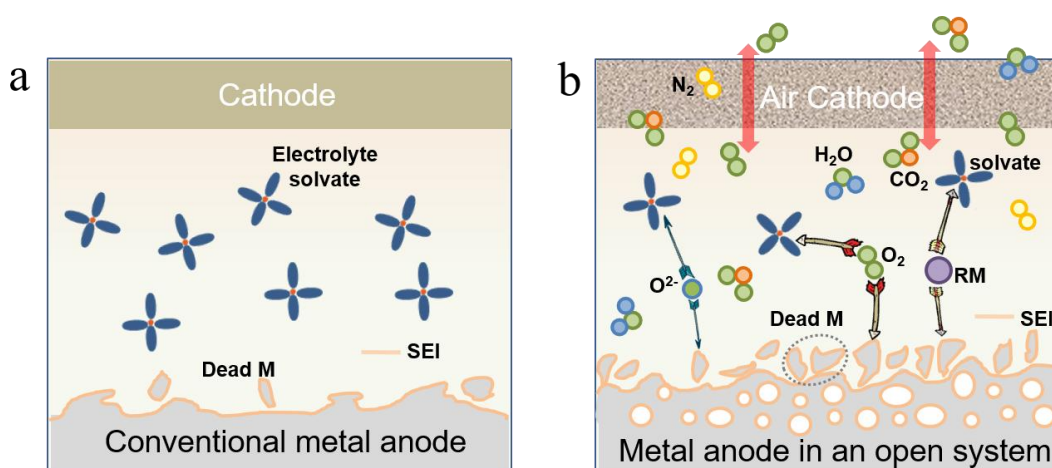


Figure 2. Challenges for the stabilization of triple-phase interfaces around the anodes in AMABs. The comparison between two-phase and triple-phase interfacial reactions of metal anodes in conventional alkali metal batterie (a) and AMABs (b).

2.1. Deterioration of electrolytes

Aprotic electrolytes between the cathode and anode have been widely used to mediate the Li^+ -ion transfer in LABs.^[76] The electrochemical performances of LABs are highly dependent on the properties of electrolytes, especially their stability against the nucleophilic attack by reactive oxygen species, such as O_2^- , O_2^{2-} , and $^1\text{O}_2$.^[24] These nucleophilic reactions could accelerate the decomposition of electrolytes.^[77] For instance, carbonate-based electrolytes used in early LAB studies were found to decompose severely owing to the nucleophilic attacks by O_2^- on the $\text{C}=\text{O}$ groups, producing Li alkyl carbonates and Li_2CO_3 .^[26] Yang and co-workers revealed that auto-oxidation via α -H abstraction occurs when mixing ether solvents with O_2 .^[78] It promotes the release of protons, esterification, and then polymerization, thus degrading the electrolyte.

Moreover, the LAB system is exposed to atmospheric moisture. The polar water molecules interact with the carbonyl groups with high electronegativity and metastable double bonds in the electrolyte components, giving rise to complex side products.^[79] Therefore, hydrophobic electrolytes with low water solubility are more favorable. To date, it is still a crucial challenge to formulate proper electrolytes in AMABs with low volatility, high hydrophobicity, and good resistance to the attack of oxygen groups.

2.2. Cross-contamination of atmospheric gases

Another main challenge for stabilizing anodic interfaces in AMABs is the cross-contamination of atmospheric O₂, CO₂, N₂, and H₂O gases.^[41, 80, 81] An open atmosphere is more likely designed to supply continuous O₂ at the cathode of AMABs. However, the simultaneous exposure of electrolytes and Li anodes to the air leads to corrosion and thus the formation of Li-ion insulating salts like Li₂O, Li₂CO₃, and LiOH at the anodic interfaces.

The crossover of oxygen was first documented by Assary *et al.*^[38] Their observations revealed the presence of multiple oxidative products at the anode, including LiOH, Li₂CO₃, CH₃Oli, CH₃Li, and polymeric layers. Also, the shuttled oxygen from the cathode reacts with the fresh Li metal and dendrites at the anode, resulting in the passivation of the anodic interface. It brings about severe polarization, shortened cycle life, and even safety concerns. Therefore, protecting the Li anode against O₂ is crucial for the safe and durable operation of LABs.

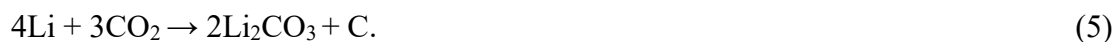
As mentioned above, H₂O is another critical corrosive gas component in ambient air,

which reacts with Li to form LiOH and H₂ through the following equation:^[41]



Similar to the above oxygen-containing species, the presence of H₂O also leads to the corrosion of Li metal. Water pollution induces solution-mediated parasitic chemical and electrochemical reactions to produce porous LiOH and LiOOH, which may destroy the SEI structure and aggravate the corrosion of the anode.^[41, 82, 83] The continuous depletion of cell components due to the irreversible transformation of the lithium anode results in a deterioration of battery cyclability.

The research community has also confirmed that the CO₂/N₂ gases degrade the electrochemical performance of LABs.^[40, 80] These gases were revealed to participate in the discharge process in a complex way, forming irreversible Li₂CO₃ and Li₃N products.^[84, 85] A higher energy barrier exists for decomposing Li₂CO₃/Li₃N than Li₂O₂, resulting in high charge overpotentials, low Coulombic efficiencies, and short battery lifespan.^[86] For example, CO₂ reacts with Li through the following equation:



Although it has been reported that protective Li₂CO₃ film can be formed after immersing the Li anode in the CO₂ atmosphere,^[87] the practical reactions involved in ambient air could be much more complex. Thus, the Li₂CO₃ product is probably not integrated into the as-generated SEI in a well-organized way. As such, it may reduce the efficiency and reversibility of the anodic reaction, increasing overpotential at the Li anode.^[88, 89]

2.3. Corrosion of metal anodes by reactive species in electrolytes

The corrosive species such as O_2^{2-} , O_2^- , and $^1\text{O}_2$ generated during the discharge process are highly nucleophilic radicals that could cause continuous anode corrosion. Various byproducts of Li_2O , Li_2O_2 , Li_2CO_3 , and insoluble ionic Li compounds would be produced.^[38, 90] Moreover, the high reactivity of the metal anode not only causes parasitic reactions with oxygen groups in the electrolyte and the introduced redox mediators (RMs).^[42] Generally, the RMs serve as mobile charge carriers in the local areas of the air cathode.^[17] They are oxidized upon charging to produce RM^+ and react with Li_2O_2 .^[42] However, RM^+ in the electrolyte could also diffuse through the electrolyte and separator to corrode the Li anode, generating the well-known redox shuttling effect.^[91]

2.4. Structure collapse of the alkali metal anodes

The degeneration of the Li metal anode mainly originates from its high activity and hostless nature. The direct contact between the alkali metal anode and O_2 leads to redox reactions that produce reduced oxygen species, such as superoxides.^[38, 92] Under ideal conditions, the final product of Li_2O helps to build a protective SEI layer to prevent further reactions between Li and O_2 .^[93] However, at the complex solid–liquid–gas triple-phase interface, breakage of the practical SEI layers easily occurs because of the severe volume fluctuation and erosion by corrosive species, exposing fresh Li metal to the electrolyte. Thus, continuous parasitic reactions happen at the anodic interface during repeated charge-discharge cycles, eventually leading to the structure collapses of Li anodes.^[94]

3. Electrolyte Engineering

The electrolyte is a critical component mediating the transfer of ionic charge carriers between the cathode and anode in an LAB. It plays a vital role in determining the solubility of oxygen, the formation pathway of Li_2O_2 , and the production of the SEI layer at the anodic interface.^[24] Indeed, corrosion of Li anodes has been extensively observed in conventional electrolytes over prolonged charge-discharge cycles.^[94] A careful selection of electrolytes is necessary for the durable operation of LABs in the open atmosphere, given the hyper-reactivity of the metallic anode and dendrite growth-derived safety concerns. Based on numerous studies over the past decades, ideal electrolytes in LABs should have the following merits: (1) good compatibility with the metal anode to produce stable SEI; (2) low volatility, poor wetting ability, and nonflammability to be compatible with the open system; (3) high chemical and electrochemical stability toward oxygen, and the reduced oxygen species of O_2^- , O_2^{2-} , and $^1\text{O}_2$; (4) a wide voltage window for efficient battery operation.^[95-97] In this section, research progress on designing functional liquid electrolytes and solid-state electrolytes toward stabilized anodic interfaces will be thoroughly reviewed.

3.1. Novel liquid electrolytes for stabilizing the anode interfaces

Liquid electrolytes are preferred in battery systems because of their easy formulation, low viscosity, large ionic conductivity, and good electrode wettability. They are generally composed of high-purity single or mixed solvents and alkali metal salts. Generally, the stability of liquid electrolytes against metal anodes and corrosive gases/species depends on the choice of electrolyte components, especially the

introduced functional additives. In the following section, various functional additives in liquid electrolytes for stabilizing anodic interfaces will be highlighted, focusing on their different functions, including constructing protective SEI, inhibiting cross-gas contamination, and alleviating attacks by corrosive species.^[98-100]

Wesley *et al.* demonstrated for the first time the durable cycling of Li anode in a straight-chain alkyl amide-based electrolyte when lithium nitrate (LiNO_3) was introduced, which effectively stabilized the SEI of Li anode and inhibited the reaction between the solvent and Li anode.^[101] Similarly, Roberts *et al.* used LiNO_3 as an effective additive to stabilize the dimethyl sulfoxide (DMSO) solvent incompatible with metallic Li.^[102] An efficient passivation film was formed, which was revealed to be self-healing and could facilitate long-term cycling once damaged. Subsequently, Kubo *et al.* introduced both LiBr and LiNO_3 in a tetramethylene glycol dimethyl ether (TEGDME)-based LAB electrolyte.^[98] The NO_3^- anion oxidizes the Li anode surface to inhibit the shuttle reaction, while the $\text{Br}^-/\text{Br}_3^-$ couple serves as an RM to facilitate oxidation at the cathode. It was also found that the mixed $\text{Br}^-/\text{NO}_3^-$ anions act synergically to significantly suppress the parasitic reaction and dendrite formation by forming a thin and solid Li_2O film (~ 10 nm) on the Li anode surface.

Sun *et al.* reported the introduction of InBr_3 as a self-defence RM in the LAB electrolyte.^[103] An In-enriched composite protective layer is formed in situ on the Li anode due to the existence of In^{3+} , which effectively suppresses the side reaction between the Li anode and the electrolyte, thus improving the anodic interfacial stability. Zhang *et al.* reported that tetraethyl orthosilicate (TEOS) as an electrolyte additive

could react with the generated LiOH at the Li surface to form a self-healing protective film (**Figure 3a**).^[104] Even after the prolonged cycling in the highly corrosive system, the destructed film can be dynamically repaired via a continuous reaction between TEOS and LiOH (Figure 3b). Therefore, the reversibility and cycle stability of Li anodes is significantly improved (Figure 3c,d).

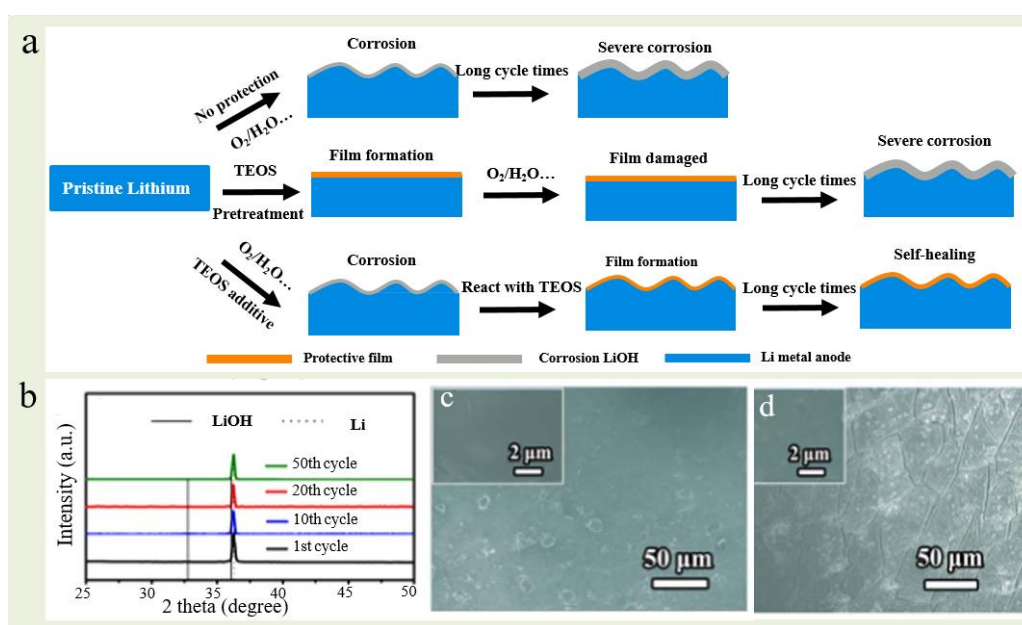


Figure 3. Liquid electrolyte additive-induced protective SEI for stabilizing the anode interfaces of LABs. (a) A comparative analysis of the protection mechanisms for three types of Li anodes. (b-d) XRD patterns and SEM images (pristine and 20th cycles) taken from TAL anodes. (reproduced with permission: Copyright 2019, Elsevier. ^[104]).

Recall that the cross-gas contamination of atmospheric O₂, CO₂, N₂, and H₂O gases is the main challenge for stabilizing anodic interfaces in LABs. Except for constructing a protective SEI at the Li anode surface, reducing the solubility of atmospheric gases and decelerating their diffusivities in the electrolyte is another efficient approach to address this issue. For example, Zhang *et al.* introduced a 10 wt % hydrophobic silica colloid electrolyte (HSCE) to protect the Li metal anode from severe corrosion and

irregular dendrite growth in the Li–O₂ battery.^[105] The results demonstrate that a lower diffusion coefficient can yield an anti-corrosion effect 980 times more effective than 0 wt % HSCE. (**Figure 4a**). The in situ coupling of CF₃SO₃[−] on silica surfaces via electrostatic interactions avoids the formation of a strong electrical field caused by anion depletion. It induces the production of a stable SEI and constrains the repeated SEI formation/breakage process. Moreover, the severe corrosion by O₂, H₂O, and other contaminants can be effectively alleviated (Figure 4b). Consequently, a stable plating/stripping process is achieved with a long anodic lifespan of 550 cycles in Li–O₂ batteries.

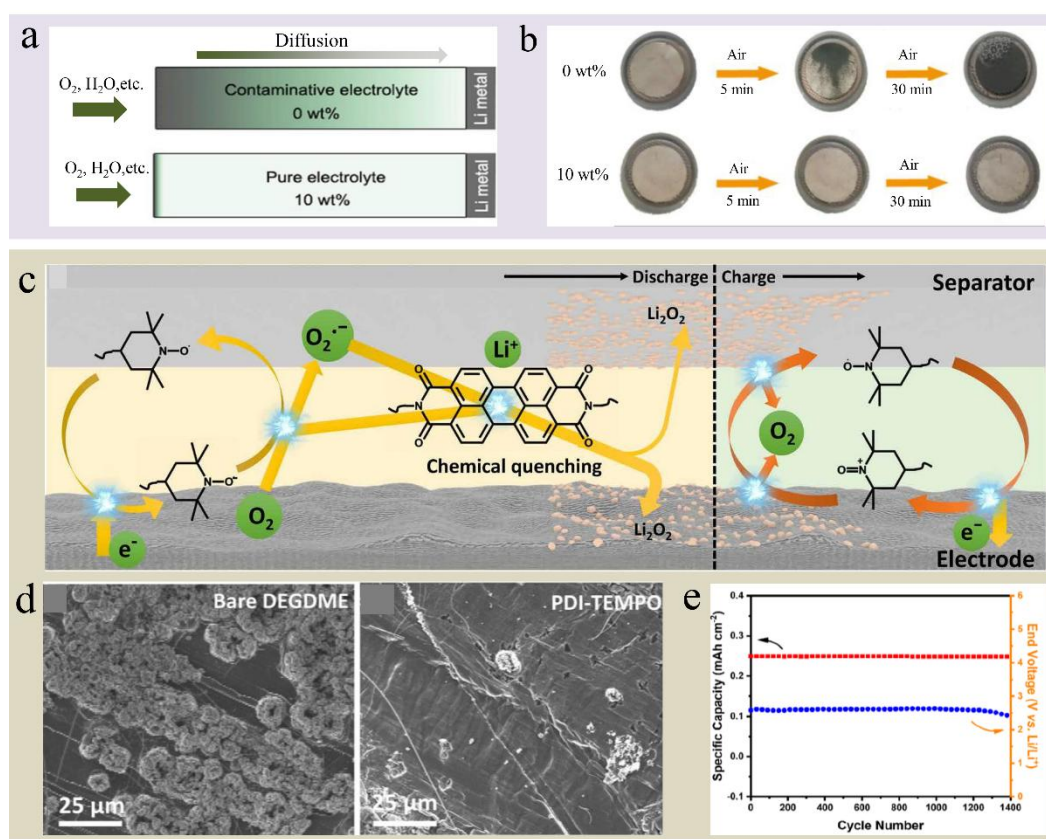


Figure 4. The use of anti-corrosion additive in liquid electrolytes for stabilizing the anode interfaces of LABs. (a) schematic representation of the anticorrosion effects of different electrolytes. (b) Optical images of the Li metal exposed to air after a different time soaking in 0 wt %

HSCE and 10 wt % HSCE.(reproduced with permission: Copyright 2020, Elsevier. ^[105]). (c) The illustration of PDI-TEMPO to comprehensively suppress parasitic reactions. (d) SEM images of the Li anodes from bare DEGDME electrolyte and PDI-TEMPO electrolyte after 10 cycles. e) The long-term cycling profile of Li-O₂ battery with 10 mM PDI-TEMPO electrolyte. (reproduced with permission: Copyright 2022, AAAS^[44]).

The introduced RMs and in-situ generated oxygen-containing groups over charge-discharge cycles are corrosive species in the electrolyte. They may accelerate the electrolyte decomposition and unstable SEI formation, thus continuously corroding the metal anode interfaces.^[100, 106, 107] As a typical example, the soluble superoxide anion O₂⁻ coming from LiO₂ may cause drastic deterioration of the electrolyte in LABs.^[108] To inhibit the attack by corrosive O₂⁻ and ¹O₂, Wang *et al.* designed and synthesized a multifunctional diimide-based quencher (PDI-TEMPO) for boosting the performance of LABs (Figure 4c).^[44] The PDI-TEMPO molecule contains a PDI backbone capable of quenching O₂⁻ and redox mediator-active TEMPO moieties to catalyze discharge and charge processes. As a result, corrosion of the metal anode is effectively inhibited, which would lead to a long cycle life (Figure 4d, e).

Chen *et al.* reported using the imidazolium cation bromide (1-methyl, 3-phenyl, 1H imidazolium bromide, IMPBr) as a tri-functional additive for LABs.^[109] It enhances the redox reaction activity at the cathode side and enables dendrite-free Li deposition. The positively charged IMP⁺ was absorbed on the Li anode surface by electric attraction and participated in the construction of a stable SEI film, thereby protecting the Li anode from the corrosion of DMSO, Br³⁻, and Br₂. Zhang *et al.* proposed to use a highly concentrated electrolyte based on LiTFSI in DMSO,^[110] which has a higher Gibbs

activation energy barrier for C–H bond scission from CH₃ in DMSO solvent, therefore improving the electrolyte stability against O₂^{•−} attack.

To summarize, this section reviews recent important progress in developing novel liquid electrolytes for stabilized anodic interfaces in LABs.^[103, 111, 112] While most reports focused on introducing functional additives for fabricating stable SEI against deterioration, interesting attempts have also been proposed to decelerate the diffusion of corrosive species in electrolytes. Also, super-concentrated electrolytes can alter the solvation structure and enhance the anti-corrosive capability against corrosive species.^[110, 113] Despite the great progress, the anodic reversibility and cycle life are still unsatisfactory. Potential safety risks exist because of easy leakage of liquid electrolytes in the open system and Li dendrite-induced short circuit issues.^[54, 114]

3.2. Solid-state electrolyte engineering

Using solid-state electrolytes (SSEs) to replace liquid electrolytes has been regarded as a practical approach to address the above electrolyte leakage and dendrite-derived safety concerns.^[115] SSEs comprise ceramics and/or polymeric materials to convey Li ions between the air cathode and the lithium metal anode.^[116] The use of SSEs in LABs is favorable for solving the (electro)chemical problems associated with liquid organic electrolytes like instability, flammability, toxicity, and volatility.^[117] The migration of reactive oxygen reduction products from the cathode to the anode can be prevented, and Li dendrite growth can also be inhibited because of their high mechanical strength.^[118, 119] In the following section, the progress in the development of solid polymer electrolytes (SPEs) and ceramic solid electrolytes (CSEs) in LABs will be

comprehensively reviewed.

SPEs have relatively higher stability than non-aqueous liquid electrolytes in LABs. It protects the Li anode from directly reacting with O_2 or H_2O . Nan *et al.* designed a freestanding, Li-ion conductive ultra-dry polymer electrolyte (UDPE) without additional liquid electrolyte (**Figure 5a,b**).^[120] UDPEs can effectively inhibit the crossover of O_2 to the Li metal anode (Figure 5c-h). Therefore, most unwanted side reactions between the liquid plasticizers and the highly active oxygen species were avoided in as-fabricated LABs. As such, the accumulation of $Li_2CO_3/LiOH$ by-products was also eliminated. As a result, the cycle life of UDPE-based LABs was two-fold longer than that using liquid electrolytes. In another study, Cui *et al.* in-situ polymerized deep eutectic solvent-based polymer electrolyte (DES-PE) on the Li anode to endow as-fabricated LABs with a robust anodic interface.^[121] The in-situ formed DES-PE prevents the penetration of O_2 , N_2 , H_2O , and other gases in the ambient air, thus effectively protecting the Li anode and boosting the anodic reversibility.

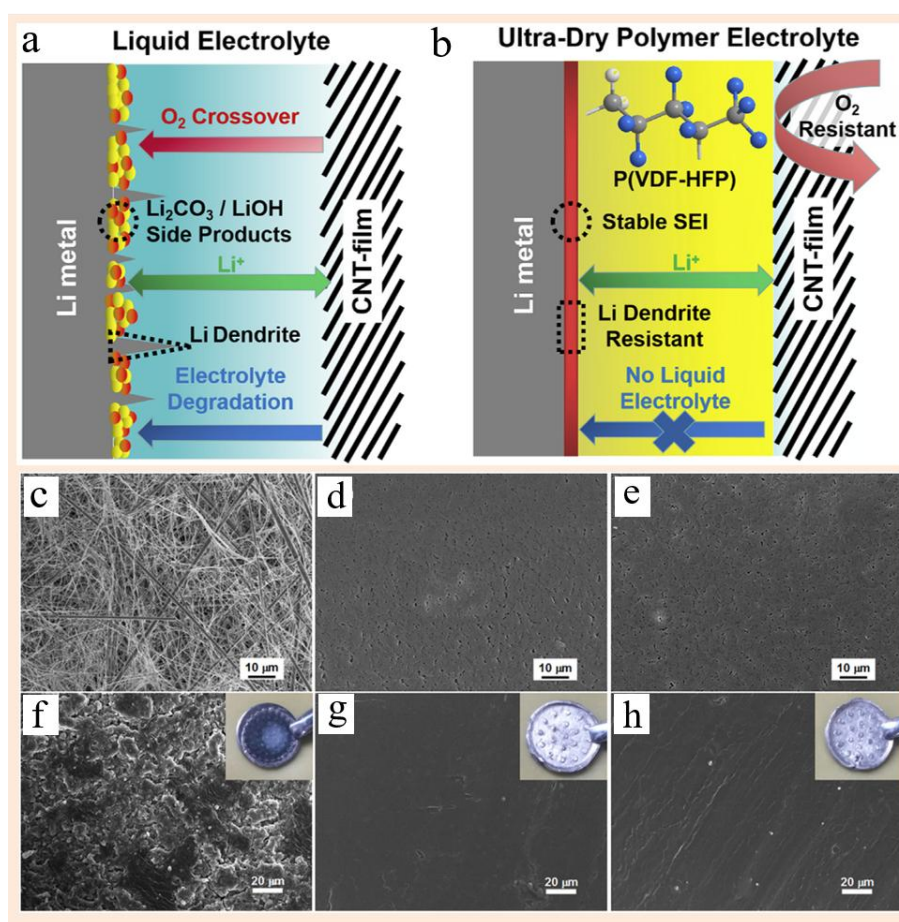


Figure 5. The construction of solid polymer electrolytes for stabilizing the anode interfaces of LABs. Schematic illustration of LABs with (a) liquid electrolytes and (b) UDPEs. SEM images of (c) GF separator, (d) PVDF membrane, (e) P(VDF-HFP) membrane, and the surfaces of the Li anodes with (f) GF, (g) PVDF membrane, and (h) P(VDF-HFP) membrane exposure to O₂ atmosphere for three days. Insets in (f-h) show the photographic images of the corresponding Li anode surfaces. (reproduced with permission: Copyright 2020, Elsevier.^[120]).

The poor oxidation resistance of SPEs hinders their practical applications, especially under high working voltages in LABs. To address this concern, CSEs with high stability against oxidation have been extensively investigated,^[122] which also have relatively higher Li⁺ conductivity and better thermal/chemical stability than SPEs. For instance, Zhou *et al.* substituted liquid electrolytes with a solid Li-ion conductor Li_{1.35}Tl_{1.75}Al_{0.25}P_{2.7}Si_{0.3}O₁₂ (LTAP), serving as both a catholyte and a Li protector.^[117] It

effectively circumvents the decomposition of liquid electrolytes, growth of Li dendrites, and parasitic reactions with mixed gas phases of O₂, H₂O, and CO₂, thereby enhancing the reversibility and cyclability of Li anodes. In a recent pioneering work, Yu *et al.* reported an integrated solid-state LAB using an ultrathin Li⁺-exchanged zeolite X (LiX) membrane with high ionic conductivity as the solid electrolyte (**Figure 6a**).^[74] This electrolyte is integrated with a cast Li anode and a carbon nanotube cathode through an in-situ assembly process. Due to the inherent chemical stability of zeolite, the degradation of electrolytes by Li metal or air is efficiently inhibited. Meanwhile, the ultra-slow dynamics of air penetration through LiXZM are favorable for impeding anodic corrosion. The Li metal protected by LiXZM was demonstrated to retain its metallic luster after 1000 hours of ageing, revealing adequate protection from air erosion (Figure 6b). In addition, the by-products of Li₂CO₃, HCO₂Li, and CH₃CO₂Li formed in conventional liquid electrolyte-based LABs are absent in the solid-state LAB using C-LiXZM. The mitigated electrolyte decomposition results in a more stable cycling performance of the LABs.

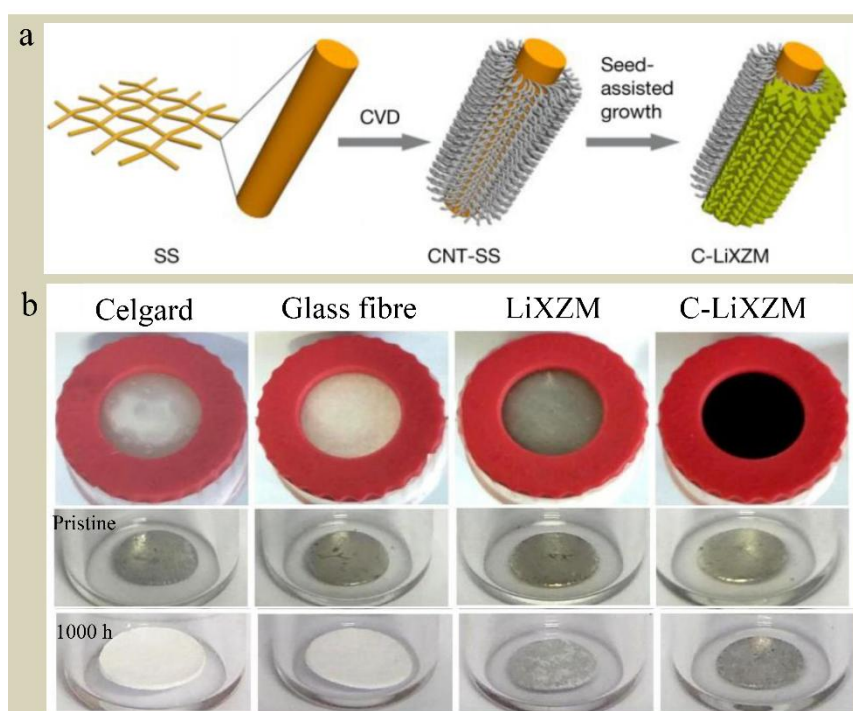


Figure 6. The construction of ceramic solid electrolytes for stabilizing the anode interfaces of LABs. (a) Schematic of the design and preparation of the integrated C-LiXZM. (b) Time-resolved optical images of Li metal inserted in the test devices sealed with Celgard separator (immersed with organic electrolyte), glass fiber separator (immersed with organic electrolyte), LiXZM, and C-LiXZM. (reproduced with permission: Copyright 2021, Springer Nature.^[74]).

Although considerable progress has been made in engineering solid-state electrolytes for high-performance LABs, the research in this field is still in its infancy. SPEs generally own poor oxidation resistance, while CSEs have limited ionic conductivity at room temperature. In addition, the poor interfacial contact between the Li anode and current CSEs is another major obstacle to obtaining reversible and durable LABs. One promising solution could be hybridizing CSEs and SPEs to integrate merits from both components toward improved (electro)chemical stability and reduced interface contact impedance.^[123] Future research should be devoted to developing high-conductivity solid electrolytes with robust interfaces for next-generation LABs.

4. Rational design of anode structure/composition

The uneven Li deposition at LAB anodes easily causes dendritic growth after repeated charging-discharging cycles, which may penetrate the separator and result in subsequent internal short circuits and thermal runaway.^[124-126] Moreover, the Li anode in LABs inevitably suffers from continuous deterioration because it is hyperreactive with H₂O, O₂, and the produced intermediates during charge-discharge. Therefore, it poses a high risk to the Li anode regarding structure collapse over prolonged cycles.^[127-129] Structure modification and rational composition design can eliminate the corrosion of Li anodes, thus stabilizing the anodic interfaces. The following section will comprehensively review and discuss the typical methods reported, including artificial SEI construction and composite metal anode fabrication.

4.1. Constructing artificial SEI layer

The physicochemical properties of SEI play a critical role in determining the electrochemical performances, especially the cycling stability of the Li metal anode and the LABs.^[130-132] Recent studies have suggested that crossover O₂ and H₂O can corrode the native SEI formed at the Li anode surface from the open air.^[111, 133] Artificial SEI layers are functional thin films pre-constructed on the Li anode surface, generally impermeable to O₂ and H₂O. Therefore, it can protect the Li anode from parasitic reactions with corrosive species, thereby improving the cycling stability of rechargeable LABs.^[134, 135]

In an early study, Osaka *et al.* extended the cycle life of Li anode in a CO₂-saturated LiClO₄/propylene carbonate electrolyte, in which the formation of Li₂CO₃ at the Li

metal surface inhibits dendritic Li deposition.^[136] Recent research revealed the in-depth mechanism of the above anode protection through combined spectroscopic characterizations and theoretical simulations.^[87] Such Li₂CO₃/C anode-protection coating can be directly conducted on a Li anode. In a custom-made electrochemical Li–CO₂ cell filled with pure CO₂, a protective coating layer composed of nanorods was built on the Li metal surface after ten discharge-charge cycles (**Figure 7a**), based on the following reaction:



The phase composition was determined to be Li₂CO₃/C by Raman tests(Figure 7b). Density functional theory (DFT) calculations revealed that the Li₂CO₃ layer endows a high energy barrier of 1.2–3.2 eV, thus effectively blocking the adsorption of N₂ and O₂ (Figure 7c,d). As a result, the Li₂CO₃-protected Li metal anodes show similar electrochemical properties in the air to those in pure oxygen (Figure 7e). Similarly, Huang *et al.* produced air-stable lithium spheres (ASLSs) with a Li core and Li₂CO₃ shell through electrochemical Li plating under a CO₂ atmosphere.^[137] The Li₂CO₃ shell is highly hydrophobic and non-reactive with O₂ and N₂ in ambient air, protecting the Li core from corrosive species. Moreover, it has a good Li⁺-ion conductivity for rapid interfacial charge transfer.

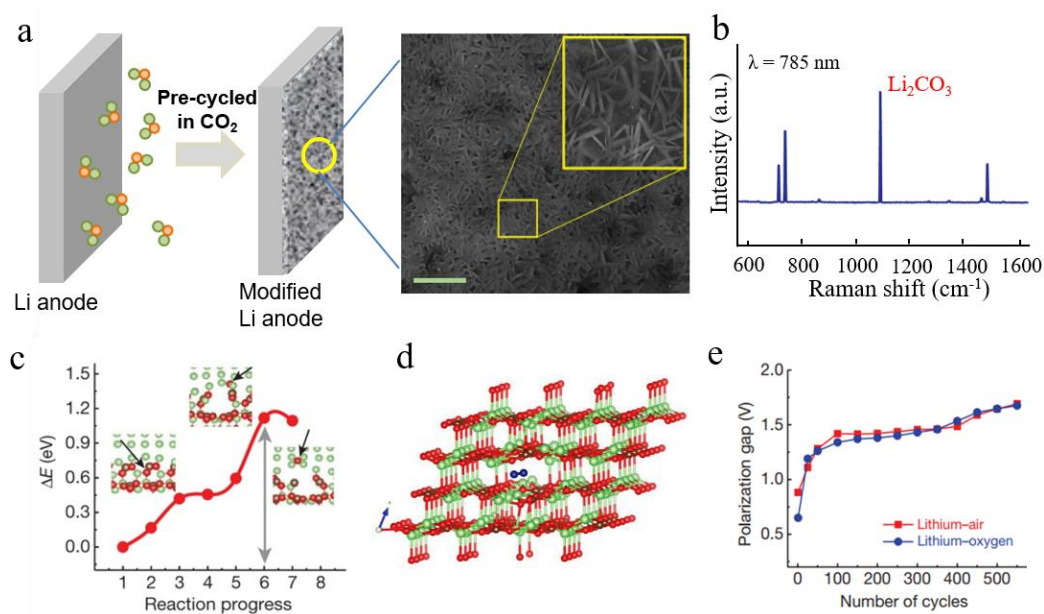


Figure 7. Constructing artificial SEI layers by pre-cycling the Li anode in CO₂ for stabilizing the anode interfaces of LABs. (a) Schematic of the synthesis process of Li₂CO₃/C layer (scale bar, 1 μm). (b) Raman spectra of the protected anode. (c) Computational analysis revealed the cleavage of the C–O bond of Li₂CO₃ at the interface and the migration of oxygen to the bulk Li (Black arrows show the presence of oxygen). (d) Computational analysis of O₂ in a Li₂CO₃. (e) The polarization gap between the lithium–air battery and the Li–O₂ battery under the same operating conditions. (reproduced with permission: Copyright 2018, Springer Nature.^[87]).

Zhou *et al.* fabricated another organic-rich protective layer on the Li surface by facile chemical reactions between Li metal and 1,4-dioxacyclohexane (DOA), which is mainly composed of ethylene oxide monomers and functions as an efficient barrier to shield the Li metal anode.^[45] Very recently, Cui *et al.* designed an iodine-containing polymer/alloy hybrid layer-based Li (IPA-Li) via the replacement reaction between zinc iodide (ZnI₂) and Li and subsequent polymerization of ethyl α-cyanoacrylate (**Figure 8a**).^[138] The high mechanical flexibility of the polymer layer not only alleviates the internal stress at the Li surface but protects Li metal from O₂/H₂O attack, thus enabling

durable storage of IPA-Li in the air (Figure 8b). The LiZn alloy nanoparticles offer many smooth Li^+ -conducting channels and afford a robust affinity with Li, which favors even Li nucleation and dendrite-free growth. The in-situ differential electrochemical mass spectrometry (DEMS) tests revealed highly reversible charge storage in as-fabricated LAB dominated by $\text{O}_2\text{--Li}_2\text{O}_2$ conversion (Figure 8c) and therefore, a low voltage polarization during charge-discharge cycles (Figure 8d).

Despite the diversity and easiness of liquid-phase reactions with Li metal to produce artificial SEI layers, they are challenging to control, which generally produces loose and inhomogeneous films on Li surfaces. As a result, uneven Li deposition and undesirable side reactions may occur. To address this issue, Zhu and co-workers fabricated a self-eliminating passivated layer on the Li surface through facile evaporation of dichlorodimethylsilane (DCDMS).^[133] The fresh Li dendrites formed in their infancy stage can be spontaneously eliminated by the Wurtz-type reaction with DCDMS because of their higher reactivity (Figure 8e). An as-generated protective layer is composed of alkali chloride and poly(dimethylsilylene), and it has multiple merits of high thermal stability, hydrophobicity, electrical insulation, and good Li^+ -ion conductivity. Moreover, the LAB with such passivated Li anodes exhibits high Coulombic efficiencies and a long cycling lifespan of over 200 cycles (Figure 8f). Likewise, Shao *et al.* proposed an effective strategy by immersing the Li metal anode in I_2 steam to create an artificial SEI (Figure 8g).^[112] This ionically conductive LiI layer not only suppresses the growth of Li dendrites but alleviates the shuttle of RMs to the Li metal anode, thereby extending the cycle life of LABs (Figure 8h,i).

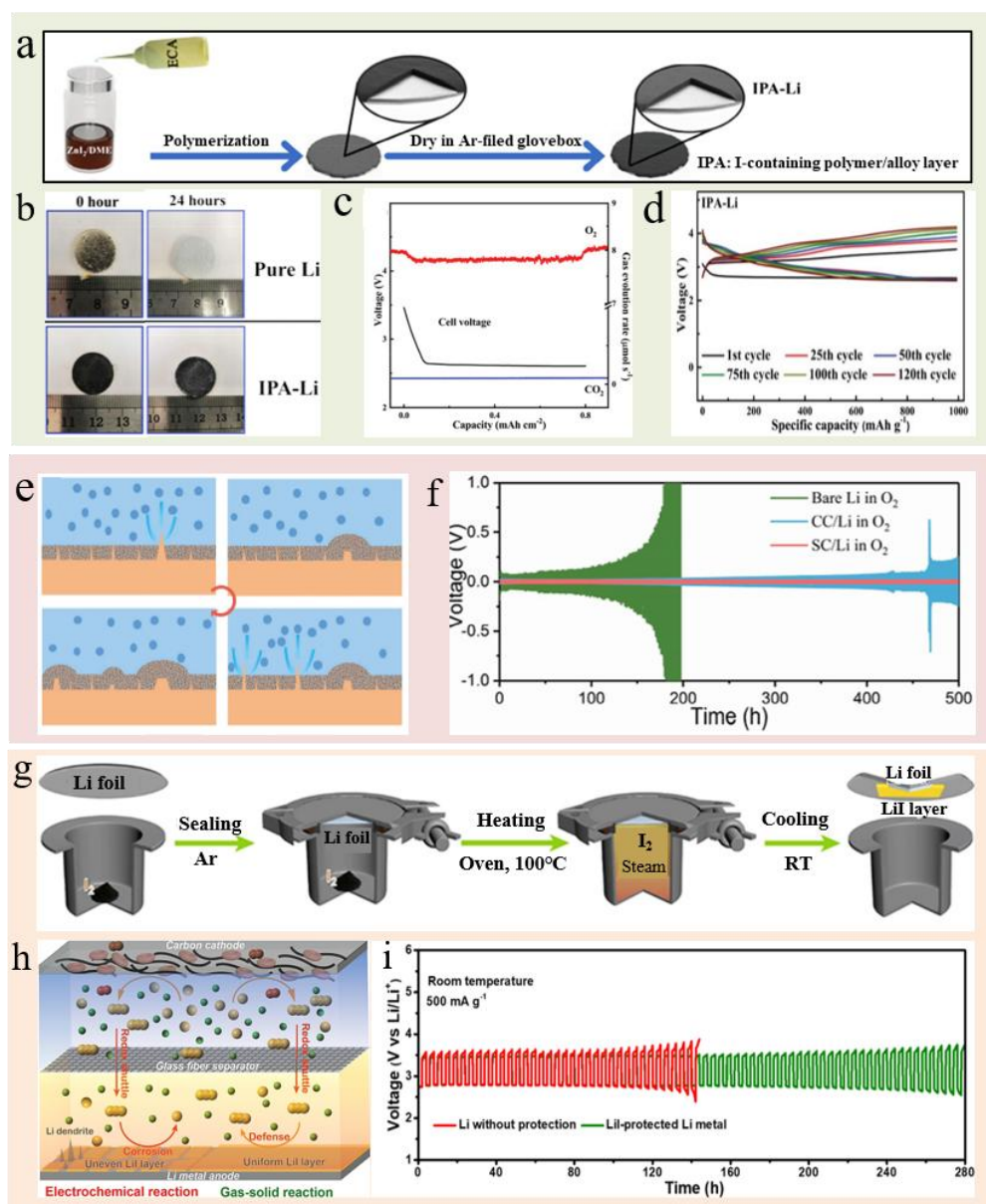


Figure 8. Constructing artificial SEI layers by chemical reactions for stabilizing the anode interfaces of LABs. (a) Schematic of the synthesis process for the IPA-Li composite. (b) Photograph images of the bare Li and IPA-Li anode exposed to the ambient air for various durations. (c) The O₂ consumption/corresponding discharge curves. (d) Voltage profiles under different cycles for IPA-Li-based LABs. (reproduced with permission: Copyright 2021, Wiley-VCH GmbH^[138]). (e) The schemes of Li deposit on SC/Li. (f) Cycling performance of the symmetric Li batteries in O₂. (CC/Li: Li metal with dichloropropane (C₃H₆Cl₂); SC/Li: Li metal reacts with LiCl/Poly(dimethylsilylene)). (reproduced with permission: Copyright 2022, Wiley-VCH GmbH^[133]). (g) Schematic illustration of the formation procedure of the protected Li metal. (h)

Shuttle mechanism and the function of the LiI protective layer. (i) Cycling performance of the LABs. (reproduced with permission: Copyright 2021, American Chemical Society^[112])

4.2. Li-containing anode design for stabilizing the interfaces

Artificial SEI forms a protective layer on the Li metal surface, which, however, does not change the inherent high (electro)chemical reactivity of Li metal anodes. The open system in LABs poses new challenges to the anodic interface stabilization except for uncontrollable Li deposition and drastic morphological changes of Li anodes in conventional Li-metal batteries.^[139, 140] Specifically, oxygen species of $\text{O}_2^-/\text{O}_2^{2-}/^1\text{O}_2$ generated during charge-discharge are high nucleophilic radicals, which catalyze electrolyte decomposition to produce a variety of reactive byproducts.^[77] Some other side products, such as LiOH, Li_2CO_3 , and ROCO_2Li , are also continuously generated on the Li anode surface^[38, 90], further deteriorating the interfacial stability.^[141]

To stabilize the anodic interfaces, novel Li-containing anodes have been extensively studied recently. For example, Peng *et al.* developed a 3D network of carbon nanotubes (CNTs) cross-stacked layer by layer orthogonally. When applied in LABs, the cycle stability of this composite Li anode was greatly improved because of the dendrite-free Li deposition and stabilized SEI.^[142] Similarly, another research group reported a Li-CNT composite anode with a self-assembled monolayer of octadecyl phosphonic acid as a tailor-designed SEI. The interwoven framework of CNTs was revealed to promote dendrite-free Li deposition within the 3D network without causing considerable volume expansion.^[143] Moreover, the artificial SEI constructed on the Li-CNT composite surface restrains the parasitic side reactions between Li metal and the electrolyte.

Although the composite anodes own enhanced mechanical stability and reduced charge/discharge polarization, extending the life-cycle of Li anodes in LABs is still a great challenge because of their high (electro)chemical reactivity. To resolve this problem, lithium-alloying composites with lower reactivity, such as Li_xSn ,^[144] LiAl_x ,^[145] and Li_xSi ,^[146] were exploited to replace Li metal. As a typical example, Zhou *et al.* developed a long-life Li-ion O_2 battery based on commercial silicon particles for the first time.^[147] Fluoroethylene carbonate (FEC) was introduced in a glyme-based electrolyte to produce a durable and deformable SEI film (**Figure 9a**). It comprises Li_2CO_3 , LiF, organic species, and polyfluorocarbon, endowing the anode with strong resistibility towards oxygen crossover effects and boosting stable cycling capability (Figure 9b). However, the limited Li source in as-fabricated LABs makes it quite challenging to maintain a long lifespan even when good protection of the alloying composite anode from corrosion reaction is realized.

Besides Li-alloying anodes, recently Zhou's group proposed an organic liquid anode of biphenyl Li (Bp-Li) complex to replace the conventional solid-phase Li metal or Li-alloying anode.^[148] When this liquid anode is utilized with a zeolitic imidazolate framework ZIF7 membrane as a separator, the notorious issues associated with Li metal anodes are well addressed (Figure 9c). Bp-Li works as a stable negative electrode at the anode side. The reactivity of Bp-Li with moisture was also studied by dropping H_2O into it, and the results in Figure 9d demonstrate its high resistance to H_2O corrosion. The ZIF-7 serves as an interlayer bridging the cathode and anode sides from the following three aspects: (1) conducting the Li^+ ions during charge/discharge; (2)

preventing the BP-Li liquid anode from shuttling to the O₂ cathode and causing short circuits; (3) constraining RMs at the anode side to get rid of their crossover. Moreover, as-fabricated organic O₂ batteries with Bp-Li anode show a superior rate performance, which benefits from the high electronic/ionic conductivity of Bp-Li and rapid Li⁺ ion transporting capability. It also delivers a high reversible specific capacity of 2000 mAh g⁻¹ at a high current density of 4000 mA g⁻¹ for 100 cycles (Figure 9d).

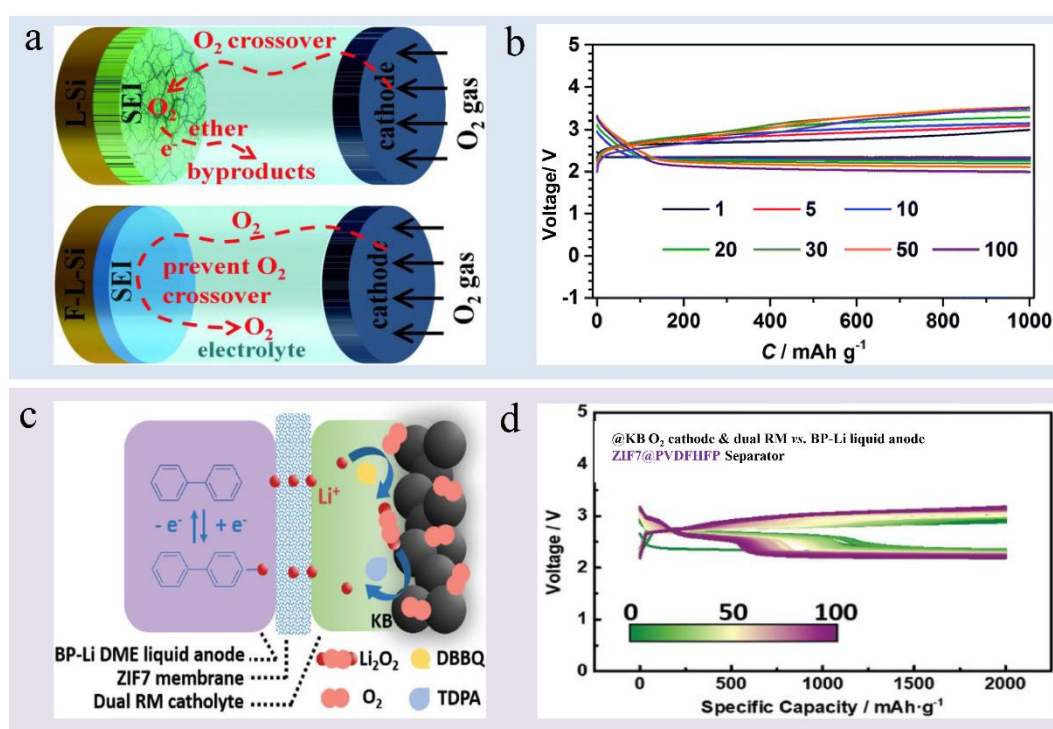


Figure 9. Design of Li-containing anodes for stabilizing the anode interfaces of LABs. (a) SEI film evolution of L-Si and F-L-Si anodes. (b) The discharge/charge curves of LABs with F-L-Si anodes. (reproduced with permission: Copyright 2020, 2016, The Royal Society of Chemistry^[147]). (c) The schematic of the organic Bp-Li-O₂ battery. (d) cycling performance of organic O₂ batteries. (reproduced with permission: Copyright 2020, Wiley-VCH GmbH^[148]).

In summary, recent progress on the rational design of Li anode structure/composition toward alleviated corrosion reaction and stabilized anodic interface has been critically reviewed. Artificial SEI layers impermeable to O₂ and H₂O can protect the Li anode

from parasitic reactions. 3D composite Li enables enhanced mechanical stability and reduced charge/discharge polarization, while other Li-containing anodes, including Li-alloying composite and liquid organic anodes, own lower (electro)chemical reactivity. Despite these advances, there are still numerous challenges to be overcome. Current artificial SEI can only protect the Li anode from the attack of single gas or corrosive species, and multifunctional protective SEI layers are required to inhibit the crossover corrosion. 3D composite Li anodes possess high reactivity and thus poor resistance to corrosion reactions. Li-alloying composites own limited Li source and therefore short lifespan, and liquid organic anodes are exposed to increased risks of cathode/anode contact and subsequent short circuits. Novel Li-containing anodes with smart compositions/structures are urgently needed for future stable AMABs.

5. Design of functional separators

A separator is a permeable membrane placed between the cathode and the anode in LABs, used to prevent internal short circuits of cells while allowing smooth transportation of ionic charge carriers.^[149] Conventional separators in LABs are porous polymeric membranes such as polyethylene (PE) or polypropylene (PP), incapable of suppressing the crossover of atmospheric gases and corrosive RMs from the cathode side.^[54, 55, 150, 151] In recent years, hazardous gases/RMs-blocking functional separators have been exploited to protect the Li anode in LABs.^[152] For example, Choi *et al.* developed a poreless polyurethane (PU) separator in LABs, which prevents H₂O and O₂ from infiltrating and gaining access to the Li anode surface while allowing Li⁺ ions to diffuse through selectively (**Figure 10a**).^[54] The Li⁺ mobility was largely promoted

due to the hydrophilic interaction between the electrolyte and the polar functional groups (Figure 10b). Due to the improved anodic interfacial stability, the LAB with the PU separator exhibited greatly improved cycling performance (Figure 10c). Similarly, Zhang *et al.* in situ fabricate a stable tissue-directed/reinforced bifunctional separator/protection film (TBF) on the surface of lithium metal.^[150] The TBF layer has excellent chemical, electrochemical, and mechanical stability. It effectively protects Li from the corrosion of oxygen species, moisture, and electrolytes, resulting in excellent anode reversibility.

RMs can facilitate the oxidation of Li_2O_2 toward reduced overpotential during charging^[33, 90, 98], yet they might also seriously degrade the Li metal anode through parasitic reactions.^[151] A proper separator design has been proposed to confine the RMs and avoid their shuttling attack on the Li metal anode. For instance, Sun *et al.* coated a polymer mixture of poly(3,4-ethylene dioxythiophene) (PEDOT) and polystyrene sulfonate (PSS) on the commercial glass fiber separator. Its robust Coulombic interaction with RMs effectively suppresses their migration toward the Li metal anode.^[153] Wen *et al.* reported the inhibition of I_3^- shuttling in LiI-involved LABs.^[154] A mixture of MXene nanosheets and bacterial cellulose (BC) nanofibers were loaded onto the glass fiber (GF) membrane (Figure 10e). The -OH functional groups on MXene surfaces served as efficient binding sites to restrain the I_3^- shuttling, and the three-dimensional porous architecture facilitated rapid Li^+ transfer. As a result, the Li anode stability was enormously improved, and the fabricated LAB exhibited a stable cycle life of up to 100 cycles (Figure 10f).

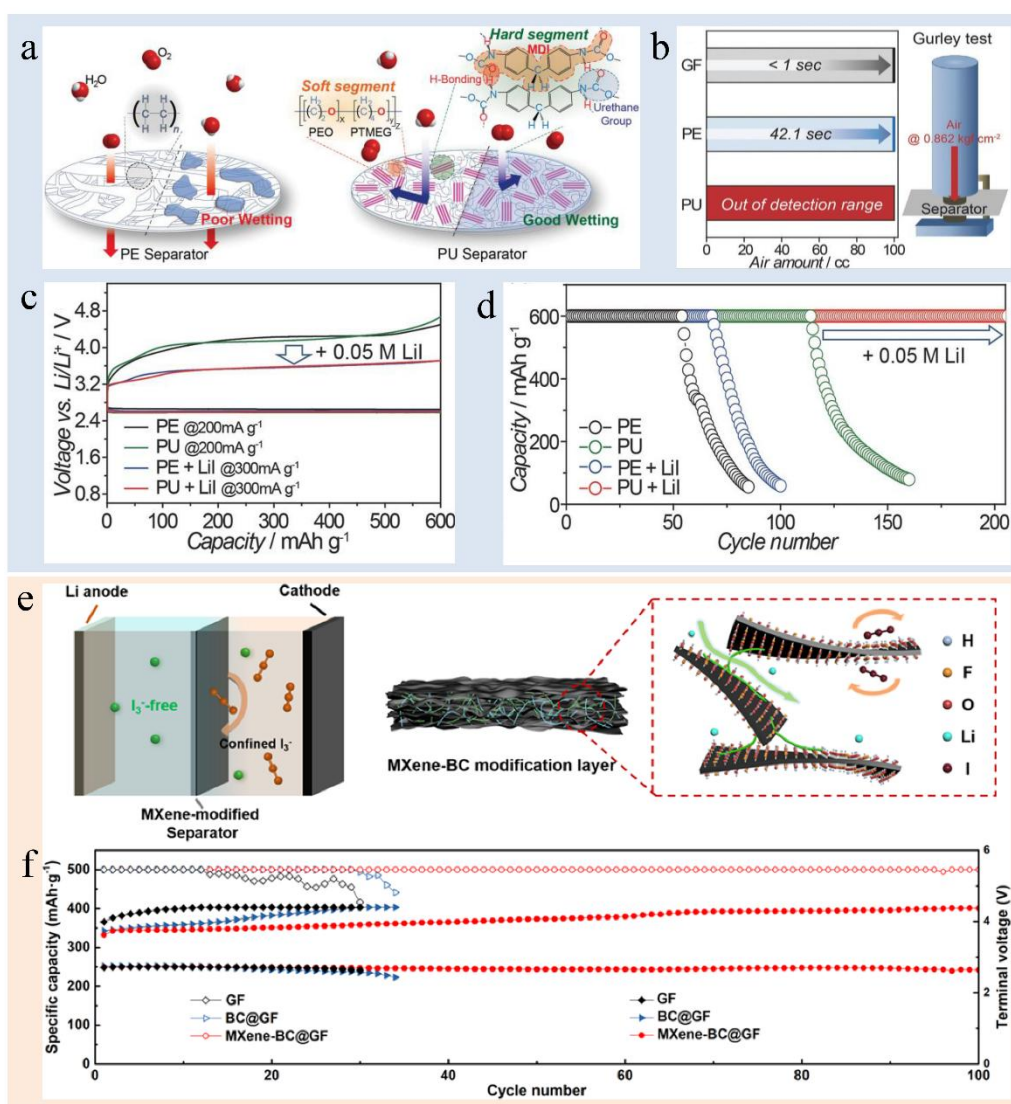


Figure 10. The design of functional separators for stabilizing the anode interfaces of LABs. (a) Illustration of the separator effect on electrolyte wetting and gas/water permeation. (b) The air permeability results of various separators. (c, d) The cycling performance of PE, PU, PE+LiI, and PU+LiI cells. (reproduced with permission: Copyright 2016, Wiley-VCH GmbH^[54]). (e) Schematic illustration of suppressing I_3^- shuttling with the MXene-modified separator in LABs. (f) Terminal discharge voltage of different separators. (reproduced with permission: Copyright 2021, American Chemical Society^[154])

Despite these progresses in developing advanced separators for suppressing corrosive gas/RM shuttling, current separators are mostly single-functional and cannot provide comprehensive protection. Moreover, the limited number of active sites for the

physicochemical adsorption of gas phases/RMs, as well as the difficulty in their sustainable functioning over prolonged charge-discharge cycles, greatly hinder their practical applications. Future development of multifunctional and durable separators in AMABs is highly desirable.

6. Anode interface stabilization in Na/K–air batteries

Na/K–air batteries (NABs/KABs) have been considered promising alternatives to LABs for large-scale energy storage applications because of the low cost and abundant resources of Na/K, as well as quite similar electrochemical properties to the Li counterparts.^[155-158] Nevertheless, the hyperactive Na and K metals are more vulnerable in the atmospheric environment, making it considerably more challenging to handle the aforementioned difficulties in anodic interface stabilization.^[158, 159] Numerous pioneering works have been reported in recent years for developing durable NAB/KAB anodes, among which representative progresses are summarized as follows.

To enable efficient Na plating/stripping in an oxygenated environment, Zhou and co-workers pre-cycled the Na metal anode in the functional electrolyte containing 2 wt.% fluoroethylene carbonate (FEC).^[160] After the preferential reduction of FEC, a durable artificial SEI film rich in NaF has been produced on the tailored Na (Tna) anode, which can efficiently suppress the O₂ crossover and undesirable side reactions (**Figure 11a**). As-constructed NABs with Tna anodes maintain stable cycling for over 300 hours in O₂, while pristine Na (Pna) anodes were short-circuited after 230 hours (Figure 11b,c).

Kang *et al.* developed a liquid Na–K alloy anode for constructing dendrite-free KABs (Figure 11d).^[161] The liquid anode provides a homogeneous and robust liquid–liquid

anode-electrolyte interface, rendering superior stability to the traditional solid–liquid interface. DFT calculations revealed the less favorable interaction of diethylene glycol dimethyl ether (DEGDME) solvents on the Na–K alloy surface (Figure 11e). Therefore, it facilitates uniform K plating/stripping and subsequently helps address the safety concerns derived from the dendrite growth.

Wu *et al.* developed a freestanding 3D sulfur-doped porous graphene network as a reactive armor to protect the K metal anode.^[73] The sulfur dopants in the graphene matrix react with the crossover species like dissolved O₂ and superoxide anions (O₂[−]) to form anionic sulfonates/sulfates, which could serve as active sites for preferential nucleation and growth of KO₂ (Figure 11f). The produced KO₂ layer on the graphene surface protects the crossover oxygen species from etching the inner fresh K metal. (Figure 11g,h). Consequently, the as-constructed K–O₂ battery with the protected K anode realizes a boosted lifespan of 140 stable cycles, three times longer than that of the K–O₂ battery with the bare K anode (Figure 11i).

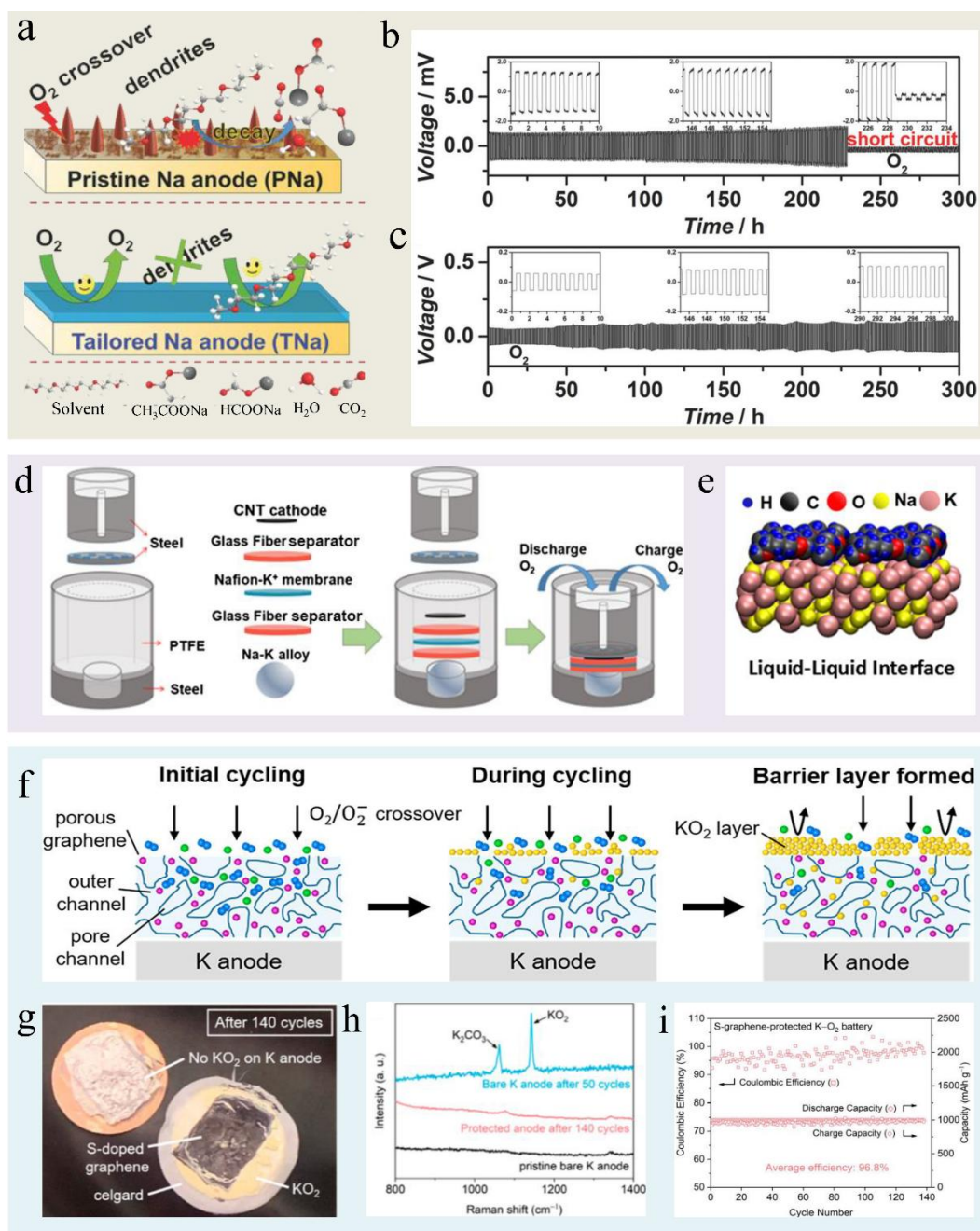


Figure 11. Examples for the stabilization of anode interfaces in Na/K-air batteries. (a) Illustration of problems on pristine Na anode (PNa) in Na- O_2 battery and illustration of improvements on TNa. (b) and (c) The effective resistibility of TNa against O_2 crossover. (reproduced with permission: Copyright 2018, Wiley-VCH GmbH^[160]). (d) K- O_2 battery configuration based on the Na-K liquid alloy as the anode. (e) Lowest energy configuration of a fully covered Na_4K_5 surface with DEGDME solvents (reproduced with permission: Copyright 2017, American Chemical Society^[161]). (f) Schematic illustration of KO_2 barrier layer on the S-doped porous graphene outer surface. (g) S-graphene-protected K anode after 140 cycles (graphene peeled

off). (h) Raman spectra of different anodes after 140 cycles. (i) Cyclability of the S-graphene-protected K–O₂ battery (reproduced with permission: Copyright 2020, American Chemical Society^[73]).

Despite the progress achieved, most of them utilized pure oxygen in the cathode, resulting in sacrificed gravimetric/volumetric energy densities.^[162] The study on stabilizing Na/K anodes in an open environmental atmosphere of NABs/KABs is still in its infancy. Challenges remain in resolving the issues caused by the high chemical reactivity of Na/K-metal interfaces and the uncontrollable morphology evolution of the Na/K anodes. The construction of in-situ/ex-situ protective films on the Na/K anode surfaces and the development of alternative anode materials with higher stability and reversibility are greatly desired.

7. Conclusions and Perspectives

AMABs hold great promise for next-generation electrochemical energy storage because of their ultra-high energy densities. However, the complicated side reactions involved at the solid–liquid–gas triple-phase interface of the anode is a formidable challenge to achieve reversible and durable metal anodes, which become a bottleneck hindering the practical applications of AMABs. In this timely review, we have critically summarized the major issues associated with the triple-phase anodic interface of AMABs, including (1) the crossover of mixing gas phases/RMs and subsequent severe parasitic reactions with the metallic anode; (2) the interference of the O₂ electrochemistry by reactive oxygen intermediates (O₂^{•-}, O₂²⁻, and ¹O₂); (3) the deterioration of uneven metal deposition and SEI inhomogeneities. Various strategies

developed to mitigate the above challenges have been comprehensively reviewed, mainly including (1) novel liquid/solid electrolyte formulation; (2) artificial SEI construction on metal anodes and Li-containing anode design; and (3) functional separator modification. These efforts have greatly improved the stability of the anode interface in AMABs.

Despite these advances, the development of stable metal anodes in AMABs is still in its infancy before the following concerns are well tackled. (i) Most liquid electrolytes developed so far have the singular function of either forming native protective SEI or boosting the intrinsic anti-corrosion capability, but the improvement of anode reversibility is far from satisfactory. Their evaporation/leakage in the open system poses another severe concern against sustainable battery operation. (ii) Integrated design of solid electrolytes and metal anodes enabling effective interfacial contact remains a significant challenge. (iii) The constructed artificial SEI layer on the metal anode shows a limited thickness and thus decelerates the ion transfer kinetics and deteriorates the electrochemical performance of AMABs. Moreover, it's still a great challenge to achieve controllable and scalable preparation of artificial SEI on highly reactive alkali metal anodes. (iv) Rational design of the anode structure/composition like 3D composite Li and Li-containing compounds can not fully eliminate the attacks by corrosive gases/intermediates/RMs; (v) It is extremely difficult to develop multifunctional separators to effectively shield corrosive gas/RM towards sustainable operation of AMABs.

The electrochemical processes involved at anode interfaces are complicated and

highly interrelated, making it unlikely to address all the above challenges by regulating individual components. Stabilizing the anodic interfaces is thus expected to be achieved from a systems engineering perspective. We present potential future research directions toward more durable metal anodes in AMABs as follows (**Figure 12**).

(1) *A more accurate understanding of the reaction mechanism at anode interfaces.*

Although many studies have uncovered the underlying interfacial reaction mechanism of metal anodes in a single O₂ atmosphere, that under an open atmosphere with mixed gases is much more complicated and yet to be revealed. Consequently, gaining a sophisticated understanding of metal anode degradation in the real working environment is highly desirable. The development of advanced experimental techniques and multiscale modeling methods is urgently needed. A recent study has revealed the correlation between the morphological evolution of the Li anode and the electrochemical performance of LOBs by complementary X-ray and neutron tomography.^[94] Cutting-edge operando characterization techniques, such as low-dose TEM imaging and X-ray computed tomography, allow direct probing of real-time electrochemical reactions at varying temporal and spatial scales. Further, by coupling with multiscale modeling methods like DFT, molecular dynamics (MD), and machine learning, a more accurate understanding of the reaction pathway and the composition evolution of electrolyte components/metal anodes/oxygen species during charge/discharge can be established. As such, more potential strategies can be proposed to precisely regulate/stabilize the anodic interfaces.

(2) *A collaborative design of advanced electrolytes and anodes.* It is essential to

consider the anode and electrolyte as an entity for achieving optimal components, microstructure, and electrochemical properties of anodic interfaces. By adopting such a holistic design approach, we can ensure that the resulting interface is well-suited to the specific requirements of the AMAB system with improved functionality and reliability. For instance, the rationally structured metal anodes coupled with properly formulated electrolytes allow the dynamic formation of protective SEI layers, enabling homogenized metal deposition and continuously alleviated interfacial parasitic reactions. The integrated design of the alkali metal anode and solid electrolyte can improve the interfacial contact and facilitate the interfacial charge transfer process in solid-state AMABs. More future research efforts are expected to be devoted to the synergistic optimization of the anode structure/composition and electrolyte formulation, which will more effectively stabilize the anodic interface, thus boosting the lifespan of AMABs.

(3) *Systems materials engineering for stabilizing the anodic interfaces.* Examining separated components is insufficient to address the scientific and technological challenges of the complicated AMAB system. Great attention should be drawn to investigating the interfaces between individual components. Systems materials engineering integrating individual components into an entire and functioning system can thus be far more effective for stabilizing the anode interfaces.^[163] The pioneering work by Yu *et al.* has constructed an integrated cathode–electrolyte–anode system with well-defined interfaces, providing a more coherent continuum among the anode, electrolyte, and cathode.^[74] Such a comprehensive system-level design is expected to

help address all challenges confronting AMABs. Therefore, after the whole cell system is evaluated as an entirety and practical performance indicators are considered, it will pave the way for their large-scale applications.^[164]

(4) *Exploration of alternative chemistries for more durable anodes in AMABs.* The investigation of new chemistries is expected to mitigate the stability challenges of anodic interfaces in AMABs. Replacing Li metal anodes based on Li plating/stripping with Li-containing compound anodes based on Li intercalation^[165] or conversion reaction^[72] could achieve improved safety, fast kinetics, and high reversibility while maintaining the low redox potential. Sealed rechargeable lithium–lithium oxide battery^[166] based on reversible interconversion between superoxide (LiO_2) and lithium peroxide (Li_2O_2) can avoid the use of gas-phase cathodes, simplifying the triple-phase interface in conventional AMABs, thus significantly alleviating the difficulty in stabilizing the anode interface. These new battery systems can therefore mitigate the degradation of cathodes, decomposition of electrolytes, and corrosion of metal anodes toward more durable AMABs. Research works in this area are in their very early stages, and more innovative efforts and designs are highly required.

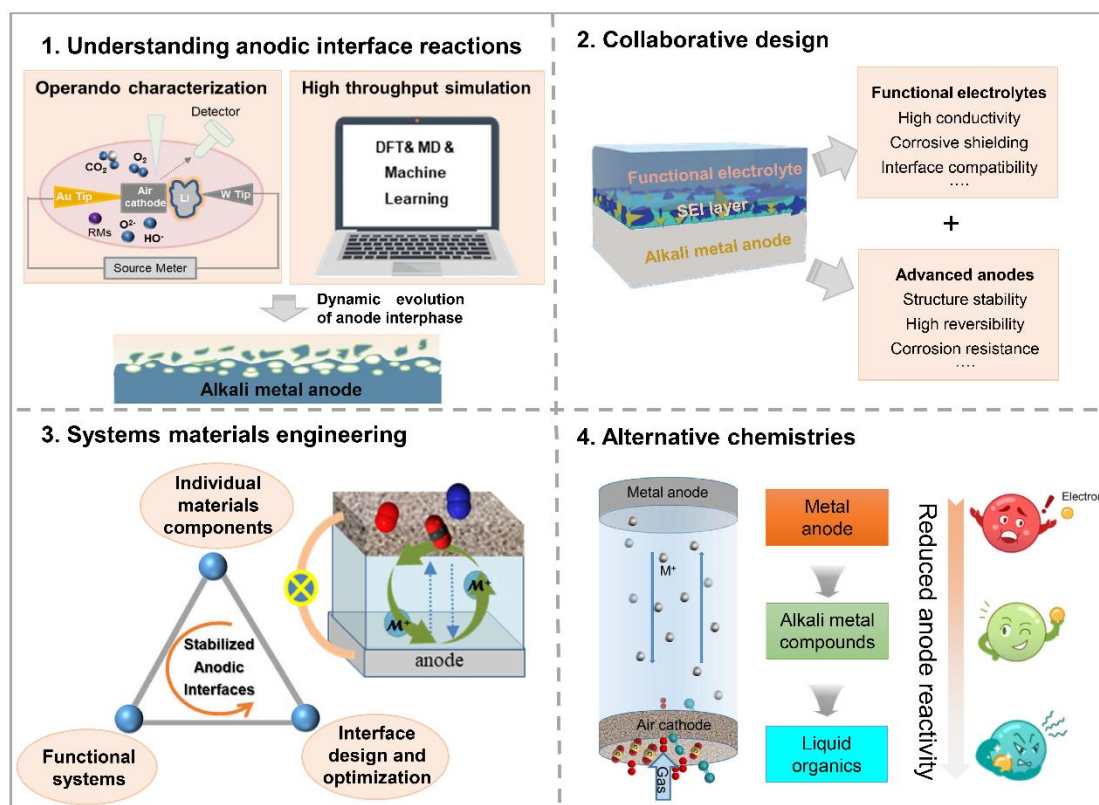


Figure 12. Outlook for the development of high-performance AMABs in the future.

Based on previously reported results and the above discussions, we conclude that there are no “one for all” strategies to address all challenges associated with the triple-phase interface of anode in AMABs. The individual components should be collaboratively designed in a systems engineering manner. While it is critical to accurately understand the reaction mechanism at anode interfaces, the investigation of new materials and new chemistries is highly encouraged. Despite numerous scientific and technological issues, this perspective is expected to provide guidelines to clarify the relationships among material composition/property, anodic interfacial behavior, and battery performance in the open system for rationally designing practical next-generation AMABs.

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Conflict of Interest

The authors declare no conflict of interest.

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