

## Li–air batteries: air stability of lithium metal anodes

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Aprotic rechargeable lithium–air batteries (LABs) with an ultrahigh theoretical energy density (3,500 Wh kg<sup>-1</sup>) are known as the ‘holy grail’ of energy storage systems and could replace Li-ion batteries as the next-generation high-capacity batteries if a practical device could be realized. However, only a few researches focus on the battery performance and reactions in the ambient air environment, which is a major obstacle to promote the practical application of LABs. Here, we have summarized the recent research progress on LABs, especially with respect to the Li metal anodes. The chemical and electrochemical deteriorations of the Li metal anode under the ambient air are discussed in detail, and the parasitic reactions involving the cathode and electrolyte during the charge–discharge processes are included. We also provide stability perspectives on protecting the Li metal anodes and propose design principles for realizing high-performance LABs.

**parasitic reaction, lithium metal anode, anode protection, Li–air batteries**

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### 1 Introduction

In the past few decades, various rechargeable battery technologies have been developed, such as lead–acid batteries, zinc–manganese batteries, nickel–metal hydride batteries, and lithium-ion batteries (LIBs) [1]. Among them, the rapid development of LIBs makes them play increasingly important roles in electric vehicles, portable electronic devices, and large-scale energy storages, which affects almost every aspect of our lives [2–4]. Also, their tremendous success enables the pioneers of LIBs to win the 2019 Nobel Prize in Chemistry. However, as the quest for high-energy-density batteries is extremely urgent and the LIBs technology almost reaches their upper energy density limit, there is now a strong appeal to develop high-capacity successors to replace LIBs [5]. To this end, new electrochemical energy storage systems have been actively explored to achieve higher energy density.

Since the theoretical energy density of aprotic lithium–oxygen batteries (LOBs) far exceeds the LIBs (Figure 1a), they have been considered as the most promising alternatives to LIBs [6]. LOBs were first proposed by Abraham in 1996 [7], and until 2012, they started to attract worldwide attention as a reversible secondary battery system [8]. Aprotic LOBs with lithium metal as the anode and oxygen as the active cathode substance are based on the reversible formation and decomposition of Li<sub>2</sub>O<sub>2</sub> (2Li+O<sub>2</sub>↔Li<sub>2</sub>O<sub>2</sub>), and Li<sub>2</sub>O<sub>2</sub> as the discharge product usually grows on the porous cathode [9]. Although it is simple, this electrochemical reaction faces many challenges for practical applications, including the instability of Li metal anodes, electrolytes, and air cathodes. Also, in the ambient air, the discharge products gradually change from Li<sub>2</sub>O<sub>2</sub> to LiOH and Li<sub>2</sub>CO<sub>3</sub> due to the presence of moisture and CO<sub>2</sub>. During the charging, the LiOH and Li<sub>2</sub>CO<sub>3</sub> are hardly to be decomposed, leading to the increase of charge overpotential and consequently resulting in the decomposition of electrolytes. This would increase the complexity of the reaction mechanism and deteriorate the

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stability of the battery. So far, LOBs have achieved significant advances in air cathodes and electrolytes, while insufficient attention has been paid to tackle the chemical and electrochemical deteriorations of the Li metal anodes, especially in the ambient air [10]. As can be seen from the scheme of lithium–air batteries (LABs) (Figure 1b), the moisture, gases, and even dust in the ambient air are prone to diffuse to the anode side to attack the Li metal anode of LABs. Not only that, the additives and reactive intermediates in the electrolyte could also corrode the Li metal anodes. These challenges make the long-term running of LABs just wild wishes. To realize practical LABs, it is urgent to develop new strategies to improve the stability of Li metal anodes not only in the reactive environment of LOBs, but also in the ambient air.

In this review, we focus on the stability of Li metal anodes in the LABs, including the reaction mechanisms of Li metal with the air components, such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the effects of electrolytes and additives on the Li anodes, and the currently available anode protection strategies. Real progress has been made in understanding the fundamental science underpinning of LABs, which explains why many previous results led to the conclusion that LABs would be difficult to move toward practicality. However, new researches on Li metal anode protection have revealed that this is not necessarily the case. No one knows when high-performance commercial LABs will be realized, but the development of truly stable Li metal anodes will make the LABs one step closer to practical applications.

## 2 The challenges of Li metal anodes

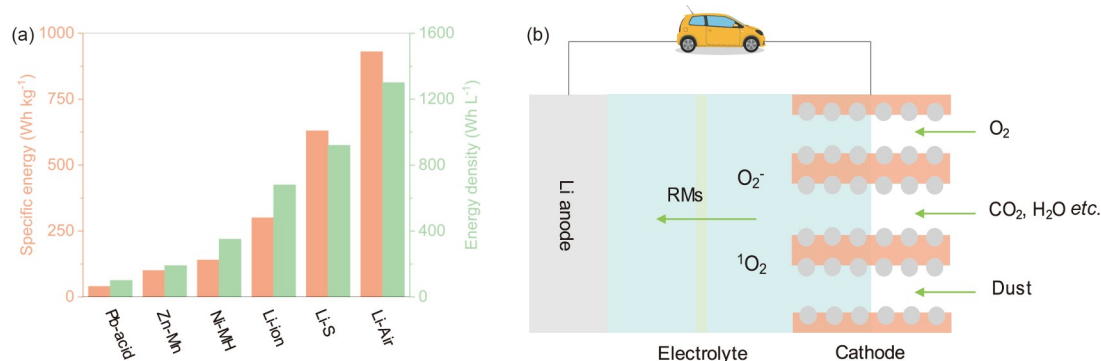
The unique semi-open structure of LABs would inevitably permit the moisture and gases to diffuse into the electrolyte during the operation [11]. Furthermore, the strong nucleophilic species, such as  $\text{O}_2^-$  and singlet oxygen, will generate during the discharge/charge process of LABs and then attack the electrolytes, resulting in their decomposition with the

production of a series of byproducts [12–15]. Likewise, some organic binders used to assemble air cathodes will also be degraded due to the  $\text{O}_2^-$  attack [16]. For the carbon-based materials, they could undergo side reactions when the charge voltage surpasses 3.5 V or in the presence of lithium peroxide [17–20]. Functional additives introduced into the electrolytes, e.g., redox mediators (RMs), could shuttle to the anode side to corrode the Li metal, and their stability toward the oxidative intermediates of LABs is still need further confirmed [21,22]. Since the separator can hardly prevent the air or the above decomposed dissolved active components diffusing from the air cathode to the Li anode, a series of parasitic reactions would occur at the Li surface with the continuous consumption of active Li and the formation of  $\text{LiOH}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{ROCO}_2\text{Li}$ , etc., significantly reducing the lifetime of LABs [23,24]. In order to promote the practicality of LABs, it is urgent to conduct in-depth research on the protection for Li metal anodes in the ambient air and should also pay more attention on the oxygen selectivity membrane (OSM) to avoid Li active species entering the LABs.

### 2.1 Reactive components toward Li metal anodes

#### 2.1.1 Water

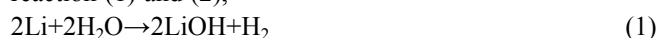
LABs are highly sensitive to water. Numerous studies have shown that even a small amount of water could have a significant impact on the reaction mechanism of LABs [25,26]. There are two recognized sources of water in LABs: moisture in the ambient air and the decomposition of electrolytes. The influence of water on LOBs includes three aspects: (1) increasing the discharge voltage platform; (2) changing the morphology of  $\text{Li}_2\text{O}_2$  discharge product with enlarged discharge capacity; (3) corroding the Li metal anode. In some cases, with a limited amount of  $\text{H}_2\text{O}$ , the effects of the first two could play a leading role. Aetukuri *et al.* [26] discovered that the discharge capacity of LOBs was enhanced by more than 4 times as the  $\text{H}_2\text{O}$  concentration increased from 200 ppm to 2,000 ppm. The  $\text{Li}_2\text{O}_2$  discharge product showed



**Figure 1** (a) Bar chart showing the practical gravimetric and volumetric specific energy densities of different battery systems. All of the battery components are taken into account. (b) The scheme of a LAB (color online).

a large annular shape, and the size and crystallinity were both improved, which was consistent with the increased capacity.

Although an appropriate amount of water could bring positive effects on the discharge capacity, it has an immeasurable impact on the cycling performance of LOBs. For example, Cho *et al.* [27] connected six Li–O<sub>2</sub> cells in series, and the anhydrous O<sub>2</sub> gas passed through the cells sequentially (Figure 2a). After the first discharge, the Li metal anodes of the first three series-connected cells were black due to the reactions with O<sub>2</sub> (Figure 2b). By contrast, the Li metal anodes of the latter three cells were gray due to the LiOH generation. This result suggests that the water amount in the electrolyte is enriched during the discharge. According to reaction (1) and (2),

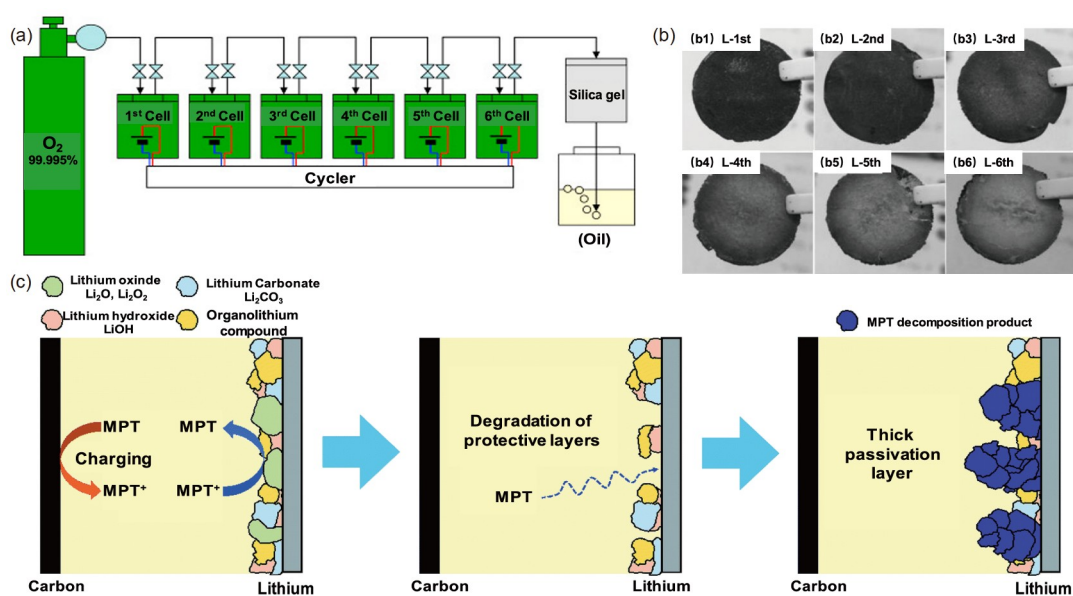


when water diffuses to the Li metal anode, LiOH is spontaneously formed on the Li anode surface, leading to increased interface impedance and charging overpotentials, and triggering a series of side reactions, such as active Li loss, electrolyte decomposition, threatening the long-term operation of LABs. Not only in LABs, the storage, transportation, and production of Li metal are also facing challenges. For example, the Li metal is typically sealed in the solid paraffin wax to preserve it from the corrosion. And inspired by this strategy, Yang *et al.* [28] proposed a wax-based coating to protect the Li metal for improving the battery performance. In laboratory, the Li metal is usually used and stored in the glove boxes filled with argon, and the water content is strictly controlled to be less than 0.01 ppm. The drying room used to assemble Li metal batteries also

keeps the dew point temperature below  $-50\text{ }^\circ\text{C}$  (relative humidity of 0.1%). Similarly, to avoid burning or exploding, soft-pack batteries need to be tested in a safe chamber filled with inert gases. For safe transportation of Li metal products, they are usually sealed in an aluminum-plastic film filled with inert gases and placed in a strong chamber. Due to the rigorous requirements of storage and use of Li metal, there is an urgent need to design air-stable Li metal, so as to promote the development of LABs.

### 2.1.2 Inactive gases in the air

The surface reactions of Li metal with various gases have been studied since 1895 [29]. The initial research interest focused on the interactions of the air and its individual component, like O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>, with Li metal [30]. These pioneering studies concluded that the Li metal did not react with dry N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> at temperatures below 160 °C, 250 °C, and 300 °C, respectively, indicating that the oxidation rate of Li metal was low in the dry gases even at high temperatures. Different from these earlier studies, the recent research exhibited contradictory results that the Li metal would be oxidized even in a dry atmosphere [31,32]. In order to clarify it, Etxebarria *et al.* [33] studied the reaction of Li metal with dry O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> via X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and density functional theory (DFT). The results show that the Li metal could react violently with dry oxygen to produce Li<sub>2</sub>O and also confirm that Li metal does not react with dry N<sub>2</sub>. For CO<sub>2</sub>, its reaction with Li metal would produce low-reactive carbon-based compounds on the Li metal surface, and thus slow down the CO<sub>2</sub> induced oxida-



**Figure 2** (a) Schematic diagram of the O<sub>2</sub> flow and cell connections. (b) Photographs of the Li metal anodes after the 1<sup>st</sup> discharge. (c) Schematic of the failure mechanism of the Li–O<sub>2</sub> cell with 10-methylphenothiazine (MPT). (a, b) Reprinted with permission from Ref. [26], Copyright 2014, Elsevier. (c) Reprinted with permission from Ref. [47], Copyright 2017, the Royal Society of Chemistry (color online).

tion of Li. Meanwhile, the XPS result demonstrates that the formation of carbon-based compounds accompanied with  $\text{Li}_2\text{O}$ , and these carbon-based compounds could not be detected when the concentration of  $\text{CO}_2$  is low (Figure 3a, b), indicating that the Li metal could be used in the absolutely dry  $\text{CO}_2$ . Chen *et al.* [34] found that the main discharge product of the battery was  $\text{Li}_2\text{O}_2$  when the  $\text{CO}_2$  concentration was below 100 ppm, and the high concentration of  $\text{CO}_2$  (>100 ppm) would promote the transformation of  $\text{Li}_2\text{O}_2$  to  $\text{Li}_2\text{CO}_3$ , resulting in electrode surface passivation. However, the effect of  $\text{CO}_2$  on the electrochemical performance could be ignored when reducing its concentration below 100 ppm. Furthermore, to shed light on the reaction pathway of  $\text{Li}_2\text{CO}_3$  growth on the Li metal surface, the reaction between Li metal and  $\text{CO}_2$  was studied by the *in-situ* characterization of ambient pressure X-ray photoelectron spectroscopy (APXPS) [35]. The results found that the oxalate as an intermediate was responsible for the formation of carbonates. Firstly, the primary lithium-based substances were observed on the Li surface and then followed by a layered structure of lithium carbonate on the top of the lithium oxide (Figure 3c, d). The reaction mechanism of the growth of  $\text{Li}_2\text{CO}_3$  on Li metal was also proposed (Figure 3e, f). The above discussion shows that a stable SEI layer composed of  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  could be formed on the surface of Li metal in a dry air environment, which prevents the further corrosion of Li metal. Therefore, LABs can be assembled in a drying room with a dew point temperature below  $-50\text{ }^\circ\text{C}$  (relative humidity of 0.1%).

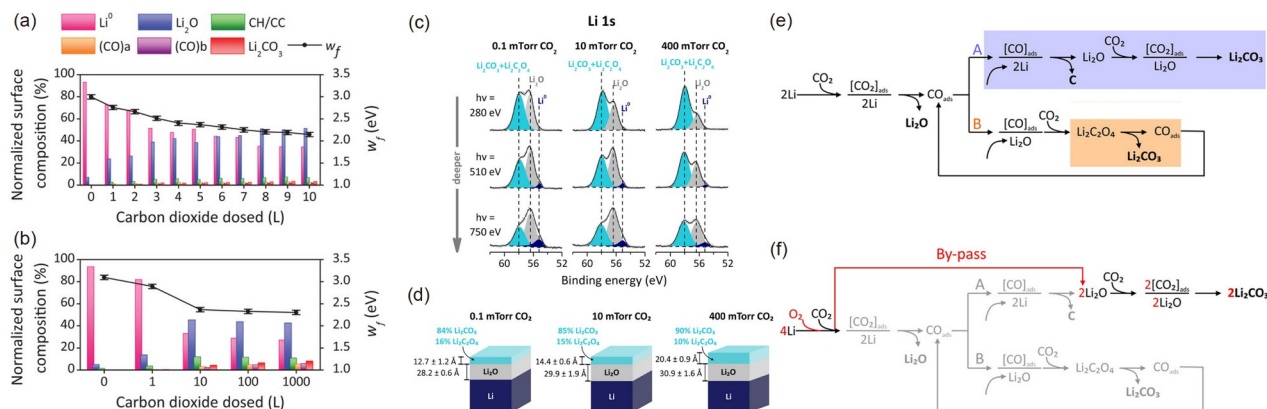
The above situation is different when water is involved. For example, the Li metal could react with  $\text{N}_2$  to produce a brown-red  $\text{Li}_3\text{N}$  surface layer when the water content is beyond 10 ppm [36,37]. Similarly, the  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  protection layer could hardly inhibit the infiltration of water molecules, and both  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  could participate in the reaction with water, which is accompanied by the color

change to black ( $\text{LiOH}$ ) and eventually white ( $\text{LiOH}\cdot\text{H}_2\text{O}$ ) [38]. The water-induced reactions between Li metal and various gases are summarized in Table 1.

Based on the above conclusions, besides the active  $\text{O}_2$ , the inactive components in the air, like  $\text{N}_2$  and  $\text{CO}_2$ , would also bring great troubles to the Li anode in LABs. As the active material of the cathode side, the  $\text{O}_2$  could also diffuse to the anode side to oxidize the Li metal. For  $\text{CO}_2$ , its effects are more brutal, despite its low concentration in the air. Since the solubility of  $\text{CO}_2$  is several times higher than that of  $\text{O}_2$  in the organic solvent of the electrolytes, the discharge product of  $\text{Li}_2\text{O}_2$  and its intermediates will react with  $\text{CO}_2$  to form lithium carbonate (a wide-bandgap insulator), leading to higher charge potentials (>4.0 V) and consequently more side reactions from the cathode and electrolyte and intensified corrosion of Li metal anodes [17]. In addition, the  $\text{CO}_2$  could also diffuse to the Li metal anode and produce a  $\text{Li}_2\text{CO}_3$  passivation layer, reducing the energy efficiency of LABs. However, our recent work not only demonstrated that the  $\text{CO}_2$ -rendered  $\text{Li}_2\text{CO}_3$  passivation layer could protect the Li anode from  $\text{H}_2\text{O}$  corroding, but could also suppress the side reactions involving the electrolyte and cathode by trapping  $\text{O}_2^-$  with  $\text{CO}_2$ , enabling the  $\text{Li}-\text{O}_2/\text{CO}_2$  batteries to run stably over 715 cycles [39]. For  $\text{N}_2$ , it could react with Li to form  $\text{Li}_3\text{N}$ , an effective SEI component to protect the Li anode, in the presence of water. However, the water is also reactive with  $\text{Li}_3\text{N}$  to produce the dangerous gas  $\text{NH}_3$  [33]. Therefore, in all links of the entire LAB manufacturing, it is necessary to pay attention to the water content at all times.

### 2.1.3 Electrolytes

The electrolyte is composed of organic solvents, lithium salts, and sometimes even additives, and its stability is affected by the properties of all the components. Early researches on LABs were mainly used liquid carbonate-based



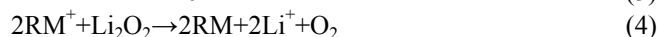
**Figure 3** Reaction characteristic analysis of Li metal and  $\text{CO}_2$ . The normalized surface composition (left vertical axis) and work function evolution (right vertical axis) of metallic Li foil with different doses of  $\text{CO}_2$ : (a) low dose range from 0 to 10 L and (b) medium dose range from 10 to 1,000 L. (c) Li 1s XPS spectra of Li foil treated at three different pressures of  $\text{CO}_2$  gases. (d) Diagram of Li surface composition distributions. (e) Pathway of the reaction of  $\text{CO}_2$  gas with the Li metal. (f) Pathway of the reaction of  $\text{CO}_2$  and  $\text{O}_2$  gases with the Li metal. (a, b) Reprinted with permission from Ref. [33], Copyright 2020, Wiley-VCH GmbH. (c-f) Reprinted with permission from Ref. [35], Copyright 2020, Wiley-VCH GmbH (color online).



**Table 1** The reactions between Li metal and various gases with or without water

Reaction substance	Without water	With water
O <sub>2</sub>	Li+O <sub>2</sub> →Li <sub>2</sub> O	Li+O <sub>2</sub> →Li <sub>2</sub> O Li <sub>2</sub> O+H <sub>2</sub> O→LiOH
CO <sub>2</sub>	2Li+2CO <sub>2</sub> →Li <sub>2</sub> CO <sub>3</sub> +CO	2Li+2CO <sub>2</sub> →Li <sub>2</sub> CO <sub>3</sub> +CO Li+H <sub>2</sub> O→LiOH+H <sub>2</sub> 2LiOH+CO <sub>2</sub> →Li <sub>2</sub> CO <sub>3</sub> +H <sub>2</sub> O
N <sub>2</sub>	Hardly reaction	6Li+N <sub>2</sub> →2Li <sub>3</sub> N Li <sub>3</sub> N+3H <sub>2</sub> O→3LiOH+NH <sub>3</sub>

electrolytes [40,41]. However, this kind of electrolytes decomposed irreversibly and produced by-products in the strong oxidative environment of LABs, making the LABs with poor reversibility [1,12]. Then, different kinds of electrolytes with improved stability were explored. Considering the insulating and insolubility of Li<sub>2</sub>O<sub>2</sub> discharge product, when designing the electrolytes, most of studies considered how to change the discharge product morphology to get increased discharge capacity, but ignored the stability of Li anodes in the electrolytes. For example, based on the concept of hard and soft acid-base (HSAB) theory by Pearson, the high donor number (DN) solvents could favor the dissolution of the discharge intermediate, like LiO<sub>2</sub>, to generate large Li<sub>2</sub>O<sub>2</sub> particles and thus a larger capacity. Therefore, various solvents with high DN values, such as DMSO and DME, were adopted to prepare the electrolytes. Nevertheless, considering that the superoxide is a strong nucleophilic attack reagent, the enhanced solubility of superoxide generally makes the solvent more susceptible to nucleophilic attack or proton extraction, as a result, producing more by-products that threaten the Li anode. Furthermore, to alleviate the high charge potential-induced cathode and electrolyte decomposition, redox mediators (RMs) were developed (such as TTF [42], DBBQ [43], TEMPO [44], LiI [45]). The mechanism of how RM facilitates the decomposition of Li<sub>2</sub>O<sub>2</sub> is shown in the reaction equation (3) and (4). It is true that RMs have unique advantages in changing the decomposition paths of Li<sub>2</sub>O<sub>2</sub>, significantly reducing the charge overpotential with suppressed side reactions. Despite the advantages, the mobile nature of RMs could corrode the Li anodes, and their stability toward the oxidative intermediates of LABs is still a challenge [46], rendering the continuous consumption of RM in the cycling process. For example, Ha *et al.* [47] found that the function of 10-methylphenothiazine (MPT) was gradually weakened during the cycling in LABs. The MPT is first oxidized to MPT<sup>+</sup> on the cathode side, and then diffuses to the Li anode and is reduced with the formation of thick passivation layers on the Li anode surface (Figure 2c). Although RMs can significantly reduce the charge overpotential, the cycle performance of LABs is not evidently improved.



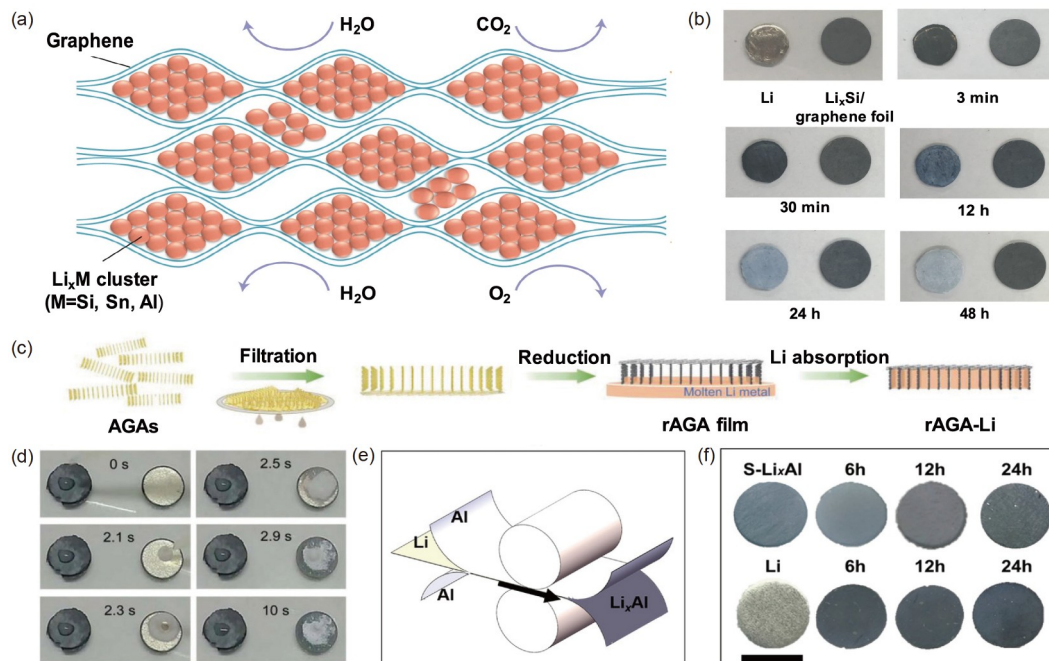
### 3 Strategies to improve the air stability of Li metal anodes

Since we know that the Li metal anode faces severe challenges in LABs, the question is how to protect it to enable the high-performance operation of LABs. To this end, there have been developed several strategies for the protection of Li anodes, such as surface design [48–52], Li metal alloys [53–55], electrolyte engineering [56–58]. Although these strategies have improved the stability of Li metal anodes to some extent, only relying on the anode protection is not enough to change the predicament of LABs. We should focus on the research of the whole LAB system by improving the stability of the cathode, electrolyte, and Li anode, and reducing the concentration of inactive gases and H<sub>2</sub>O entering the LABs simultaneously.

#### 3.1 Li composite anode design

Considering the large volume change, unstable interface, and dendrite growth of Li anode during repeated plating/stripping, confining the Li into an active/inert host has been demonstrated to be an effective approach to alleviate the above issues [59]. Especially, the architectural design of Li composites and Li metal alloys could accommodate the volume change and guide uniform Li plating/stripping at high current densities. However, the use of low-capacity active or inactive host materials would bring about the reduction of battery-operating voltage and energy density.

For improving the air stability of Li metal anodes, we could design hydrophobic host materials since they could provide a shielding effect for preventing the internal lithium from the corrosion by the air components. Among the reported hydrophobic hosts, the graphene could act as effective frameworks of Li or Li metal alloys to suppress the dendrite growth and air/water infiltration. For example, Cui *et al.* [60] reported a series of lithium-containing foils consisting of densely pack Li<sub>x</sub>M (M = Si, Sn, or Al) nanoparticles that were encapsulated by graphene sheets (Figure 4a). These Li<sub>x</sub>M/graphene foils remained stable in the ambient air for 2 days (Figure 4b) due to the protection of graphene sheets. To prevent the air corrosion of Li metal, Dong *et al.* [61] designed a layered-structure Li metal anode that combined a vertical stratiform host and a hydrophobic surface layer (Figure 4c). Benefiting from the protection of the hydrophobic graphene, the rAGA-Li exhibited the ultra-high stability in contact with water when exposed to the air (Figure 4d). Further, Li *et al.* [62] found that the Li<sub>x</sub>Al alloy possessed outstanding air stability. After exposure to the humid



**Figure 4** (a) Schematic illustration of the unique  $\text{Li}_x\text{M}$ /graphene structure. (b) Photographs of the Li metal and  $\text{Li}_x\text{Si}$ /graphene foils exposed to the ambient air for different times. (c) Schematic illustration of the fabrication procedures of rAGA-Li. (d) Optical images of the time-dependent evolution of rAGA-Li (left) and Li foil (right) after direct contact with water. (e) Scheme of the industrial production process of roll-to-roll prelithiation of the Al foil. (f) Photographs of the S- $\text{Li}_x\text{Al}$  foil and fresh Li foil exposed to the air after different times. (a, b) Reprinted with permission from Ref. [60], Copyright 2017, Springer Nature. (c, d) Reprinted with permission from Ref. [61], Copyright 2020, Wiley-VCH GmbH. (e, f) Reprinted with permission from Ref. [62], Copyright 2021, Wiley-VCH GmbH (color online).

air for 24 h, the color of the  $\text{Li}_x\text{Al}$  foils only slightly changed, while the Li metal was completely oxidized (Figure 4e, f). For  $\text{Li}_x\text{Sn}$  alloy, a similar phenomenon was also discovered [63]. Although these results indicate that the air stability of the Li anode could be improved by introducing hydrophobic host or alloying, the feasibility of these strategies in LABs is questionable, as Li metal anodes would be also attacked by oxidative intermediates  $\text{O}_2^-$  [64] and RMs in LABs.

### 3.2 Surface protection of Li metal anodes

Before the Li metal can become a viable anode in LABs, the challenge of Li corrosion needs to be overcome. Although the structure and composition design could enhance the air stability of Li, it still can hardly make the Li metal avoid the attack from the Li activity components during battery cycling. To deal with these issues, we need to get a deeper understanding of the Li corrosion mechanism in LABs and put forward effective strategies. Since the concept of solid electrolyte interphase (SEI) was proposed by Peled in 1979 [65], the SEI formed by the spontaneous reaction of Li metal and electrolytes has become an issue part of battery research [66,67]. Owing to the high chemical/electrochemical reactivity of Li metal, almost all electrolytes could be reduced to form a stable SEI and then passivate the Li anode. Although the construction of a stable SEI in Li metal batteries can inhibit the growth of Li dendrites and alleviate the as-

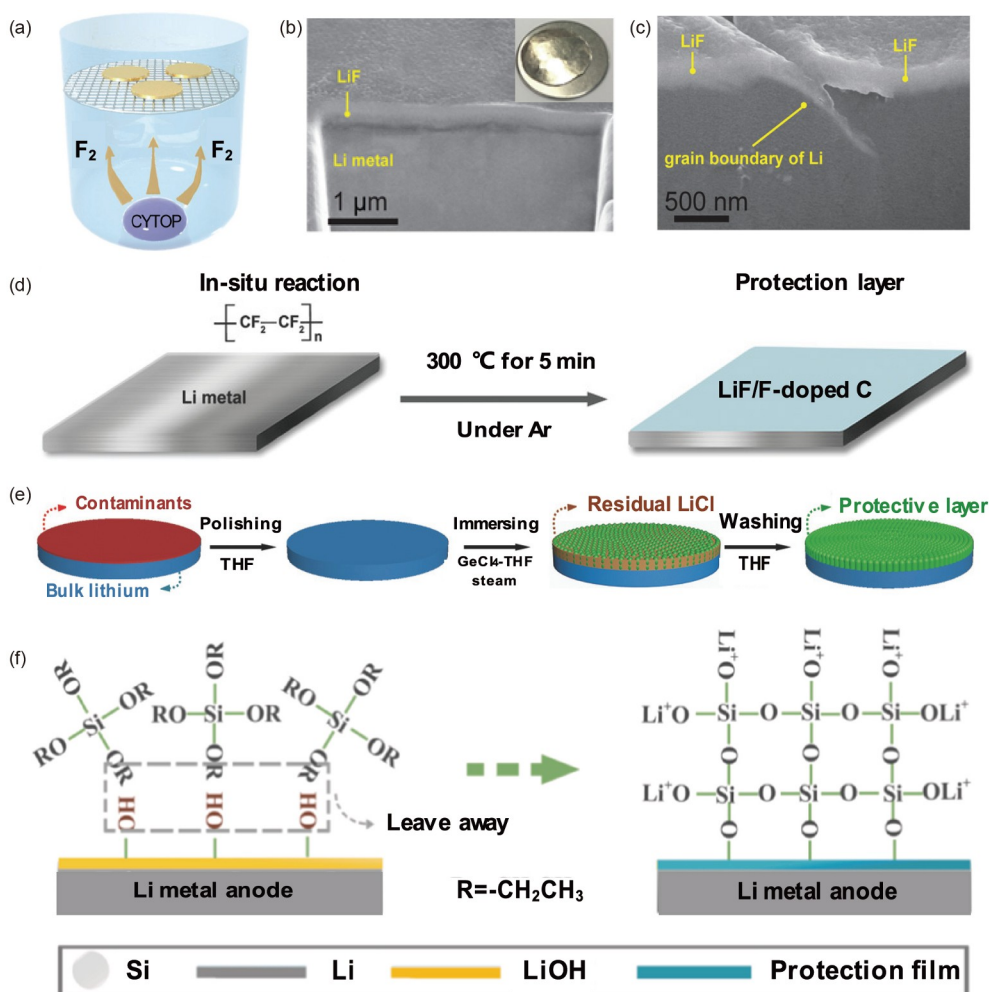
sociated side reactions, designing a stable SEI for the Li anodes in LABs is complicated due to their semi-open nature and high oxidative environment, especially in the presence of water. In pure oxygen atmosphere, Aurbach *et al.* [68] found that the SEI components mainly included  $\text{Li}_2\text{O}$ , LiF,  $\text{Li}_2\text{CO}_3$ , and carbonate substances. Togasaki *et al.* [69] found that a trace of  $\text{H}_2\text{O}$  could regulate the SEI components and produce  $\text{Li}_2\text{CO}_3$  and LiF layers to prevent the occurrence of side reactions during cycling. Similarly, Zhang *et al.* [70] revealed that trace amounts of water (25–50 ppm) could facilitate the formation of homogeneous and dense LiF-rich SEI layers on the surface of Li metal anodes. When increasing the water content, the SEI gradually became a porous layer dominated by LiOH, which was difficult to prevent the reaction of fresh Li metal with the active components in LABs. Therefore, a stable SEI layer not only needs to passivate the Li anode and prevent Li dendrites growth, but the most key character is water resistance. In this consideration, a SEI layer with sufficient hydrophobicity and electrolyte permeability may realize the full protection of Li metal anodes. An ideal SEI protective layer should have the following characteristics: (1) hydrophobicity and compactness to reduce the water and gas permeation to the Li anode; (2) electrochemical and chemical stability to avoid any side reactions with the Li metal and electrolyte, and retain original structure and composition after long-term cycling; (3) good elastic deformation ability to tolerate the volume

change of Li anodes and to keep close contact with the electrode; (4) high  $\text{Li}^+$  conductivity to reduce the interfacial impedance. At present, there are two commonly used methods for preparing the protective layers, which are *in-situ* chemical or electrochemical reaction methods, and *ex-situ* methods like the artificial interface layer design.

### 3.2.1 *In-situ* protective layers

The highly reactive nature of Li could enable it to react with multitudinous chemicals to *in-situ* construct protective layers closely attached to its surface, preventing the corrosion from water in the air and other reactive components in the electrolyte. For example, by taking advantage of the *in-situ* spontaneous reaction between the gas and Li metal (Figure 5a–c), Cui *et al.* [71] developed a surface fluoridation process that used the fluoropolymer-containing perfluoro (1-butenyl vinyl ether) polymer (CYTOP) as a precursor to produce  $\text{F}_2$  gas for reacting with the Li metal, forming a

homogeneous and dense LiF coating on the Li–Si alloy. Due to the low solubility of LiF in water, this protective layer made the Li–Si alloy anode keep stable in the humid air (about 40% relative humidity, RH). Similarly, Zhang *et al.* [72] prepared a multifunctional composite LiF/F-doped carbon gradient protective layer on the Li anode surface by one-step reaction between the molten Li and PTFE (Figure 5d). This well-designed gradient protective layer could enable dendrite-free plating/stripping and corrosion-resistant Li metal anodes in both ether- and carbonate-based electrolytes. Although these inorganic protective layers, such as LiF [53],  $\text{LiN}_x\text{O}_y$  [73], contribute to the stabilization of Li metal anodes, they can only regulate the deposition of Li metal and hinder the growth of Li dendrites, but are not optimal for blocking the moisture and gas penetration. Therefore, organic protective layers or composite protective layers with hydrophobicity and compactness have been developed to solve the multiple challenges of Li anodes faced in the LABs.



**Figure 5** (a) Schematic illustration of the *in-situ* reaction of Li metal and fluorine gas. (b, c) Cross-sectional focused ion beam (FIB)-scanning electron microscopy (SEM) images of the LiF-coated Li metal. Schematic illustration of the formation of (d) LiF/F-doped C, (e) Ge/GeO<sub>2</sub>/Li<sub>2</sub>CO<sub>3</sub>/LiOH/LiCl/Li<sub>2</sub>O, and (f) Si–O-containing self-healing lithium protection films. (a–c) Reprinted with permission from Ref. [71], Copyright 2017, American Chemical Society. (d) Reprinted with permission from Ref. [72], Copyright 2020, Wiley-VCH GmbH. (e) Reprinted with permission from Ref. [74], Copyright 2018, Wiley-VCH GmbH. (f) Reprinted with permission from Ref. [75], Copyright 2019, Elsevier (color online).

Zhou *et al.* [74] designed a composite protective layer composed of Ge,  $\text{GeO}_x$ ,  $\text{Li}_2\text{CO}_3$ , LiOH, LiCl, and  $\text{Li}_2\text{O}$  by soaking the Li metal in organic  $\text{GeCl}_4$ -THF vapour (Figure 5e). It was shown that the protected Li metal was more stable than the pristine one, especially when being exposed to water. When using the protected Li metal electrodes to assemble symmetric cells, they could realize 500 stable cycles at  $3 \text{ mA cm}^{-2}$  in wet electrolytes. Even in humid  $\text{O}_2$  gas (45% RH), the Li- $\text{O}_2$  batteries with the protected Li anode could be stably discharged and charged for more than 150 cycles. Targeting to address the continuous corrosion of Li anodes, Zhang's group [75] proposed an *in-situ* self-healing method by utilizing the spontaneous reaction between the tetraethylorthosilicate and LiOH (the dominated component of the harmful surface corrosion layer on the Li anode, Figure 5f). The formed protective film could be dynamically repaired during cycling, prolonging the lifetime of LABs. Furthermore, the Li metal could also react with some polymers to form flexible and elastic polymer-based protective layers. Guo *et al.* [76] prepared a highly elastic smart polymer-based protective layer by *in-situ* reaction of the Li metal with polyacrylic acid to accommodate the significant volume change of the Li anode. Chen *et al.* [77] exploited the spontaneous reaction of ureido-pyrimidinone (Upy) groups with Li metal to construct a self-stabilizing and strongly adhesive supramolecular polymer-based protective layer on the Li anode. Because of its remarkable sealing ability and elasticity, the LABs with the polymer layer-protected Li anodes exhibited excellent cycling stability in the humid air.

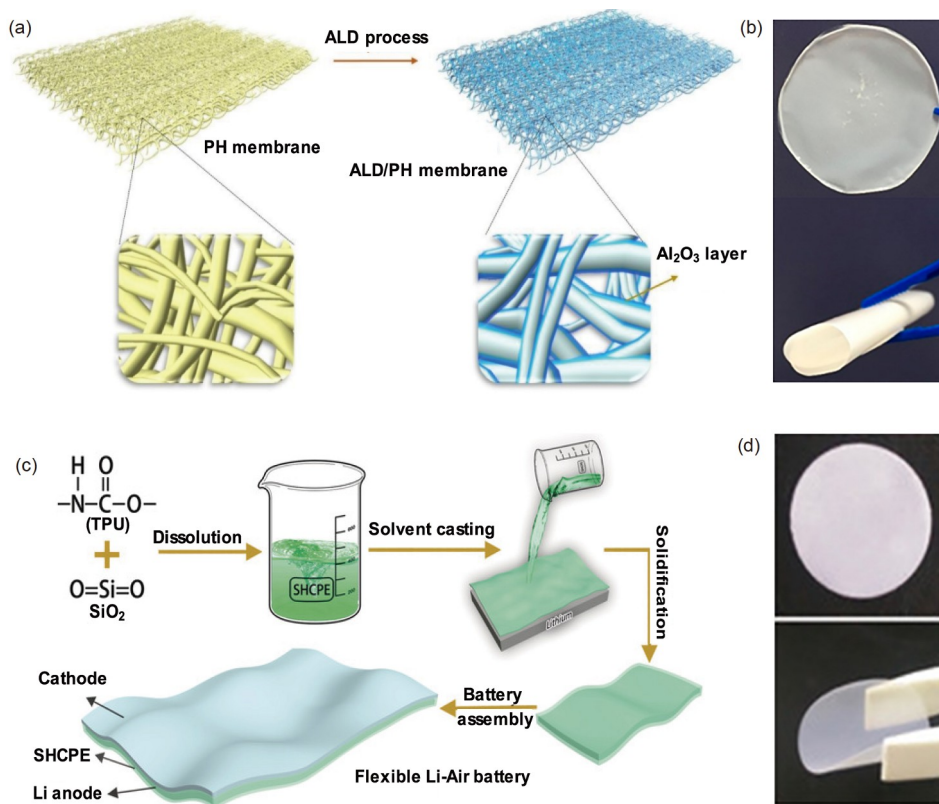
Benefiting from the highly reductive ability of Li metal, dense inorganic, elastic organic or composite protective layers can be *in-situ* formed on the surface of Li metal anodes under various conditions. Although this kind of *in-situ* protective layers could effectively protect the Li anodes from dendrite growth/volume change/corrosion, it is difficult to control the reaction process and the thickness of the protective layers, which might lead to large impedance and poor Li-ion transport. Currently, to obtain thinner protective layers, a large amount of diluent is usually used to reduce the concentration of reactants, which would lead to cost increase in large-scale production, and thus solvent recovery should be considered in the future. Meanwhile, due to the complexity of the reaction inside the battery, it is difficult to design appropriate technological parameters for mass production. In summary, *in-situ* protective layers provide the opportunity for the full stabilization of the Li metal anodes in the ambient air, but more efforts are still needed to meet the requirement of practical applications.

### 3.2.2 *Ex-situ* protective layers

Compared with *in-situ* protective layers, *ex-situ* protective layers can be controllably synthesized by physical or chemical methods. The physical methods include chemical va-

por deposition (CVD) [78], atomic layer deposition (ALD) [79,80], and physical vapor deposition (PVD) [81]. For chemical methods, they usually use chemical reagents to fabricate a thin, flexible film and then transfer it to the Li anode surface. Different from chemical methods, the physical deposition technology could prepare ultra-thin protective films with the precise thickness control to adapt the volume change and block the corrosion of Li anodes. It should be noted that thicker coatings would increase the resistance for conducting  $\text{Li}^+$ , although they generally have higher tolerance to water corrosion. Since the elaborate design of CVD-grown atomically-thin protective layers could simultaneously possess high chemical/electrochemical stability, mechanical strength, and flexibility, they have been considered as good choices to prevent the corrosion of Li anodes. However, the high deposition temperature of CVD and the lack of large CVD equipments have hindered its practical application in the battery field. In addition to CVD technology, Hu *et al.* [82] used ALD to coat an  $\text{Al}_2\text{O}_3$  film on the surface of the poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) separator (ALD-PH) (Figure 6a, b), endowing the ALD-PH separator with higher ionic conductivity and high affinity to the Li anode. In contrast to other separators in Li metal batteries, the Li metal in ALD-PH separators had a smooth surface with no distinct dendritic lithium growth. Even after 100 cycles, the surface of the Li anode still exhibited no obvious change, indicating that ALD-PH separators could to some extent inhibit the growth of lithium dendrites. Despite their effectiveness, the CVD, ALD, and other physical deposition methods have put forward extremely high requirements for production equipment and technology. The production process is complicated, and the coating material is limited, which is not easy to be promoted for large-scale application. The chemically synthesized protective layers, like polymer and composite coatings, are more widely studied in LABs. Since the flexibility and water resistance of this kind of protective layers can be regulated by selecting appropriate chemicals and reaction conditions, they have been considered as the most preferred methods to protect the Li anodes. Also, the chemically synthesized protective layers are easy to scale up and can be well matched with the existing battery manufacturing processes. As shown in Figure 6c, d, inspired by the umbrella protection effect, Zhang *et al.* [48] fabricated a polymer electrolyte film with high flexibility, hydrophobicity, and stability by using thermoplastic polyurethane and hydrophobic  $\text{SiO}_2$  nanoparticles to restrain the corrosion of the Li anode and improve the capacity and cycle life of LABs in the ambient air. Liu *et al.* [83] constructed a composite layer with polyethylene oxide/lithium aluminum titanium phosphate/wax. This composite layer could enable highly reversible and dendrite-free lithium plating/stripping under abusive operating conditions, including in the ambient air, up





**Figure 6** (a) Schematic of the fabrication process of the ALD/PH membrane. (b) Digital images of the ALD100/PH separator at 25 °C. (c) Schematic of the fabrication process of the SHCPE membrane. (d) Digital images of the SHCPE separator at room temperature. (a, b) Reprinted with permission from Ref. [82], Copyright 2019, American Chemical Society. (c, d) Reprinted with permission from Ref. [48], Copyright 2019, Wiley-VCH GmbH (color online).

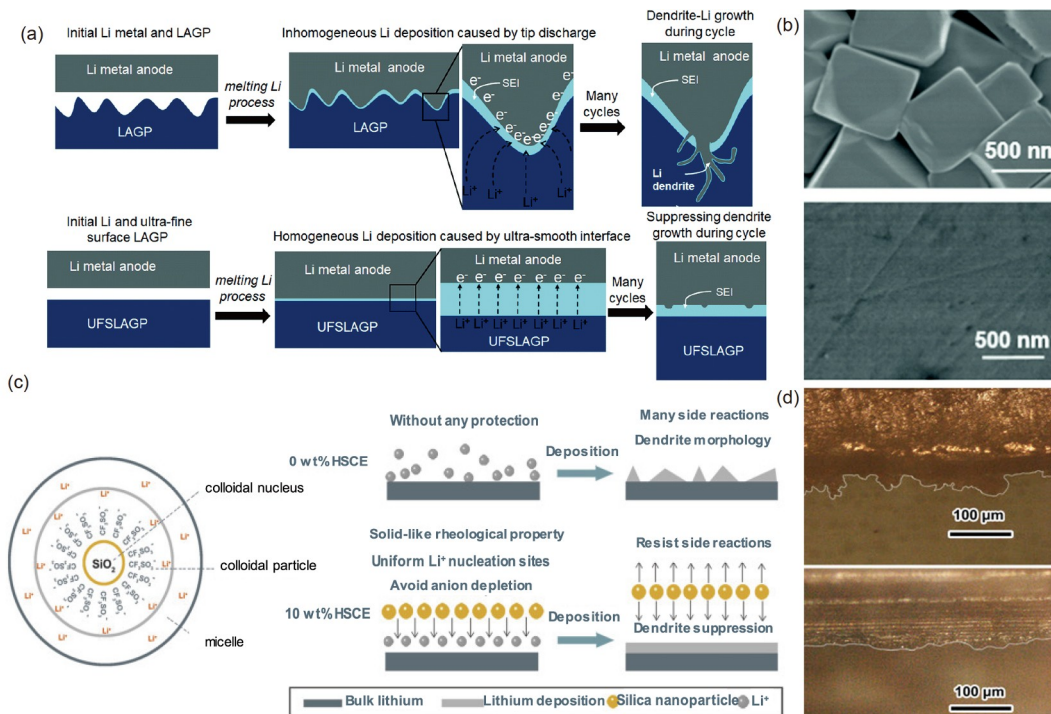
to 99% humidity, and even in electrolytes containing large amounts of water. Although these protective films clearly hinder the corrosion of Li metal, some side effects, such as high interfacial impedance and sacrifice of power density, still exist. Therefore, how to eliminate the adverse effects of the chemically synthesized protective film remains an unsolved problem.

Furthermore, designing a SEI protective layer can only retard the Li anode corrosion and lithium dendrites growth, but not completely solve these challenges. Therefore, it is particularly critical to reduce the water content inside the battery as well as regulate the plating and stripping of Li metal.

### 3.3 Electrolyte alternatives

As above mentioned, the strategies, like the structure and composition modification of the Li anodes, the regulation of *in-situ* protective layers, and the design of *ex-situ* protective layers could delay the corrosion of the Li anodes. However, the strong volatility and the electrochemical instability of liquid electrolytes still hinder the development of high-performance LABs. Consequently, lithium-ion-conducting ceramics, polymers, and hydrophobic ionic-liquid electrolytes have been considered to replace the organic liquid

electrolytes to conquer their shortcomings. Among these alternative electrolytes, the all-solid-state electrolytes, like inorganic ceramic electrolytes, with the high voltage window and excellent electrochemical/chemical stability could significantly prolong the lifetime of Li anodes by completely isolating the Li anode from the attack of the reactive components in the ambient air and inhibition of the dendrite growth. Nevertheless, the low conductivity of the all-solid electrolyte and the point-to-point contact between the cathode/anode are extremely unfavorable for the transport of  $\text{Li}^+$  ions, resulting in limited reaction areas and thus the low capacity and poor rate capability for LABs [84,85]. To address these problems, Xu's group [85] fabricated integrated LABs by directly casting the molten lithium on one side of a  $\text{Li}^+$ -conductive zeolite membrane and the ionic-liquid electrolyte and cathode material on the other side. Benefiting from the stability of the zeolite electrolyte and the sufficient contact between each battery component, this solid-state battery realized long cycling performance and high capacity in the ambient air. To tackle the point-to-point contact-induced Li dendrite growth, Zhou *et al.* [86] fabricated a solid electrolyte with ultra-smooth/flat surface by simple nanopolishing the  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$  (LAGP) (Figure 7a, b). The good contact between the electrolyte and Li anode could homogenize the  $\text{Li}^+$  flux, and consequently suppressed the



**Figure 7** (a) Schematic demonstration of the Li deposition and growth on/in LAGP with protrusions or ultra-fine surface (UFSLAGP). (b) SEM images of LAGP and UFSLAGP. (c) Schematic of the ion-adsorption condition of micelle in 10 wt% HSCE and the dendrite-suppression effect during Li deposition process in 0 wt% and 10 wt% HSCE. (d) *In-situ* optical microscopy images of the Li deposition in 0 wt% and 10 wt% HSCE for 60 min. (a, b) Reprinted with permission from Ref. [86], Copyright 2018, the Royal Society of Chemistry. (c, d) Reprinted with permission from Ref. [87], Copyright 2019, Elsevier (color online).

dendrite growth and prolonged the lifespan of the all-solid-state LAB. Although the adoption of all-solid-state electrolytes could moderate the challenges of the liquid electrolyte and Li anodes, the performance of the solid-state LABs is still inferior to that of the LABs with liquid electrolytes. To address this dilemma, the researchers adopted a compromised strategy by combining the solid ion-conductive/non-conductive particles with liquid electrolytes or ionic liquid electrolytes to form gel electrolytes. For example, Zhang's group [87] prepared a gel electrolyte by *in-situ* coupling the  $\text{CF}_3\text{SO}_3^-$  groups of the Li salt with the hydrophobic silica nanoparticles (Figure 7c). With the help of the seed crystal effect and solid-like rheological properties, the 10 wt% hydrophobic silica-based electrolyte enabled a stable anode-electrolyte interface to realize the dendrite-free Li deposition/dissolution (Figure 7d) and reduce the interfacial impedance by 45 times. Besides, the hydrophobic nature of the electrolyte made the lithium sheets maintain smooth surface and shiny luster even after being placed in the humid air for 30 min. In addition, Zhang *et al.* [88] mixed the ionic liquid electrolyte and solid LAGP powders to prepare hybrid gel electrolytes for LABs. Due to the low volatility and hydrophobicity of ionic liquid, this hybrid electrolyte enabled the LABs to achieve a Coulombic efficiency of 99.5%, significantly improving the capacity retention from 45% to 60% after 100 cycles.

The use of polymer electrolytes in LABs could date back to 1990 when Abraham *et al.* [7] first adopted polyacrylonitrile-based films as a solid-state electrolyte to realize the charge and discharge of LABs. Limited by the low ionic conductivity and relatively poor electrochemical stability toward the strong oxidative environment of LABs, the polymer electrolytes have not become the mainstream electrolytes for the LABs. However, from the perspective of performance and applicability, the polymer electrolytes will play indispensable roles in the future LABs, especially in the solid-state LABs. Jang *et al.* [89] studied the effect of the PVDF-HFP electrolyte on the cycling stability of LABs. The coating of the PVDF-HFP electrolyte on the Li anode surface could reduce the interfacial resistance during discharge-charge processes and inhibit the Li dendrite growth, thereby improving the cycling lifetime of LABs. Ein-Eli *et al.* [90] prepared a PEO-based polymer electrolyte and operated the LABs at temperatures above its melting point. Compared with the LAB with the TEGDME-based electrolyte, the discharge overpotential of the PEO-based cell was only 80 mV, and most notably, the charge voltage was reduced by 400 mV. Although various alternative electrolytes have been developed, their properties are still not satisfactory for enabling high-performance LABs. Moreover, most of these electrolytes are just simply copied from other battery systems. It is frustrating that they have not been specifically

designed according to the use environment and reaction mechanism of LABs.

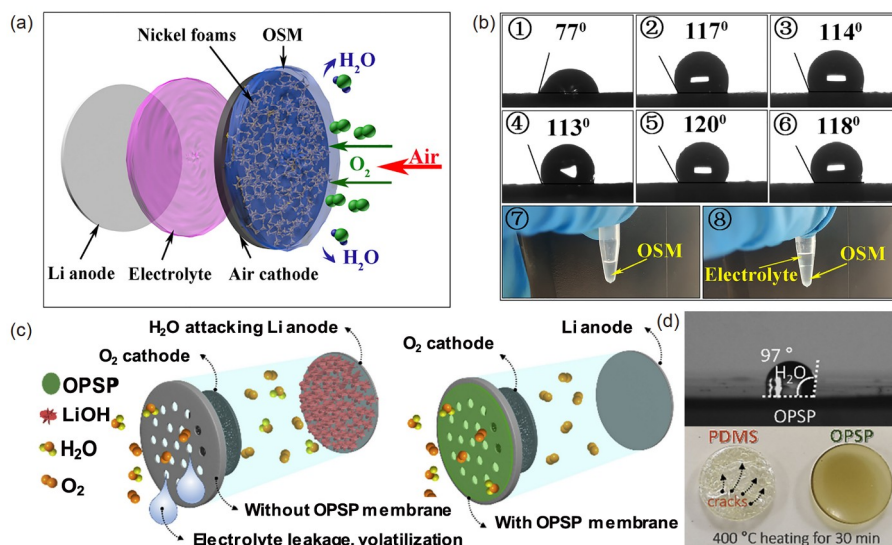
### 3.4 Introduction of oxygen-selective membranes

Different from LIBs, LABs are a semi-open system that brings new challenges to the organic liquid electrolytes and Li metal anodes. Therefore, in addition to the direct protection of the Li anodes and the design of stable electrolytes, we could also start with the structure engineering of the LABs, like the introduction of oxygen-selective membranes (OSMs) at the outside of the cathode to improve the permeability of oxygen and repel other gas molecules in the air, avoiding the inactive gas-rendered side reactions for both the cathode and Li anode. Then the question is how to design an OSM that could just selectively diffuse the  $O_2$  molecules. This is a really tough task because the kinetic diameters of  $H_2O$  (0.289 nm) and  $CO_2$  (0.330 nm) are smaller than the Knudsen diffusion value of  $O_2$  (0.346 nm) [2,91]. Hence, only a few studies on OSMs have been reported so far due to the aforementioned limitations.

Ruan *et al.* [92] prepared a perfluorocarbon silicone oil OSM and attached it to the outside of the cathode shell (Figure 8a, b), remarkably improving the electrochemical performance of LABs in the ambient air. Amici *et al.* [93] designed a silicone oil-supported PVDF–HFP membrane and used it as the OSM. Benefiting from the oxygen selectivity of silicone oil and the hydrophobicity of PVDF–HFP, the cycling performance of LABs in the air was comparable to the cell in pure oxygen. Later, Huang *et al.* [94] fabricated a perfluoropolyether (PFPE) oxygen-permeable waterproof membrane. With this membrane, the stability of both the

lithium anode and lithium peroxide was significantly improved, and the evaporation of organic liquid electrolyte was greatly suppressed. As a result, the LABs could stably operate for 144 cycles in the ambient air with a relative humidity of about 30%. To further improve the performance of LABs, Shao *et al.* [95] added silica nanoparticles to polydimethylsiloxane to prepare a kind of hydrogen-bonded cross-linked flexible OSMs (Figure 8c, d). The water resistance,  $O_2$  permeability, and high heat resistance of this newly designed OSM could enable the coin-type (700 h) and pouch-type LABs to stably operate in harsh conditions.

To sum up, although various strategies have been developed to protect the Li anodes, how effective are they? The performance of LABs with the Li anodes protected by different strategies is summarized in Table 2. There is only limited research of using the Li alloy in LABs because the alloy anodes can hardly get rid of the corrosion by water and  $CO_2$ . The all-solid electrolytes have also been attempted to solve the corrosion of Li anodes by air and electrolyte components, but its large interface resistance and poor ion conductivity leads to unsatisfactory performance in LABs. By contrast, the gel polymer electrolytes with flexibility, water resistance, and stability could extend the battery lifetime, but suffer from large overpotentials. Although these strategies could solve the Li corrosion to a certain extent, it is still hardly to prevent the corrosion of Li anodes originally. Therefore, some OSMs have been developed to prevent the moisture and gases from entering into the LABs but failed to achieve the original goal due to the poor oxygen selectivity of the designed OSMs. As a result, it is still a long way to research and develop stable electrolytes and powerful OSMs. Only relying on the cooperation of different strategies can



**Figure 8** The application of oxygen-selective membranes in LABs. (a) Sketch of a Li–air cell assembled with OSM. (b) Photographs of the water contact angles on the OSM and the immiscible between the electrolyte and OSM. (c) Schematic illustration of the LABs in the ambient air with and without OPSP. (d) The contact angle of water on the OPSP and the thermo-tolerance and stress–strain properties of PDMS and OPSP. (a, b) Reprinted with permission from Ref. [92], Copyright 2018, Elsevier. (c, d) Reprinted with permission from Ref. [95], Copyright 2020, Elsevier (color online).

**Table 2** Performance of LABs with the Li anodes protected by different strategies

Type	Current (mA g <sup>-1</sup> )/Limit capacity (mAh g <sup>-1</sup> )	Cycle life	Relative humidity	References
Li alloy+SPE	500/1000	135	/	[52]
<i>ex-situ</i> +SHCPE	200/500	95	/	[47]
<i>ex-situ</i> +HDHPC	500/1000	110	40%	[48]
<i>In-situ</i> +Li-GeCl-THF	200/1000	150	45%	[71]
<i>In-situ</i> +DES-PE	500/1000	300	45%	[50]
LAGP	400/1000	31	/	[82]
Zeolote SSE+IL	500/1000	149	/	[81]
SiO <sub>2</sub> -LiI-PVDF	100/500	100	15%	[56]
LiI-GPE	200/1000	400	15%	[57]
OSMs+PFC-PDMS	200/500	42	68%	[88]
OSMs+PFPE	100/500	144	30%	[90]
OSMs+OPSP	500/1000	166	30%	[91]

make the practical application of LABs come in the earliest time.

#### 4 Summary and outlook

The air instability of Li metal anodes is one of the crucial factors that hinder the application of LABs in the real air environment. In the past several years, various strategies have been proposed to solve the issues that Li anode faced, including the composition and structure design of Li anodes, surface modification with *in-situ/ex-situ* protective films, replacement of organic liquid electrolytes with all-solid electrolytes, gel electrolytes, or composite electrolytes, and the introduction of oxygen-selective membranes outside the cathode. Although these efforts have shown improvements in mitigating the instability of Li anodes, the realization of completely stable Li anodes remains to be explored and there is still a long way to go. In-depth studies on the degradation mechanisms of Li anodes together with the coordinated protection of Li anodes by multiple strategies may have the opportunity to bring Li metal anodes to practical applications.

As a battery system, besides the requirement of a stable Li anode, the status of other battery components should also focus. First, the charging voltage should be kept below 3.5 V due to the high voltage sensitivity of carbon cathode degradation, electrolyte decomposition, and singlet oxygen generation. To reduce charge overpotential, catalysts and RMs have been explored. Although the use of catalysts can decrease the charge voltage at the initial stage of operation, with the deepening of charging states, the voltage gradually polarizes to more than 4.0 V to induce side reactions. Meanwhile, the discharge products would transform from Li<sub>2</sub>O<sub>2</sub> to LiOH and Li<sub>2</sub>CO<sub>3</sub> when the battery runs in the ambient air. Therefore, it is very important to develop cata-

lysts that could efficiently decompose the LiOH and Li<sub>2</sub>CO<sub>3</sub> and maintain the low charge voltage in the whole process, thereby suppressing the sides reactions associated with the cathode and electrolyte, and avoiding the corrosion of the Li anode. For reducing the charge voltage, utilizing RMs is more efficient than the catalysts due to the use of their own oxidation voltages to decompose the Li<sub>2</sub>O<sub>2</sub>. Although they are effective, the mobile nature of RMs could corrode the Li anode, and their stability toward the oxidative intermediates of LABs is still a question. It is necessary to overcome the shortcomings of prior studies and propose the strategies to maintain low charge potential and high stability of catalysts and RMs during the long-term cycling. In addition, it is also important to keep an eye on the development of other new catalysts, such as photocatalysts.

Identifying the internal reasons of electrolyte decomposition and the details of the composition of decomposed products is paramount for designing stable electrolytes. Previously, the discharge intermediates, such as lithium superoxide, were considered to be the main initiators for the electrolyte decomposition. But in the case of K-O<sub>2</sub> batteries, even after thousands of times cycling, the parasitic reactions originating from the chemical reaction between the superoxide and electrolyte were still limited, revealing that the electrolyte decomposition might not be directly related to the superoxide. And recent studies have found that the singlet oxygen rather than the superoxide plays a major role on facilitating the electrolyte decomposition [96]. Therefore, it is necessary to explore the origin of singlet oxygen and design singlet oxygen quenchers to alleviate its rendered parasitic reactions and consequently protect the Li anode from the corrosion. Furthermore, due to the volatility and instability of liquid electrolytes, it is still necessary to develop other alternative electrolytes.

Oxygen-selective membranes (OSMs) have the possibility of blocking the environmental Li-reactive components, like



H<sub>2</sub>O, CO<sub>2</sub>, N<sub>2</sub>, to enter the LABs. However, it is worth noting that the materials with high oxygen permeability tend to be more easily to diffuse CO<sub>2</sub>. It remains to explore a kind of OSMs that have the ability to block all unwanted gases. If this can be realized, the developed truly OSMs will greatly promote the application of LABs in the real air environment.

Since LABs are semi-open systems, the selection of electrolytes is particularly important. Current research mainly focuses on organic liquid electrolytes. However, their strong volatility, high flammability, and poor stability make them be difficult to be applied in practical LABs. On these grounds, solid electrolytes would be good choices for next-generation LABs because they can avoid volatility and flammability, and also hinder the corrosion of the Li anode by water and other gases. However, the poor contact between the solid electrolyte and electrodes brings large interfacial resistance, leading to poor electrochemical performance and sometimes even the growth of lithium dendrites inside the electrolyte [97]. The preparation of composite electrolytes that integrate the advantages of inorganic solid electrolyte and polymer electrolyte while get rid of their shortcomings could be a possible way to conquer the above challenges. Nevertheless, the currently available composite electrolytes cannot meet the rigorous requirements of constructing a high-performance LAB. More work should be done to develop inorganic/polymer electrolytes with high ionic conductivity, electrochemical/chemical stability, and explore the way of how to prepare composite electrolytes to maximize each component's strengths. It is important to understand the various characteristics of electrolytes in LABs and develop suitable electrolytes for LABs rather than duplicates.

In addition, the development of any protection strategies is premised on understanding the mechanism of Li anode degradation. However, due to the surface passivation induced by the high chemical reactivity of Li metal, it is particularly difficult to study the real passivation reactions at the nanoscale. This originates from the lack of effective tools to characterize the structural and chemical properties of both the SEI and Li anodes due to their fragile nature. With the development of advanced characterization techniques, such as cryogenic electron microscopy (CEM) [98,99], *in-situ* TEM [100], *operando* 3D microscopy [101], neutron depth profiling (NDP) [102], synchrotron X-Ray tomography [103], MAS nuclear magnetic resonance (MAS NMR) [104], they are expected to be applied in LABs to help understand the characteristics of Li anodes in the complex environment of LABs and support the formulation of more beneficial proactive strategies to realize the design of truly stably Li anodes.

It is also very important to establish a scientific evaluation system for fully assessing the effectiveness of the existing strategies on the performance of Li anodes. As shown in Table 2, the Li anodes protected by different strategies have

been tested under different conditions, making it hard to draw conclusions of which strategy is more effective. Only under the conditions with the same variables can convincing conclusions be drawn to promote the development of stable Li anodes for LABs. Therefore, it is urgent to develop a set of scientific evaluation standards and provide a set of scientific testing systems for Li anodes and LABs. Certainly, this requires the joint efforts of scientists over the world, and we look forward to this day as soon as possible.

Li alternative anodes might also provide some possibilities [105]. For example, Scrosati *et al.* [106] replaced the Li anode with a lithiate silicon-carbon anode, making the Li<sub>x</sub>Si-O<sub>2</sub> battery realize an energy density of 980 Wh kg<sup>-1</sup> and successfully cycled for 15 times. Similarly, Zhou *et al.* [107] designed a Li-ion oxygen battery with an energy density of 678 Wh kg<sup>-1</sup> and a lifetime up to 100 cycles by using the commercial silicon particles as the anode. Although using Li alternative anodes could avoid some issues that the Li anodes face. However, the low Coulombic efficiency and the continuous consumption of the limited lithium sources would eventually lead to the premature death of Li-ion oxygen batteries. This requires the development of large-capacity alternative anodes with high Coulombic efficiency and stable electrode/electrolyte interface.

In summary, this review introduces the challenges faced by the Li metal anodes in the LABs and the corresponding protection strategies in detail. Despite the effectiveness, the currently available strategies still cannot solve all the issues that the Li anodes faced. More efforts should be devoted to further improve the stability of Li anodes in the system level. Only when a perfectly stable Li anode could be realized, can the practical application of LABs be hopeful.

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**Conflict of interest** The authors declare no conflict of interest.

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