第 40 卷　第 5 期
2025 年 10 月

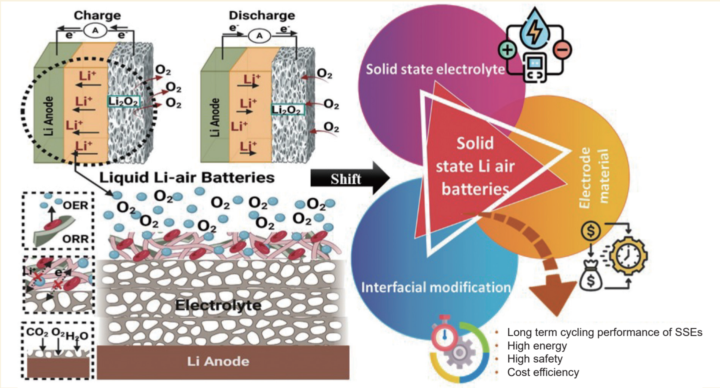
新型炭材料（中英文）
New Carbon Materials

Cite this: New Carbon Materials, 2025, 40(5): 1038-1073　　Read Online　　Review

Current problems in Li-air batteries and ways to solve them

Humaira Rashid Khan[1], Abdul Latif Ahmad[1,*], Asim Ali Yaqoob[2]

(1. *School of Chemical Engineering, Universiti Sains Malaysia, Engineering campus, Seri Ampangan*, 14300 *Nibong Tebal, Seberang Perai Selatan, Pulau Penang, Malaysia*;
2. *City of Oxford College, Oxpens Rd, Oxford OX1 1SA, United Kingdom*)



Abstract: The energy production system must be completely transformed to reach net zero emissions by 2050, and advanced battery technologies will play a pivotal role in helping downstream sectors transition to sustainable energy sources. Li-air batteries (LABs) provide a fascinating "beyond Li-ion" option because of their ultrahigh theoretical energy density, which far surpasses conventional lithium-ion batteries. However, LABs face significant hurdles in practical implementation, including electrolyte instability, irreversible electrodes, poor cycling performance, and low-rate capability. This review provides a detailed analysis of recent progress in LAB systems, highlighting innovative approaches such as electrolyte stabilization, electrode modification, and interfacial engineering to address these challenges. It evaluates current strategies for overcoming these problems and outlines targeted research directions aimed at resolving the remaining obstacles in LAB technology. The progress made so far indicates a way to realize practical LABs with a specific energy density potentially comparable to gasoline, which could revolutionize electric transportation.

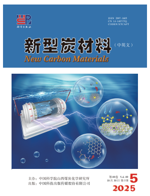
Key words: Lithium-air batteries；Aqueous and non-aqueous electrolytes；Dendrite formation；Parasitic reactions；Hybrid membranes

1 Introduction

The increasing consumption of fossil fuels has significantly impacted the ecosystem of the entire globe, resulting in exacerbated greenhouse effect, poor air quality, ozone layer depletion and ocean level elevation[1–2]. In recent years, there has been significant investment in renewable energy sources such as solar and wind energy to address environmental issues. However, the imbalanced energy distribution in time and space leads to ineffective utilization of clean energy sources, and still remains a challenging issue to overcome[3]. At the 26th Conference of the Parties, governments affirmed their commitment to the International Energy Agency's (IEA) landmark objective of reaching net zero emissions by the year 2050[4–5]. The shift towards renewable and low carbon emission electricity sources is a crucial strategy for rebuilding global energy supply and achieving net zero emissions, as electricity has become an outstanding area sector in the energy system. The International Energy Agency (IEA) states that the power sector accounted for 36% of all energy-related CO_2 emissions in 2020[6–7]. It is estimated that the electricity demand will increase to 42 000 TWh by 2050, highlighting the necessity for reliable electrical energy storage systems[8].

Electrochemical energy storage technologies offer high flexibility and compatibility, making them a preferred choice for the energy market. Therefore, it is

Received: December 19, 2024
Revised: March 14, 2025
Accepted: March 14, 2025
DOI: 10.1016/S1872-5805(25)60976-0
CSTR: 32158.14.S1872-5805(25)60976-0



of urgent need to develop novel energy devices for a sustainable society. Over the past two decades, research has shifted towards electrochemical energy production and storage techniques such as supercapacitors, fuel cells, and rechargeable batteries[9]. Rechargeable batteries effectively address energy storage and release issues by reducing power grid pressure by storing energy at peaks and releasing it at troughs[10]. Recently, a new generation of rechargeable lithium-ion batteries has emerged as an intriguing new energy source for modern electronics and transportation. However, despite recent advancements, the specific power and energy densities of lithium-ion batteries are still lower than that desired for long-range electric vehicles. While some advanced Li-ion batteries (e.g., $LiFePO_4$ at ~200 Wh/kg, Nickel-Cobalt-Manganese at 200–300 Wh/kg) are used in Electric vehicles, there is a growing need for even higher energy densities to extend range and reduce battery weight[11]. The development of metal air batteries (MABs) has been based on the deficiencies in lithium-ion batteries and continuous research and development of rechargeable batteries, which have led to the development of advanced battery technology for electric vehicles.

The concept of using lithium in metal-air batteries dates back to the 1970s, with patented technology for non-rechargeable primary lithium air cells[12]. A 1996 study demonstrated a theoretical energy density comparable with gasoline, sparking interest in this technology. In the early 2000s, researchers tackled technical barriers around stability, electrolytes, oxygen electrodes, and rechargeability. In 2009, IBM researchers reported a lithium-air cell cycling 500 times, demonstrating the potential as a secondary rechargeable device[13]. By 2011, lithium-air batteries (LABs) gained mainstream attention and hype as a potential breakthrough.

This review examines the challenges and advances in rechargeable LABs. It introduces LAB technology, analyzes working mechanisms, components, and configurations, and addresses hurdles impeding commercialization, such as air constituent effects, cathode design constraints, parasitic reactions, and anode instability. Advanced mitigation strategies, including oxygen-selective membranes, optimized cathode architectures, electrolyte formulations, and lithium metal protection techniques, are discussed. The article explores future research directions and potential breakthroughs. It aims to provide researchers and industry professionals with an understanding of the state-of-the-art in LAB technology, its limitations, and its trajectory towards practical implementation in next-generation energy storage systems.

2 Overview of Li-air battery technology

LABs, also referred to as Li–O_2 batteries, convert chemical energy into electrical energy through electrochemical reactions between lithium at the anode and oxygen (O_2) at the cathode[14]. Introduced in 1976 by Littauer and Tsai in an aqueous system[15], the concept was later advanced by Abraham et al.'s in 1996 through a study on non-aqueous LAB using an organic polymer electrolyte[16]. Although initially overlooked due to technical challenges, LABs have gained renewed interest in recent years owing to their exceptional theoretical energy densities.

The theoretical energy density of LABs ranges from 1000 to 2000 Wh/kg, depending on the electrolyte, membrane, and cathode design[17], with calculations reaching up to 3458 Wh/kg[18]. This is remarkably close to that of gasoline (around 13 000 Wh/kg) and significantly higher than conventional Li-ion batteries (100–265 Wh/kg). The extraordinary energy density stems from the battery's unique chemistry, where lithium metal serves as the anode and ambient oxygen as the cathode active material. The lightweight nature of oxygen, which is drawn from the surrounding air rather than stored within the battery, contributes to this high energy density. Fig. 1 illustrates the comparison of theoretical vs. practical energy densities of various metal-air batteries, highlighting the superior potential of LABs. The inset in Fig. 1 also shows the trend in LAB research, demonstrating growing interest in this technology. Theoretical calcu-

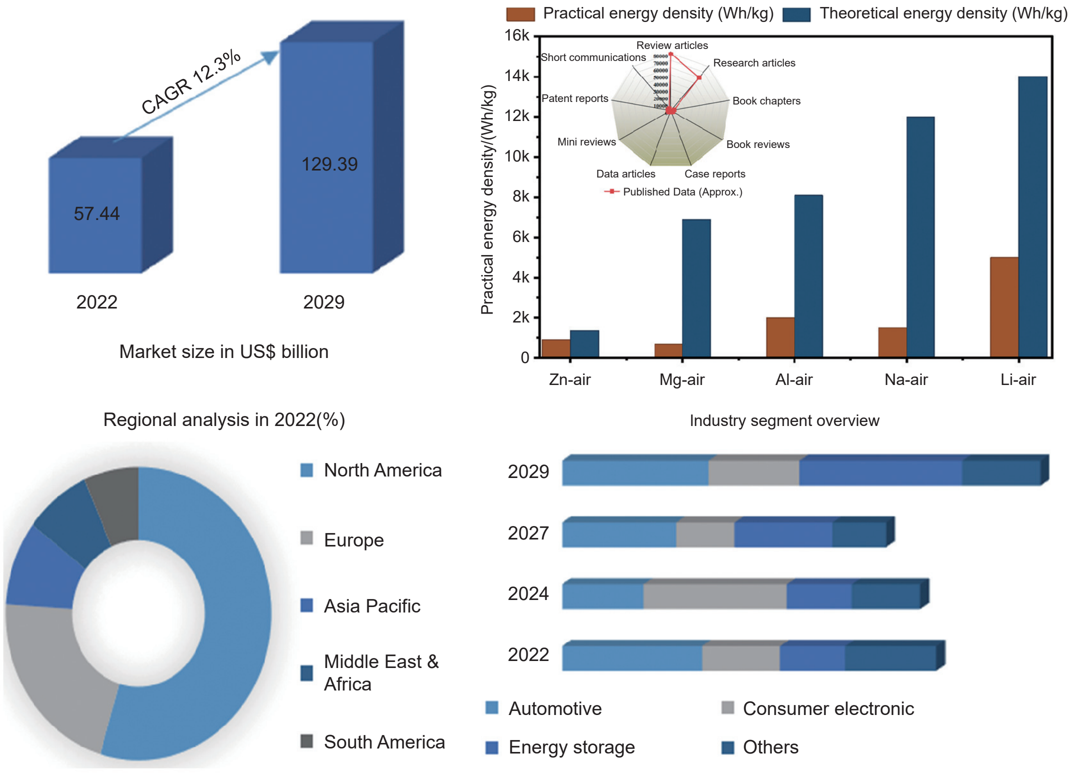


Fig. 1 Lithium-air battery market, theoretical vs. practical energy densities of various metal-air batteries (inset) trend in research LABs. (The data obtained from Scopus and cross checked from web of science)

lations, focusing solely on the mass of active reactants[19], show that for a non-aqueous electrolyte solution, the energy density of a LAB is approximately 3458 Wh/kg. Notably, when excluding the mass of oxygen, the theoretical energy density can reach as high as 14 000 Wh/kg, surpassing most metal-air batteries. These exceptional energy densities make LABs a promising solution for electric vehicles, potentially enabling ranges of over 500 miles per charge, comparable to gasoline-powered vehicles[20].

The working mechanism of LABs involves a metallic lithium anode, a perforated air cathode, and an electrolyte that acts as a separator between the 2 electrodes, as illustrated in Fig. 2. During discharge, lithium metal oxidizes at the anode, releasing lithium ions (Li^+) and electrons. The lithium ions migrate through the electrolyte toward the cathode while the electrons flow through the external circuit. At the cathode, atmospheric oxygen gets reduced, producing oxygen anions that combine with lithium ions to form solid lithium peroxide (Li_2O_2). The chemical reactions in a LAB with a non-aqueous electrolyte are as follows:

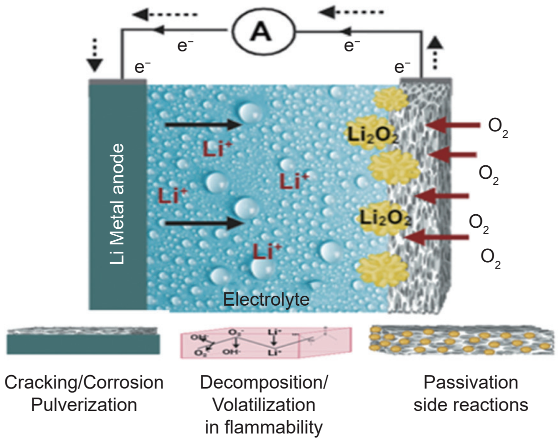


Fig. 2 Operating mechanism and challenges in LABs

At anode:

$$\mathrm{Li} \rightarrow \mathrm{Li}^+ + \mathrm{e}^- \tag{1}$$

At cathode:

$$\mathrm{O_2} + \mathrm{e}^- \leftrightharpoons \mathrm{O_2^-} \tag{2}$$

$$\mathrm{O_2^-} + \mathrm{Li}^+ \rightleftharpoons \mathrm{LiO_2} \tag{3}$$

$$\mathrm{LiO_2} + \mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Li_2O_2} \tag{4}$$

Overall reaction:

$$\mathrm{Li} + \mathrm{O_2} \rightleftharpoons \mathrm{Li_2O_2} \tag{5}$$

These reactions represent the electrochemical process occurring in a lithium-air battery during discharge[21]. At the anode (1), lithium ions are released, and electrons are generated. At the cathode (2-4), lithium ions are intercalated into the cathode material (typically a lithium transition metal oxide), and the electrons from the anode reduce the cathode material[22]. The overall reaction (5) shows the formation of lithium oxide (Li_2O_2) as the discharge product in a lithium-air battery[23], which is a promising next-generation battery technology with higher theoretical energy density compared to conventional lithium-ion batteries.

LABs can be classified into four distinct categories based on the type of electrolyte employed: non-aqueous/aprotic, aqueous, hybrid and solid-state (Fig. 3). Each configuration presents unique characteristics, advantages, and challenges that significantly influence their performance and potential applications.

Non-aqueous/aprotic LABs utilize organic liquid electrolytes and are characterized by their high energy density and simple cell design. In these systems, the key reactions involve the oxidation of lithium at the anode and the reduction of oxygen at the cathode[24]. The chemical reactions at the anode and cathode of an aprotic LAB are:

At anode:

$$Li \rightarrow Li^+ + e^- \tag{6}$$

At cathode:

$$2Li + O_2 + 2e^- \rightarrow Li_2O_2 \tag{7}$$

$$4Li + O_2 + 4e^- \rightarrow Li_2O \tag{8}$$

While this configuration offers promising energy densities, it faces challenges due to the insolubility of discharge products (Li_2O_2, Li_2O) in the electrolyte, leading to cathode pore blockage and reduced oxygen penetration[25]. Recent research has focused on enhancing electrolyte stability and developing efficient catalysts for oxygen reduction and evolution reactions.

Aqueous LABs, developed by Visco et al. in 2004[26], employ water-based electrolytes that can be either acidic or alkaline. The chemical reactions of aqueous LAB are different depending on the acidic or basic nature of the electrolyte and are as follows:

Reaction in acidic medium:

$$4Li + O_2 + 4H^+ \rightarrow 4LiOH + H_2O + Li^+ \tag{9}$$

Reaction in alkaline medium:

$$4Li + O_2 + 2H_2O \rightarrow 4LiOH \tag{10}$$

Aqueous LABs benefit from high ionic conductivity and better solubility of discharge products. However, they require robust protection of the lithium anode from water reaction, which has been a focal point for recent developments in advanced protective membranes.

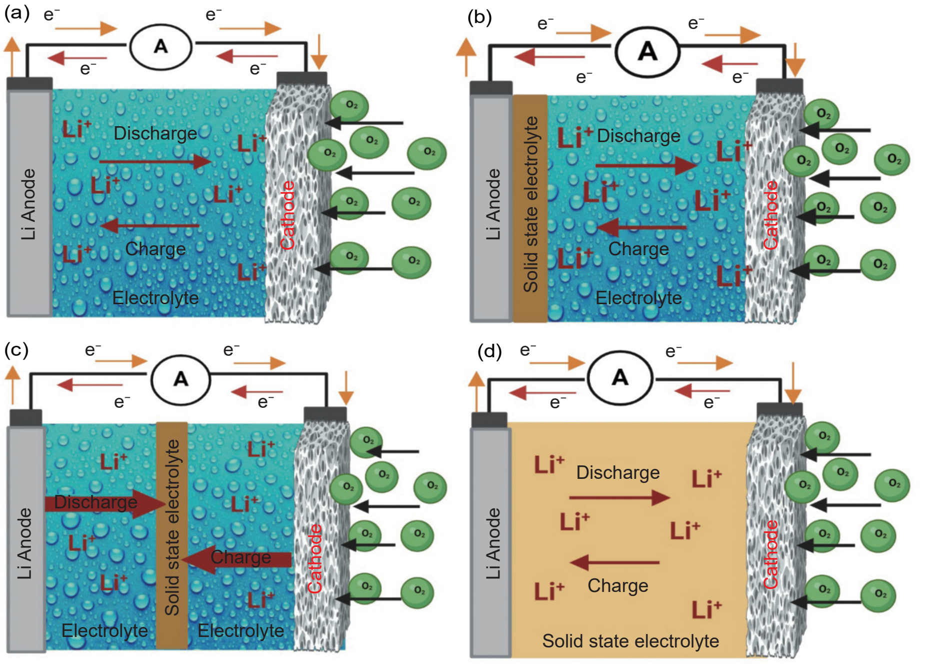


Fig. 3 Configuration of various LABs. (a) Aprotic/non-aqueous, (b) aqueous, (c) hybrid and (d) solid state LABs

Hybrid LABs represent an innovative approach that combines elements of both non-aqueous and aqueous systems. These batteries feature a metallic lithium anode in an organic electrolyte and a carbon cathode in an aqueous electrolyte, separated by a solid-state electrolyte membrane. The reactions occurring at the respective electrodes in this system can be represented in the following chemical reactions[27]:

At anode:

$$4Li \rightarrow 4Li^{+} + 4e^{-} \tag{11}$$

At cathode:

$$4e^{-} + O_2 + 2H_2O \rightarrow 4OH^{-} \tag{12}$$

Overall, cell reaction:

$$4Li + O_2 + 2H_2O \rightarrow 4Li^{+} + 4OH^{-} \tag{13}$$

During the discharge process, there is a continuous flow of O_2 from the atmosphere to the perforated cathode that facilitates the reduction reaction. Similarly, Li ions are generated at the anode that move from the non-aqueous solution to the aqueous solution through the separator. Hybrid battery have been designed to manage discharge products and moisture effects in aprotic systems, eliminating clogging issues in perforated cathode due to discharge products. They have a lower power density, which is a drawback in long-term operations, primarily due to the Li-ion conducting membrane[28].

Solid-state LABs, introduced by Kumar and colleagues in 2010 had different prospective[29], employing all solid-state components, including electrodes and electrolyte. The primary reactions in these systems are like those in non-aqueous LABs, but the solid-state nature of the electrolyte introduces unique characteristics. The redox reactions taking place at the electrodes of solid-state LABs are represented as:

$$2Li + O_2 + 2e^{-} \rightarrow Li_2O_2 \tag{14}$$

or

$$4Li + O_2 + 4e^{-} \rightarrow 2Li_2O \tag{15}$$

These batteries offer enhanced safety and stability, particularly in challenging environments with temperature fluctuations or vibrations. Immediate fabrication, which makes them ideal for power conservation and transformation processes[30]. Both inorganic and organic (polymeric) solid-electrolyte compounds have made great advances in improving these properties. There has been a recent uptick in the use of solid-state electrolyte in chemical and electrical energy storage systems. However, compared to the liquid electrolyte, electrical transmission is worse in the solid state. The higher current density requires an operating temperature higher than the surroundings[31]. Innovative solid electrolyte battery mechanisms may revolutionize the charging industry due to their cost-effectiveness, extended life duration, and safety. However, improvements in electrical conductivity, electrolytic interfacial integration, chemical equilibrium, and morphological aspects are needed to make these batteries practical energy-storing devices[32]. Recent research works have explored novel glass-ceramic electrolytes and polymer-ceramic composites to address these issues.

Despite their promising potential, LABs face significant challenges that hinder commercialization. These include limited cycle life, electrolyte instability, cathode degradation, and the formation of lithium dendrites, which pose safety risks[33]. Additionally, the practical energy density achieved in real-world applications is lower than theoretical calculations due to factors, including the weight of other battery components and system inefficiencies. The main challenges include the cracking of anode material, corrosion of the electrolyte, combustibility, passive side reactions, and discharge of cathodic material[34] (Fig. 2). These challenges cause further complexity in the system and hinder the practical application of LABs. To address these issues and optimize the performance of LABs, it is crucial to understand the intricate air electrochemistry and the anode degradation mechanism, as well as to develop stable electrolytes[35]. The redox reactions occurring in LABs for the energy conversion process rely on specific components, each designed to overcome operational challenges and improve overall performance. In the following section, we will discuss the main components of LABs and their roles in addressing these challenges.

2.1 Components of LABs

2.1.1 The Li anodes

Li metal anodes in LABs have high theoretical specific energy densities, offering the most negative potential and unmatched gravimetric capacities of 3860 mAh/g compared to conventional graphite or silicon-based anodes[36]. Lithium metal anodes in LABs enable full utilization of the air cathode's oxygen reduction capacity during discharge, boosting overall battery performance. The low redox potential and high theoretical capacity of lithium metal anodes contribute to excellent energy density[37]. However, when paired with organic liquid electrolytes in LABs, lithium metal anodes present safety risks, such as potential short-circuits and fires from dendrite formation or electrolyte leakage. Lithium metal offers high energy density but also faces challenges like lithium dendrite formation, unstable solid electrolyte interphase, rapid volume fluctuations, and continuous electrolyte decomposition. Dendrites can cause internal shorts, reducing cycling lifetimes to 50 cycles, which is below acceptable standards[38]. Despite these challenges, the lithium metal anode remains crucial for lithium-air batteries' theoretical possibilities. LABs face more challenges than LIBs due to the semi-open oxidizing environment, which can lead to complex side effects on the Li anode and electrolytes, such as electrolyte degradation and Li metal corrosion[39]. O_2 dissolution can lead to electrolyte degradation, generating H_2O and causing Li metal corrosion, thereby significantly affecting the electrochemical performance of LABs[40]. It is crucial to develop a practical approach to effectively prevent the contamination of lithium metal.

2.1.2 The O_2-breathing cathodes

Oxygen-breathing cathodes play a key role in the performance and viability of LABs by utilizing atmospheric oxygen as the reactant, contributing to the battery's high energy density. These cathodes facilitate the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), essential for the charge and discharge processes of the battery[41]. Numerous studies have focused on advancing electrocatalysts for O_2-breathing cathodes, emphasizing noble metals[42], transition metal oxides[43], and carbides, which are crucial for enhancing the reversible performance of LABs and reducing their operational potential[44]. Effective catalysts inside the O_2-breathing cathodes aid in the formation and degradation of Li_2O_2, facilitating the mass transfer of Li_xO_2 intermediates[45].

O_2-breathing cathodes can allow oxygen intake while excluding contaminants such as CO_2 and H_2O, enabling the use of ambient air. This exclusion of contaminants, made possible by materials like nano-engineered metal oxide-graphene aerogel matrix composites (NMOGAM), helps maintain the cathode's structural integrity and improves the overall electrochemical performance of the battery[46]. The unique properties of O_2-breathing cathodes enable enhanced capacity and cycle life, with hybrid cathodes combining Li-rich layered-oxide with O_2 components showing significantly higher discharge capacities and extended cycle life[47]. Catalytic materials such as Co_3O_4/Ru and potassium-doped cathodes further improve capacity, cycle life, and round-trip efficiency[48]. Advanced carbon materials like boron-doped reduced graphene oxide and carbon nanotubes can enhance structural stability and oxygen diffusion in O_2-breathing cathodes. Despite challenges like electrode disintegration and capacity fading, ongoing research into hybrid and composite materials aims to improve catalytic efficiency and durability, highlighting the potential for revolutionizing energy storage in applications like electric vehicles.

2.1.3 Conventional electrolytes

Electrolytes for LABs are categorized into 4 predominant categories: aqueous electrolytes, aprotic electrolytes, solid-state electrolytes (SSEs), and ionic liquid electrolytes[49]. The chemical reactivity of an oxygen electrode is affected by the type of electrolyte, as depicted in Fig. 4. Both non-aqueous and solid state lithium-air battery (SSLAB) systems have comparable chemical reactions, whereas aqueous systems follow different electrochemical reaction routes because their cathodes are exposed to the aqueous electrolytes which are mostly basic in nature[50]. The ORR in the discharge process is intricate, including many electron-transfer reactions with O_2-related molecules (O_2^-, OH^- and HO_2^-), that play an integral part in the reversible synthesis and degradation of LiOH[51]. Non-

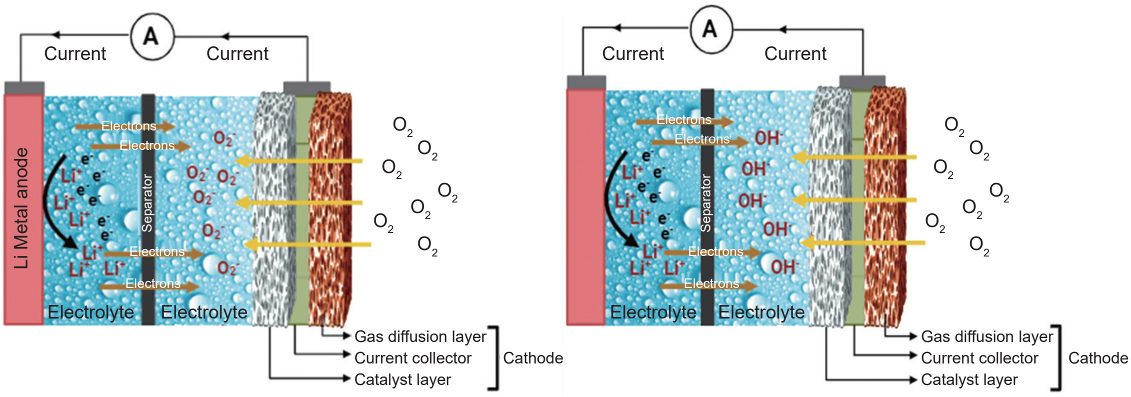


Fig. 4 Properties and mechanisms of LABs: (a) non-aqueous and (b) aqueous electrolyte

aqueous LABs have gained considerable interest in recent years for their higher energy storage capacity as compared to aqueous batteries[52]. Non-aqueous electrolytes for LABs require an elevated oxygen dissolution, lithium-ion transfer ability, significant solvation impact, and a stable electrochemical range, usually achieved by dissolving lithium salts in non-aqueous solvents. However, the semi-open design of non-aqueous electrolytes can rapidly deplete the configuration of LABs, resulting in safety issues and short circuit. In addition to this, blocking the air breathing porous structure of the electrode might cause severe polarization and irreversible electrochemical reactions. Therefore, novel electrolyte systems for LABs should be explored to meet the requirements of high-power density and stable processes. The ORR that occurs during the discharge process is complex.

LABs show great promise, but practical application is hindered by several challenges. To unlock the potential of these batteries, researchers are developing innovative designs and solutions to overcome limitations, improve performance, and ensure safety and reliability. This review critically assesses recent advancements to provide an overview of progress towards realizing the full potential of next-generation LAB technology.

3 Challenges in the advancement of Li-air batteries

The development of LAB technology represents one of the most exciting yet challenging limits in energy storage research. While these systems promise exceptional theoretical energy densities, the path from laboratory concept to practical implementation is covered with intricate challenges that limit multiple scientific disciplines. At the intersection of electrochemistry, materials science, and engineering, LABs represent a complex interaction of phenomena that simultaneously offer immense potential and pose significant obstacles. The hurdles facing Li-air technology are not only incremental but fundamental, requiring innovative solutions that push the boundaries of our current understanding and capabilities. From the molecular-level interactions at electrode surfaces to the macroscale engineering of cell structure, each aspect of LAB development presents unique difficulties that demand novel approaches and breakthrough technologies. As we delve into these challenges, we uncover the landscape where innovative research meets practical limitations, where the promise of revolutionary energy storage faces the realities of material limitations and system complexities. This section explores the multifaceted challenges (Fig. 5) that researchers and engineers must overcome to transform LABs from an enticing theoretical concept into a viable, high-performance energy storage solution for the future.

3.1 Effect of air constituents on electrochemistry of LABs

Atmospheric components significantly impact lithium-air battery performance. Traces of moisture, N_2 and CO_2 can form LiOH and Li_2CO_3, leading to increased overpotential and reduced cyclability[53]. We noted that these side reactions occur even in Li-O_2

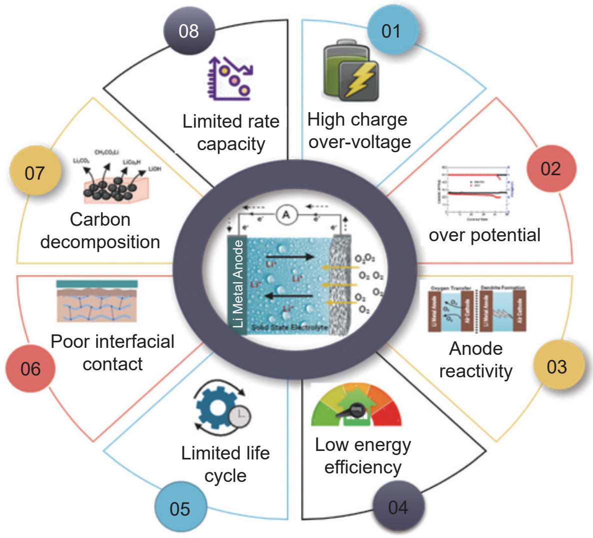


Fig. 5 Visual representation of the ongoing challenges confronted by LABs

cells due to solvent decomposition and electrode degradation. Paradoxically, minute quantities of H_2O and CO_2 may enhance performance, but higher concentrations ($>1.0\times10^{-3}$) prove detrimental. Understanding these processes is crucial for optimizing Li-air cell design, even with air-filtering membranes. Effective management of these chemical interactions is key to mitigating unwanted reactions and improving the long-term stability of practical lithium-air batteries. The impact of N_2 on cell performance, while present, is less pronounced compared to H_2O and CO_2. Hence, we emphasize that the elucidation of these chemical processes is crucial for optimizing lithium-air cell designs to mitigate undesired reactions and enhance cycling stability.

3.1.1 Effect of N_2 on the performance of battery

Nitrogen gas, constituting approximately 78% of atmospheric air, exhibits minimal impact on the oxygen reduction reaction in LABs. Several studies have successfully cycled in ambient air conditions, with limited evidence of nitrogen involvement in oxygen electrochemistry within typical electrochemical testing ranges (2–4.5 V)[54]. This apparent inertness of N_2 towards reduced oxygen species and its lack of redox activity within this potential window is advantageous for LAB development. The electrochemical reduction of N_2 to form Li_3N requires significantly lower potentials, with an estimated equilibrium voltage of approximately 0.46 V versus Li^+/Li, corresponding to a formation free energy (ΔG^0) for Li_3N between −129 and −135 kJ/mol[55]. This electrochemical inactivity of nitrogen in the operational voltage range of LABs simplifies cathode reactions and eliminates the need for complete O_2/N_2 separation from air. These characteristics can potentially facilitate the development of more practical and efficient LAB systems.

3.1.2 Effect of CO_2 on the performance of battery

Unlike nitrogen, "carbon dioxide significantly impacts the electrochemistry of nonaqueous LABs". It readily reacts with reduced oxygen species, particularly superoxide and peroxide[56]. The interaction between CO_2 and Li_2O_2 produces lithium carbonate (Li_2CO_3) as shown in reaction (16), which has several consequences[57–58]. This reaction can trigger side reactions with aprotic polar electrolytes, facilitated by intermediates like peroxydicarbonate. Furthermore, the transformation of Li_2O_2 into Li_2CO_3 intensifies polarization during battery recharge, resulting in increased overpotentials and faster battery degradation[59].

$$\begin{gathered} Li_2O_2 + CO_2 \rightarrow Li_2CO_3 + 1/2O_2 \\ \Delta G^0 = -166.6\ \mathrm{kJ/mol} \end{gathered} \tag{16}$$

The superoxide anion (O_2^-), being a strong nucleophilic and effective charge transferring species[60], reacts with CO_2 to form various peroxycarbonate species including CO_4^-, CO_4^{2-} and $C_2O_6^{2-}$[61]. These reactions have been confirmed through in-situ Raman spectroscopy studies by Qiao et al.[62]. The dominant electrochemistry shifts from O_2/O_2^- to $O_2^-CO_2/C_2O_6^{2-}$ as the CO_2/O_2 ratio in the cell atmosphere increases (reactions 17, 18 and 19). In Li-free electrolytes, peroxycarbonate species are observed without carbonate formation. However, in the presence of lithium ions, Li_2CO_3 becomes the primary discharge product.

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \tag{17}$$

$$O_2 + CO_2 + 2e^- \leftrightarrow CO_4^{-2}, \qquad E^\circ = 2.89\ \mathrm{V} \tag{18}$$

$$O_2 + 2CO_2 + 2e^- \leftrightarrow C_2O_6^{-2}, \qquad E^\circ = 3.27\ \mathrm{V} \tag{19}$$

$$O_2 + 2CO_2 + 4e^- + 4Li^+ \leftrightarrow 2Li_2CO_3, \quad E^\circ = 3.27\ \mathrm{V} \tag{20}$$

The nature of the cation significantly influences the stability of peroxycarbonate anions. Softer cations like tetrabutylammonium (TBA^+) stabilize the soft peroxydicarbonate anion more effectively compared to the harder Li^+, preventing further conversion to carbonate (reaction 20)[63]. Electrochemical pressure measurements have indicated that approximately 1.33 electrons are used per gas molecule during the discharge reaction involving CO_2 and O_2.

In summary, CO_2 contamination in LABs contributes to significant deterioration of the electrolyte by reacting with reduced oxygen species to form Li_2CO_3. This carbonate compound is difficult to oxidize back reversibly, and its accumulation leads to further degradation of both the electrode and electrolyte, potentially due to the generation of singlet oxygen during charging. Additionally, CO_2 contamination increases the charging overpotential, imposing more stringent requirements on both the cathode and electrolyte to maintain reversible Li_2O_2 formation. Avoiding the generation of Li_2CO_3 is critical in LABs unless novel strategies are developed to improve oxygen recovery. Qiao et al. explored the use of a $Li^+(DMSO)_3$ complex in a concentrated LiTFSI/DMSO electrolyte, leveraging the stabilization of $C_2O_6^{2-}$ by the softer TBA^+ ion[62]. In this system, DMSO molecules effectively screen the Li^+ charge, minimizing interactions between Li^+ and $C_2O_6^{2-}$, which shifts the dominant charging reaction from Li_2CO_3 decomposition at 4.2 V to the decomposition of soluble $Li_2C_2O_6$ species at 3.5 V.

3.1.3 Effect of H_2O on the performance of battery

Lastly, we explore the influence of water on nonaqueous oxygen electrochemistry. In LABs, water contamination can originate from various sources, including oxygen supply tubing, electrolytes, or cell components. The incorporation of a water trap for moisture removal would significantly increase the overall weight and volume of the battery, thereby reducing its competitiveness compared to other battery technologies. Furthermore, water can enter the system as a contaminant due to imperfect cell sealing, residual moisture in the oxygen supply tubing, electrolyte, or other cell components, posing additional challenges for the performance of battery. Gasteiger et. al.[64] revealed that water presence, ranging from hundreds to thousands of 10^{-6}, either as an electrolyte additive or due to cell leakage, significantly enhanced $Li\text{-}O_2$ cell capacity. Remarkably, water did not alter the fundamental nature of the discharge product, which remained Li_2O_2[65]. This phenomenon extends to water-in-salt $Li\text{-}O_2$ batteries, which, despite lacking organic solvents and thus avoiding solvent decomposition issues during cycling, still produce Li_2O_2 as the primary discharge product. Notably, the reaction between water and Li_2O_2 to form LiOH is thermodynamically favorable. These findings underscore the complex role of water in $Li\text{-}O_2$ systems and its potential to influence cell performance without necessarily changing the core electrochemical processes[66].

Several studies suggest that in water-containing $Li–O_2$ cells (with water concentrations at or below a few thousand 10^{-6}), the conversion of Li_2O_2 to LiOH is kinetically slow. Specifically, the presence of water does not readily result in Li_2O_2 being transformed into LiOH, likely due to the slow kinetics of (equation 6).

$$\begin{gathered}2Li_2O_2 + 2H_2O \rightarrow 4LiOH + O_2 \\ \Delta G^0 = -152\ \mathrm{kJ/mol}\end{gathered} \tag{21}$$

When LiOH creates a protective layer on Li_2O_2, further conversion requires water protons to move through the LiOH to reach the Li_2O_2 core, causing oxygen to be released from the core. This protective effect may lessen at higher water levels as LiOH becomes more soluble, making it easier for Li_2O_2 to change into LiOH. For example, the research studied by Xia et al.[67] on how moisture impacts battery chemistry using a Ketjen black cathode and LiTFSI/TEGDME electrolyte found that LiOH and Li_2O_2 were discharge products. The carbon-based cathode struggled to decompose LiOH effectively, leading to significant polarization during recharging. The findings suggest that while Li_2O_2 conversion to LiOH may alleviate some effects, it doesn't fully resolve LiOH-induced polarization. However, some moisture-related effects like improved capacities and decreased degradation offer interesting areas for future research.

Water significantly affects both the cathode and anode in LABs. Cho et al.[68] demonstrated that H_2O

exposure leads to the formation of a porous lithium hydroxide (LiOH) surface layer on the anode, as evidenced by the grayish appearance of cells exposed to moisture during discharge. The porous LiOH layers are ineffective in protecting the lithium anode, contributing to the growth of dendritic lithium structures during charge-discharge cycles[69]. LABs operating at 40% relative humidity also experience Li anode volume expansion and LiOH formation[70]. High H_2O levels (>2000 ppm) degrade both the cathode and anode, emphasizing the need for effective strategies to remove excess water from LABs.

3.2 Porosity constraints in air cathode design

The performance of LABs is primarily limited by the air cathode, which accounts for most of the cell's energy delivery and voltage drop. Studies show that while the anode potential remains stable at ~ 0.02 V vs. Li^+/Li, the air cathode contributes significantly to the overall voltage decrease[71]. This emphasizes the need for air electrode optimization to enhance cell performance. Non-aqueous electrolyte systems in LABs offer higher cell capacities compared to aqueous configurations, but present unique challenges at the air electrode-electrolyte interface. These findings underscore the importance of focused research on air cathode development to overcome current limitations in LAB technology.

In practical applications, non-aqueous LABs often fail to reach their theoretical energy potential, due to the early termination of discharge. This premature termination occurs before the entire pore volume of the air electrode is filled with Li_2O. Research suggests that the discharge process stops because the lithium oxide precipitates clog the pore openings, preventing further oxygen intake and hindering lithium-ion transport into the deeper pore spaces. As a result, even though a substantial portion of the pore volume remains unoccupied, the discharge process stops[72].

Further research studies have shown that air electrode pores are not fully filled with lithium oxides by the end of discharge, with only a fraction of the total pore volume utilized. This usable pore fraction varies across experiments, with reports indicating values of approximately 47% (at 1.96 mg cm^{-2} cathode carbon loading)[73], 7% and as low as 3% (at 12.57 mg cm^{-2} cathode loading)[74]. Further calculations reveal that under discharge conditions, lithium oxides accumulate randomly near the pore openings, and typically within 20% of the pore radius from the orifice. This non-uniform filling significantly limits the overall efficiency of the air cathode in non-aqueous LABs. Studies on air electrodes with various carbons without added catalysts suggest that discharge termination in LABs is caused by pore cavity barriers rather than the blockage of active charge-transfer sites. This is supported by the lack of correlation between carbon pore surface area and discharge capacity, contradicting the expected outcome if active site blocking were the primary issue.

However, research findings[75] demonstrate no such correlation between carbon pore surface area and discharge capacity. Instead, a strong positive correlation has been observed between average pore diameter and discharge capacity. This relationship strongly suggests that pore geometry, rather than surface area, is the critical factor in determining cell performance. Furthermore, impedance data confirms the hypothesis that pore orifice clogging is the predominant factor in cell discharge termination. Additionally, if the active center barrier were the primary mechanism, finer dispersions of catalytically active centers across the surface would require greater amounts of precipitates to block them. Notably, studies have shown that the performance of carbon finely loaded with Fe_2O_3 is comparable to that of carbon merely mixed with Fe_2O_3 powder[76]. Nevertheless, it should not be entirely dismissed that discharge termination may, under certain conditions, also be linked to the blockade of active reaction sites by precipitates. This analysis suggests that one avenue for enhancing energy performance of the battery involves developing novel cathode materials capable of accommodating substantial amounts of Li_2O_2 without compromising oxygen and Li^+ transport through pore blockage. The capacity of carbon to accommodate precipitates is closely related to its pore structure. Materials with meso- and macro-sized pores have demonstrated the ability to accommodate significant amounts of Li-peroxide precipitate without impeding oxygen and Li^+ transfer[77].

In summary, the optimization of air cathode architecture remains a critical challenge in realizing the full potential of LABs. Future research should focus on developing novel cathode materials with optimized pore structures that can accommodate substantial amounts of discharged products without compromising oxygen and lithium-ion transport. Strategies such as hierarchical pore designs, advanced carbon materials with tailored meso- and macropores, and innovative catalyst dispersions could potentially address the issues of pore clogging and non-uniform product deposition. By overcoming these limitations, we can pave the way for next-generation LABs with significantly improved energy density and cycle life, bringing us closer to their theoretical performance capabilities.

3.3 Parasitic reactions at carbon cathode

The degradation of carbon cathodes through parasitic reactions and interface corrosion presents a significant challenge in the development of high-performance lithium-oxygen (Li-O_2) batteries. Despite its widespread use as a host material for Li_2O_2, susceptibility of carbon to degrade under operating conditions necessitates a thorough understanding of the underlying mechanisms to improve battery longevity and efficiency. Carbon has emerged as the predominant material for Li_2O_2 accommodation in LABs, owing to its favorable properties including low density, cost-effectiveness, high electrical conductivity, processing versatility, and relative stability. The chemical resilience of carbon cathodes in the presence of reactive oxygen species is paramount for achieving battery reversibility. Extensive research efforts have been directed towards elucidating the degradation mechanisms of carbon cathodes, particularly under high overpotential conditions.

Multiple factors have been identified as influencing carbon degradation in Li-O_2 batteries, including charging overpotentials, electrolyte composition, surface defects, and carbon functionalization[78]. McCloskey et al.[79] pioneered the investigation of carbonaceous cathode oxidation in the presence of Li_2O_2 and a highly oxidative environment, leading to Li_2CO_3 formation through specific reactions shown in equations (7 and 8). Thermodynamic analysis (ΔG^0) indicates that the reaction between Li_2O_2 and the carbon cathode to form Li_2CO_3 is highly favorable, suggesting substantial Li_2CO_3 formation at the Li_2O_2-carbon interface by the end of discharge.

$$\begin{gathered}\mathrm{Li_2O_2 + C + 1/2O_2 \rightarrow Li_2O_3} \\ \Delta G^0 = -542.4\ \mathrm{kJ/mol}\end{gathered} \tag{22}$$

$$\begin{gathered}\mathrm{2Li_2O_2 + C \rightarrow Li_2O_3 + Li_2O} \\ \Delta G^0 = -533.6\ \mathrm{kJ/mol}\end{gathered} \tag{23}$$

Interestingly, only minimal Li_2CO_3 byproduct formation has been observed during discharge, particularly in ether-based electrolytes. To further explore this approach, Xu et al.[80] employed solid-state ^{13}C nuclear magnetic resonance spectroscopy on a ^{13}C-enriched (99%) carbon cathode post-discharge, comparing it to a naturally abundant carbon cathode. This innovative approach provided valuable insights into the carbon degradation mechanisms and the formation of byproducts at the molecular level.

The ^{13}C NMR signal for Li_2CO_3 would be anticipated to be significantly greater, approximately 2 orders of magnitude higher, than that from a carbon cathode with natural carbon abundance, if the creation of Li_2CO_3 were directly induced by a reaction with the ^{13}C-enriched carbon cathode. However, such a rise in signal was not detected, and Li_2CO_3 was readily eliminated by solvents[81]. This suggests that the Li_2CO_3 seen during discharge is probably not directly caused by corrosive carbon but rather a result of electrolytic degradation[82]. The kinetics of the Li_2O_2-carbon reactions are slow, though it is thermodynamically possible. In addition, superoxide (O_2^+, LiO_2) and singlet oxygen are further reactive oxygen species that can cause corrosion of carbon at the carbon-electrolyte interface. The degree of corrosion depends on the nature, crystal structure, and morphological aspects of the carbon cathode[83]. Studies by Bruce, Shao-Horn, and colleagues have demonstrated that carbon cathodes, such as graphitic carbon or reduced graphene oxides that possess a high density of oxygen-containing functional groups (e.g., C=O, C—O, C—OH, COOH) show diminished stability in LABs[84]. Specifically, superoxide species generated during discharge can oxidize carbon at defect sites, leading to the formation of Li_2CO_3.

Itkis and colleagues have demonstrated that the crystallinity of carbon cathodes significantly influences their chemical stability, with well-arranged carbon configurations being advantageous for a stoichiometric Li_2O_2 reaction[85]. In contrast, the charging process presents a different scenario. McCloskey, Bruce, and their team utilized ^{13}C-labeled carbon electrodes in combination with naturally abundant ether-based electrolytes, and they tracked CO_2 evolution during charging using differential electrochemical mass spectrometry (DEMS). Their observations revealed that while $^{12}CO_2$ was emitted at all charging voltages, significant amounts of $^{13}CO_2$ were detected only when the voltage exceeded 3.8 V. This finding suggests that electrolyte decomposition occurs across all charging voltages due to reactions involving Li_2O_2, $Li_{2-x}O_2$, LiO_2, and singlet oxygen, whereas direct carbon corrosion manifests only at higher charging voltages, with CO_2 resulting from the electrochemical breakdown of Li_2CO_3[86]. Furthermore, they discovered that charging after discharging with ^{18}O-labeled $Li_2{}^{18}O_2$ led to a mixture of ${}_{12}C_{16}O_2$, $^{18}O_2$, indicating that the oxygen in CO_2 originates from both Li_2O_2 and the electrolyte[79]. McCloskey and collaborators proposed that, as charging progresses, parasitic reactions at both the Li_2O_2-electrolyte and Li_2O_2-carbon interfaces lead to the accumulation of Li_2CO_3 over repeated cycles. This accumulation was later validated using X-ray absorption near edge structure (XANES) spectroscopy (total electron yield mode) and ^{13}C–^{13}C 2D homonuclear correlation NMR spectroscopy[77]. The NMR cross-peaks between ^{13}C resonances of Li_2CO_3 and the carbon electrode indicated proximity, suggesting direct contact. The formation of these interfacial Li_2CO_3 films significantly contributes to increased polarization during charging, thereby promoting further parasitic reactions. To mitigate carbon corrosion and limit the formation of interfacial Li_2CO_3, it has been recommended that the charging voltage for carbon-based Li−O_2 batteries be maintained below 3.5 V[87]. These findings underscore the complex interactions between carbon cathodes, reactive oxygen species, and electrolyte components in lithium-air batteries, highlighting the need for ongoing research to develop strategies for reducing carbon degradation and improving the stability and performance of cathode materials in advanced battery systems.

3.4 Lithium metal anode instability

Lithium metal is considered one of the most promising anode materials due to its outstanding specific capacity of 3860 mAh/g, which is calculated based on the lithium mass in the fully charged state of the battery[88]. This material is integral to achieving the high energy density often cited for LABs[89–90]. While extensive research has focused on cathode (electro)chemistry, comprehensive studies on the lithium metal anode in non-aqueous LABs remain limited. In several fundamental investigations that emphasize cathode performance, $LiFePO_4$ (LFP) is frequently substituted for the Li metal anode to mitigate complications arising from anode degradation. However, achieving the high specific energy potential of LABs requires addressing the challenges related to lithium metal anodes in future research.

The lithium metal anode faces a significant challenge in the form of detrimental morphological alterations during repetitive stripping and plating cycles. Specifically, at lower current densities, mossy structures develop on the lithium metal surface that are characterized by compact porous microstructures, while at higher current densities, dendritic growth occurs, manifesting as spiny projections extending outward from the lithium metal surfaces, as opposed to the desired smooth plating on the lithium metal surface[91]. The formation of dendrites poses a critical safety risk, as they have the potential to penetrate the separator and contact the oxygen electrode, resulting in an electrical short circuit within the battery.

3.4.1 Atomic-scale mechanisms of dendrite formation

Recent advances in characterization techniques have revealed that Li dendrite formation follows nonclassical nucleation pathways, challenging traditional theories of electrodeposition. At the atomic scale, the process involves complex prenucleation clusters (PNCs) that serve as intermediate stages before stable dendrite formation. These PNCs, typically 1–2 nm in diameter, have been directly observed through in-situ transmission electron microscopy during early-stage Li electrodeposition. During the initial stages, multiple small current spikes in chronoamperometric measurements indicate the presence of transient PNCs, providing a lower bound estimate of critical nucleus radius between 29–89 nm depending on the applied potential[92].

The morphological evolution of Li dendrites exhibits distinct patterns in solid electrolytes, categorized as “straight”, “spalling”, “branching”, and “diffuse” structures (Fig. 6a-d). Each morphology represents different growth mechanisms: straight dendrites show uniform propagation, spalling indicates mechanical degradation of the electrolyte, branching demonstrates tip splitting during growth, and diffuse patterns suggest more distributed Li penetration[93]. The growth rate of these dendrites shows a directly proportional relationship with the applied current (Fig. 6e), where higher currents accelerate dendrite propagation and increase the risk of short circuits.

Time-resolved in-operando imaging has provided unprecedented insights into the dynamic nature of dendrite evolution. In-situ SEM observations have revealed that Li dendrite growth initiates cracks and drives their propagation through the solid electrolyte (Fig. 6f). This process begins with crack nucleation (marked by yellow dotted lines) followed by progressive dendrite advancement, demonstrating the coupled nature of mechanical damage and electrochemical deposition[94]. Moreover, recent studies using liquid-cell TEM have captured the existence of disordered nanoclusters that can undergo reversible structural fluctuations between amorphous and crystalline states, providing direct evidence of nonclassical nucleation pathways[95].

Surface diffusion mechanisms play a decisive role in determining whether deposited Li atoms contribute to uniform plating or dendritic growth. Mo-

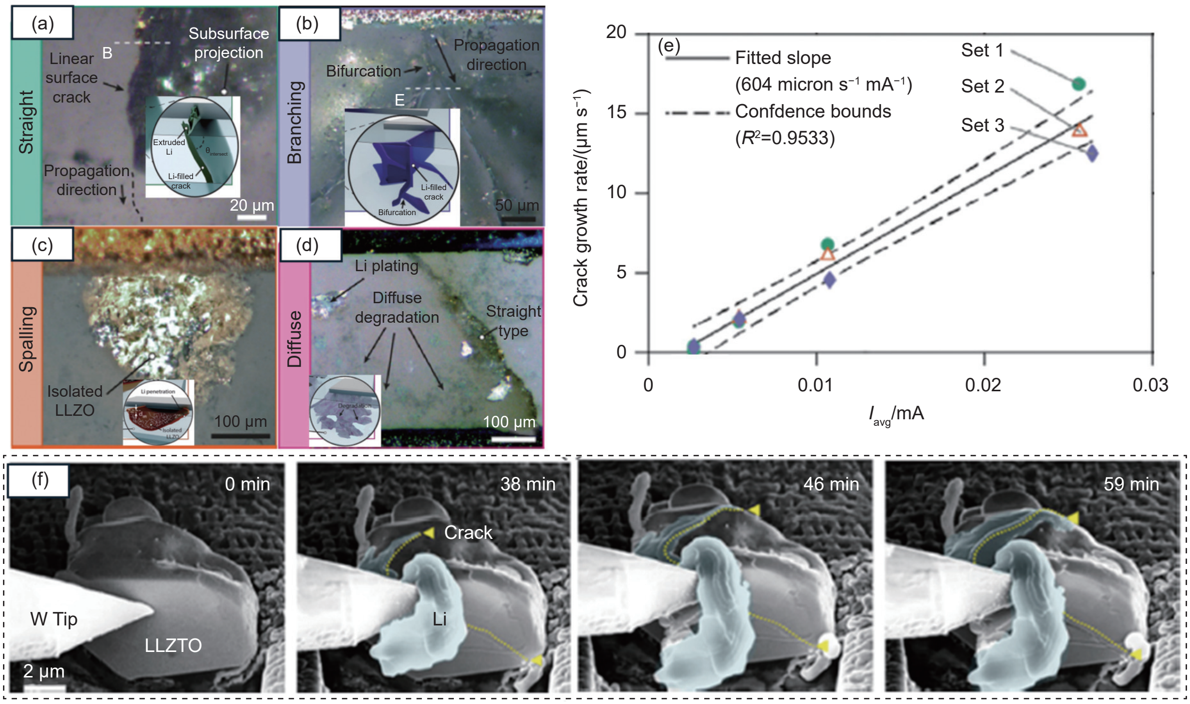


Fig. 6 Morphological analysis of lithium-induced degradation in solid electrolytes: (a-d) Different failure modes observed in LLZO, including straight surface cracking, branching patterns, spalling and diffuse degradation. (e) Quantitative relationship between current and crack growth rate with fitted slope analysis[93]. (f) Time-resolved SEM images showing progressive lithium deposition and crack evolution in LLZTO over 59 min[92]. (Copyright permission granted from Ref: [92,93])

lecular dynamics simulations have revealed that Li adatoms face a significantly higher surface diffusion barrier compared to other metals like magnesium, which explains their greater tendency to form dendrites[96]. For example, as Mg shows a surface diffusion barrier of only 0.01 eV and tends to form uniform deposits, the higher diffusion barrier of Li impedes atom mobility and promotes irregular structure formation. This inherent limitation in surface mobility, coupled with the size-dependent plasticity of Li at the nanoscale, creates a complex interplay between electrochemical and mechanical factors during dendrite growth[97].

The atomic-scale processes are further complicated by the presence of grain boundaries and other structural defects in solid electrolytes. These features create preferential pathways for both ion transport and dendrite propagation, with recent studies showing that grain boundaries can exhibit up to 50% lower shear modulus compared to bulk material, making them particularly susceptible to dendrite penetration[98].

3.4.2 Microstructural effects on dendrite propagation

The propagation of Li dendrites is fundamentally controlled by microstructural features, particularly grain boundaries and interfacial characteristics in solid electrolytes. It has been revealed from different research works that grain boundaries serve as preferential pathways for dendrite growth due to their dual nature: they act both as high-diffusivity channels for Li ions and as mechanically vulnerable regions susceptible to dendrite penetration[99]. In-situ electron microscopy studies have revealed that dark regions appearing in cycled solid electrolyte pellets (Fig. 7a, b) correspond to Li dendrite penetration through interconnected pores and along grain boundaries, ultimately leading to catastrophic short circuits[100]. This penetration is particularly severe when grain boundaries are oriented perpendicularly to the interface between the solid electrolyte and Li electrodes.

The interface between Li metal and solid electrolyte plays a decisive role in dendrite evolution through multiple mechanisms. To address these interfacial and microstructural challenges, various strategies have been developed and implemented. Table 1 provides a comprehensive comparison of different approaches for controlling Li dendrite growth in solid electrolytes, evaluating their practical effectiveness, advantages,

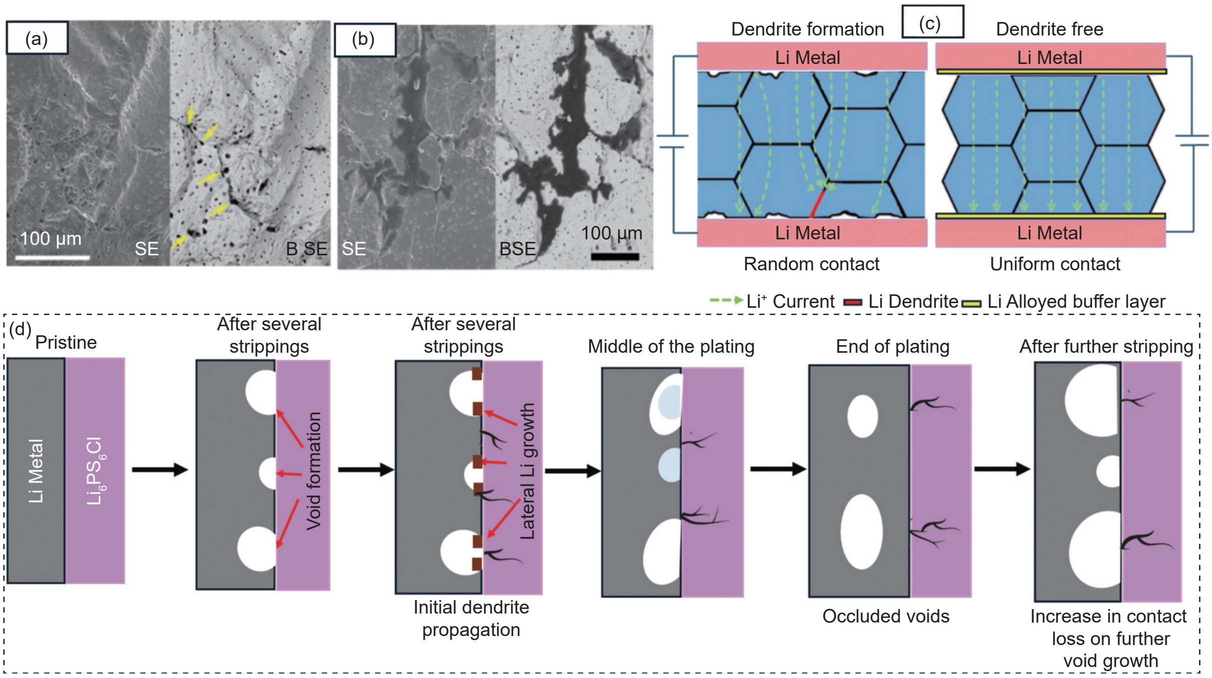


Fig. 7 Lithium dendrite characterization: (a) Cycled pellet showing darkened regions[100]. (b) SEM/BSE imaging of intergranular dendrite growth[111]. (Copy right permission granted from Ref. [100,111]) (c) Critical current density (CCD) for dendrite initiation at varying temperatures[102] (Reproduced from Ref. [102]) (d) Schematic representation of void-mediated dendrite formation mechanism above CCD during Li stripping[103] (Reproduced from Ref. [103])

and limitations. Each strategy targets specific aspects of the dendrite formation mechanism, from surface modification to structural design.

Among these strategies, interface engineering strategies like coating and chemical modification have shown promising results in improving critical current density and cycling stability. For instance, as shown in Table 1, grain boundary modification through Li_2CO_3 and LiOH addition can increase the CCD from 0.15 to 0.6 mA/cm^2[101]. However, each approach presents specific challenges in terms of processing complexity and scalability that must be considered for practical applications.

As illustrated in Fig. 7c, the quality of interfacial contact significantly influences current distribution and subsequent dendrite formation[102]. The formation and evolution of voids during the stripping process presents another critical challenge. When the current density exceeds the critical threshold during stripping, voids form at the interface between Li metal and solid electrolyte (Fig. 7d). These voids subsequently serve as nucleation sites for dendrite formation in following cycles[103]. Three-dimensional synchrotron X-ray tomography has revealed that void formation is particularly prevalent in regions with up to 96% relative density, highlighting the importance of achieving near-perfect density in solid electrolytes[104].

Various research findings have identified multiple strategies for controlling dendrite propagation through microstructural engineering. For instance, introducing thin layers of materials like $LiAlO_2$ on grain surfaces can increase the CCD from 0.4 to 0.75 mA/cm^2 at room temperature[112]. Similarly, coating MoS_2 layers on solid electrolytes has shown promise in alleviating dendrite growth by modifying the interfacial properties. The incorporation of LiI into sulfide-based solid electrolytes has demonstrated effectiveness in improving Li transport at the interface while suppressing dendrite nucleation[113].

The achievement of high Coulombic efficiency remains paramount for practical applications. Application of batteries in electric vehicles demand over 1000 charge/discharge cycles with a Coulombic efficiency of 99.98% to maintain 80% capacity retention[106]. The advancement in electrolyte engineering has shown promising results, with some systems approaching 99.9% efficiency through careful control of interfacial chemistry and mechanical properties[110]. Time-resolved in-operando neutron depth profiling has provided valuable insights into the origin of dendrite formation by monitoring dynamic evolution of Li concentration profiles during deposition, revealing the critical role of electronic conductivity in dendrite initiation.

Despite the challenges faced by LABs, researchers have been actively exploring various strategies to mitigate these issues and push the boundaries of LAB technology. By addressing the limitations associated

Table 1 Comparison of strategies for controlling Li dendrite growth with specific merits and demerits

Strategy	Material	Method	Key advantages	Main limitations	Performance improvement	Ref.
Surface coating	LLZO	MoS_2 layer deposition	• Improves interfacial contact • Reduces resistance	• Complex coating process • Uniformity challenges	Dendrite growth suppressed at standard operating conditions	[105]
Pore engineering	LLZO	Surface pore filling with liquid electrolyte or Si nanoparticles	• Better interfacial contact • Enhanced ion transport	• Partial loss of solid-state benefits • Processing complexity	Effective reduction in dendrite nucleation	[106]
Grain boundary modification	LLZTO	Li_2CO_3 and LiOH addition	• Higher ionic conductivity • Better mechanical stability	• Complex processing • Control challenges	CCD increased: 0.15 → 0.6 mA/cm^2	[101]
Interface layer	LLCZN	$LiAlO_2$ thin layer coating	• Reduces electronic conductivity • Suppresses dendrite nucleation	• Requires precise thickness control	CCD increased: 0.4 → 0.75 mA/cm^2	[107]
Chemical doping	LPS	LiI incorporation	• Better Li transport • Improved interface stability	• Higher material costs • Conductivity effects	Significant increase in CCD	[108]
3D architecture	LLZTO	Acid etching process	• Larger interface area • Lower local current density	• Complex fabrication • Scale-up challenges	Stable long-term cycling achieved	[109]
Hybrid design	LLZO/LATP	Combined solid/liquid electrolyte	• Enhanced interfacial contact • Better ion transport	• More complex system • Partial loss of solid benefits	Improved cycling stability	[110]

with the cathode, anode, and electrolyte components, as well as the overall cell design, considerable progress has been made towards realizing the full potential of LABs. The next section will explore recent advancements and emerging solutions that have potential for overcoming the challenges discussed earlier and paving the way for the practical implementation of high-performance LAB systems.

4 Mitigation strategies in Li-air batteries

4.1 Preventing moisture and CO_2 contamination on Li electrodes using oxygen-selective membranes

The use of non-aqueous LABs under ambient conditions requires the effective exclusion of moisture and carbon dioxide from the cell environment. This challenge has been addressed with the introduction of oxygen-selective membranes (OSMs), which allow oxygen to pass through while blocking moisture and carbon dioxide from reaching active sites[114]. The idea of using membranes for moisture control was first proposed by Muthiah et al.[115], who suggested polyvinylidene fluoride (PVDF)-Teflon amorphous fluoropolymer (AF) as a hydrophobic material for LABs, although they did not evaluate its electrochemical performance. Crowther and coworkers[116] advanced the practical use of OSMs by applying Teflon-coated fiberglass cloth, achieving a notable 94% capacity increase. Their work also optimized $LiBF_4$ concentration across various electrolytes, including propylene carbonate, 1,2-dimethoxyethane, dimethyl carbonate, and tetraethylene glycol dimethyl ether, with testing at 23 °C and 23% relative humidity. This research marks a significant step forward in developing LABs suitable for operation in real-world atmospheric conditions. To further advance these early developments, recent research has shifted towards quantitatively evaluating key performance metrics of OSMs, such as permeability and selectivity, to enhance their role in stabilizing LAB performance under ambient conditions. The effectiveness of OSMs is determined by both oxygen permeability and transmission rate[117]. The permeability (P) is defined as

$$P = DS \tag{i}$$

where D is the diffusion coefficient ($cm^2\ s^{-1}$) and S is the solubility coefficient. This relationship can be expressed in terms of oxygen transmission rate (OTR) normalized for membrane thickness as:

$$P = cm^3(gas)cm\ cm^{-2}\ s^{-1}mm\ Hg^{-1}$$

Here cm^3 (gas) is a molar quantity calculated at STP that can be used to determine the solubility coefficient. The units for P are expressed in Barrer that can be expressed as:

$$1\ Barrer = 10^{-11}cm^3(gas)cm\ cm^{-2}s^{-1}mm\ Hg^{-1} \tag{ii}$$

The maximum current density (i_{max}) supported by an OSM is directly related to oxygen flux (j_{O2}) through the relationship:

$$i_{max} = nFj_{O2} \tag{iii}$$

where n represents the electron equivalents per mole of oxygen and F is Faraday's constant[118]. To achieve long-term electrochemical stability in LABs operating under ambient conditions, it is imperative to develop OSMs with high oxygen permeability ($P > 100$ Barrer) while simultaneously minimizing water vapor permeation to prevent anode corrosion and electrolyte degradation. This, in turn, ensures a stable oxygen reduction reaction (ORR) environment, reducing parasitic side reactions and enhancing overall LAB efficiency.

Various studies have investigated the essential properties of OSMs for LABs, highlighting 4 critical characteristics: high oxygen diffusion to maintain battery capacity[119], strong hydrophobicity to prevent moisture ingress, carbon dioxide blockage to avoid Li_2CO_3 formation, and reduction of electrolyte evaporation during operation[120]. As illustrated in Fig. 8, OSM design strategies primarily focus on physical regulation (optimizing porosity and thickness) and chemical regulation (incorporating O_2-favorable materials).

Recent experimental studies have demonstrated remarkable progress across various OSM material categories. PVDF-HFP membranes modified with nanosponges have achieved impressive stability, enabling 145 cycles over 1450 h at RH 17%[121]. The incorporation of dextrin-nanosponge particularly enhanced CO_2

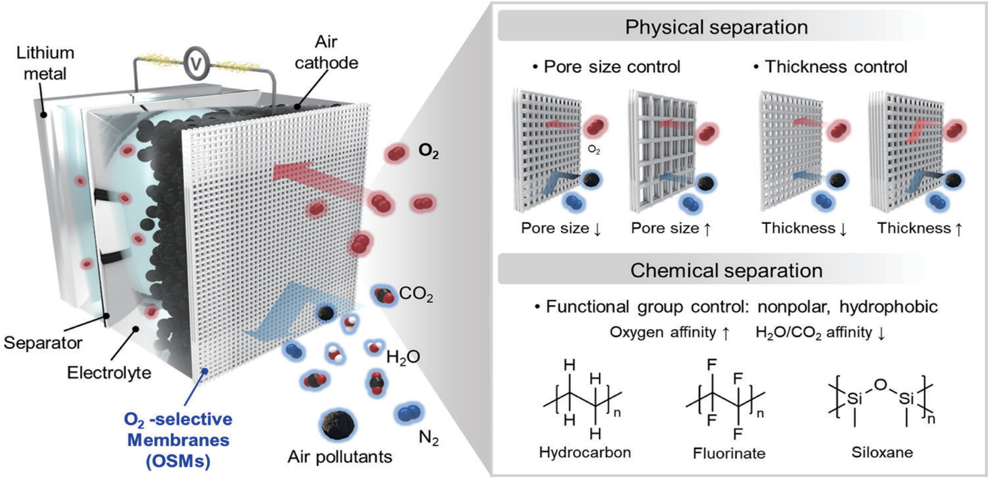


Fig. 8 Overview of approaches to design O_2-selective membranes for the ambient operation of LABs

blocking through functional group interactions while maintaining oxygen transport pathways. In parallel, Zhang et al.[122] demonstrated enhanced LAB performance using silicone oil-loaded OSMs on Teflon films (PTFE) and porous metal sheets. At 20% RH, the battery operated for 16.3 days, achieving 789 mAh/g capacity and 2182 Wh/kg specific energy while maintaining selectivity of 2.5–5.0 mol O_2/mol H_2O, compared to 5.5 days, 267 mAh/g, and 704 Wh/kg for PTFE-only barriers. Similarly, Zou et al.[123] utilized silica-aerogel OSMs, achieving 165 cycles at 500 mA/g in dry conditions and 130 cycles at 45% RH, compared to 55 cycles and 12 cycles without OSMs, respectively. The application of OSM promoted the Li_2O_2 formation over LiOH (Fig. 9a-f).

Significant advances have also been made in composite membrane architecture. Cao et al.[124] developed composite membranes incorporating polydopamine-coated metal organic framework crystals (CAU-1-NH_2) into polymethylmethacrylate (PMMA), achieving 1480 mAh/g and 66 stable cycles at 30% RH. The synergistic combination of $-NH_2$ (MOF), $-OH$ (dopamine), and $C=O$ (PMMA) functional groups created effective barriers against contaminants while maintaining oxygen transport. Additionally, Wang et al.[125] demonstrated the efficacy of a low-density polyethylene (LDPE) film as OSM for LABs. LDPE films have shown remarkable performance with oxygen permeability of 40.3 Barrer and low water permeability of 0.825 g m^{-2} day^{-1}. When coupled with a LiI redox mediator (RM), this configuration achieved significant stability of 610 cycles in ambient air (5% RH) without detectable Li_2CO_3 formation, a common failure mode in LABs due to parasitic side reactions. Similarly, Amici and coworkers[126] found that polyvinylidene fluoride co-hexafluoropropylene (PVDF-HFP) OSMs provided 640 mAh/g at 17% RH, significantly outperforming non-OSM configurations and protecting the lithium anode. This improvement was attributed to enhanced hydrophobicity and oxygen transport properties, which stabilized the Li-air interface during prolonged cycling

The development of perfluorinated compounds has further expanded OSM capabilities and practical applications as active material. PFPE-based membranes on Celgard substrates demonstrated exceptional stability with 144 cycles at 100 mA/g, achieving capacities of 7843 mAh/g at 30% RH[127]. The successful use of these compounds stems from the combination of high oxygen solubility and strong hydrophobicity. The comprehensive experimental results presented in Table S2 demonstrate significant improvements in cycle stability (>100 cycles), capacity retention at higher relative humidity (30%–50% RH), and enhanced current density tolerance with newer materials.

Recent advancements in OSM design have concentrated on optimizing the balance between membrane thickness, surface area, and oxygen permeation distance[128]. These efforts have led to the develop-

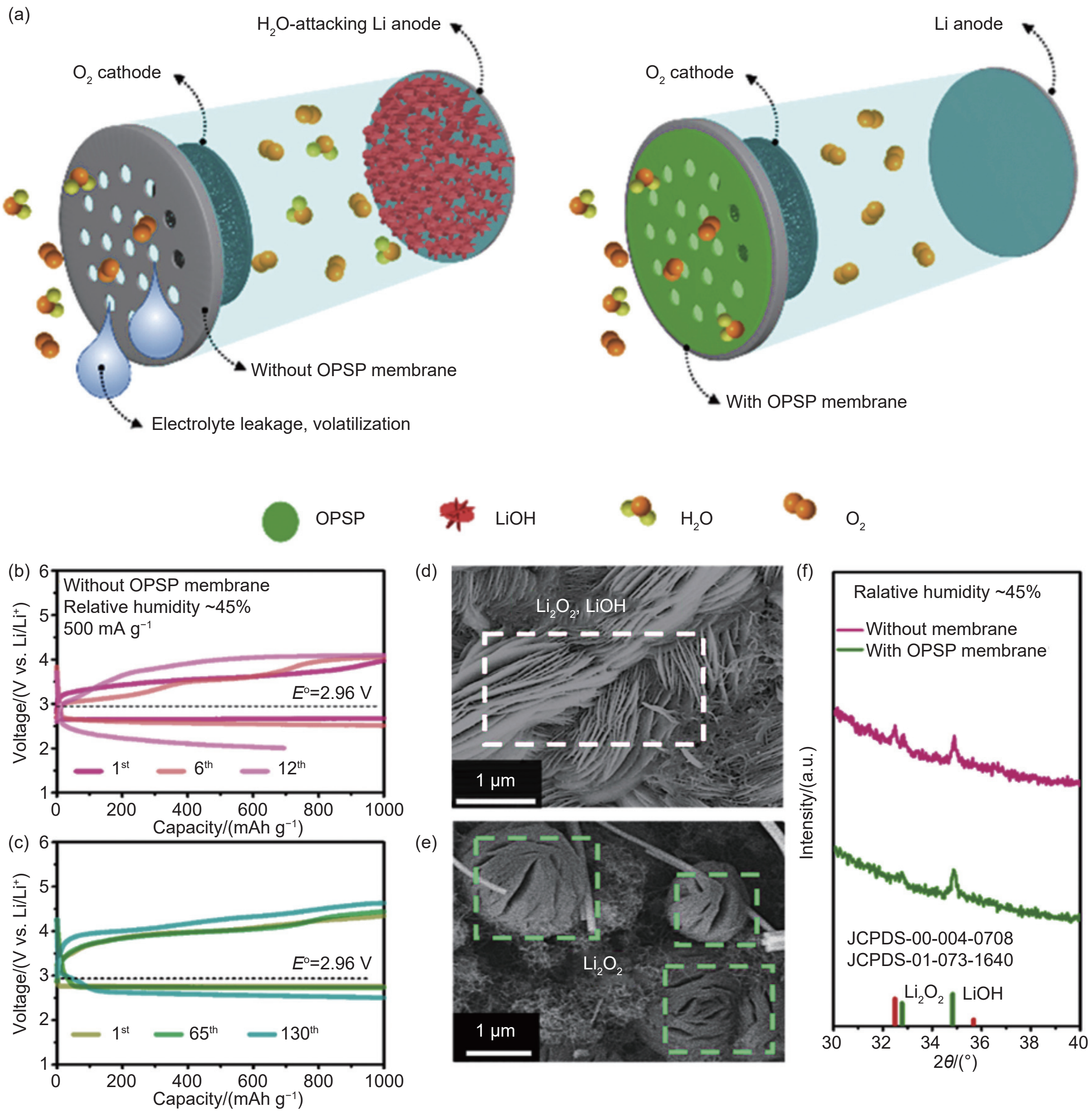


Fig. 9 Characteristic O_2-selective membranes: (a) Graphic illustration. (b-c) Cycling comparison and discharge products. (d-e) SEM. (f) XRD patterns of LABs in ambient air with/without OPSP[123]. (Copyright permission granted from Ref. [123])

ment of hierarchical structures that combine micro- and macro-scale features, surface modifications to enhance selectivity, and innovative composite architectures that leverage multiple material properties[129]. The incorporation of catalytic components has also demonstrated potential for improved oxygen transport. Despite the significant progress made in this field, there remain opportunities for further optimization of oxygen permeability, selectivity, and long-term stability. These improvements can be achieved through the exploration of novel composite architectures, the implementation of advanced fabrication techniques, and the enhancement of mechanical stability for extended operation[130]. Current design strategies have emphasized integrated approaches, such as the direct application of protective layers to electrode surfaces.

Future research in this area should prioritize the development of novel architectures that minimize transport resistance while maintaining high selectivity[131]. This goal may be achieved through the investigation of hierarchical structures or the utilization of advanced composite materials that can more effectively manage the competing demands of oxygen transport and contaminant blocking. By focusing on these research directions, scientists and engineers can continue to push the boundaries of OSM technology, ultimately leading to more efficient and sustainable energy systems.

4.2 Ideal cathode strategies for LABs

A rechargeable non-aqueous LAB must exhibit 4 essential characteristics to be considered high performing (Fig. 10). These key attributes include: (1) High specific capacity. (2) High round-trip efficiency. (3) Good rate capability. (4) Excellent cycling performance[132]. The cathode plays a pivotal role in determining these characteristics, acting as the primary source of these desirable properties. Considering this, the following discussion will delve into the critical strategies and approaches necessary for developing an optimal cathode design. By focusing on these cathode-centric methods, we aim to elucidate the pathways towards achieving the exceptional level of performance required in non-aqueous LABs, addressing each of the four crucial aspects in detail.

4.2.1 Increasing specific capacity efficiency

The discharge process in non-aqueous LABs is characterized by the accumulation of lithium peroxide (Li_2O_2) within the cathode's pores, as this discharge product does not dissolve in the organic electrolyte. Consequently, the capacity of the battery is directly determined by the cathode's ability to accommodate these products. Various research studies by S Monaco et al.[133], EM Ryan et al.[134] and P Andrei[19], have observed that discharge can be abruptly terminated when pores become blocked, preventing further oxygen diffusion to reaction sites. To address this challenge, several strategies have been proposed, including the use of highly active catalysts, optimizing catalyst loading, and ensuring uniform distribution of electrode materials. These approaches aim to enhance the structure of cathode, improving pore utilization and boosting specific capacity. Additionally, the insulating nature of Li_2O_2 presents another hurdle, as its growth during discharge leads to passivation and promotes battery degradation[135]. However, further research in this field suggests that modifying the adaptive properties and morphology of Li_2O_2 could potentially improve discharge capacity. These complex interactions between cathode structure, Li_2O_2 formation, and overall battery performance highlight the multifaceted challenges in developing high-capacity LABs, driving ongoing research to explore innovative solutions and unlock the full potential of this promising energy storage technology[136].

4.2.2 Increasing round trip energy efficiency

Non-aqueous LABs operate through two primary reactions: the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during recharge. The slow kinetics of these reactions often result in a significant voltage gap between charge and discharge processes, even at low current densities. This voltage deviation leads to low round-trip efficiency, despite the coulombic efficiency (charge in/charge out) potentially approaching

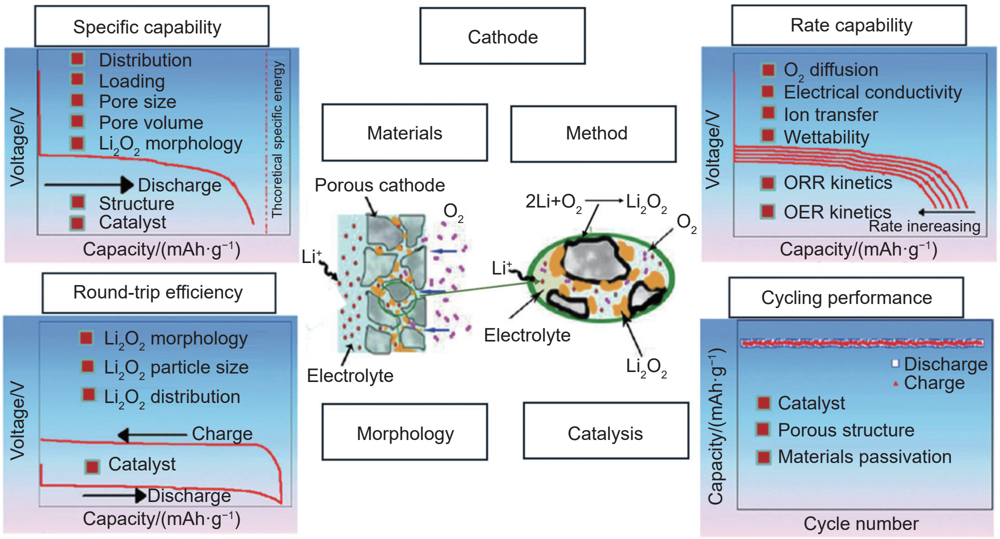


Fig. 10 Strategies for designing an optimal cathode for non-aqueous LABs (Reproduced from Ref [144])

100%. To address this issue, researchers have focused on developing bi-functional catalysts that exhibit catalytic activity for both ORR and OER. These catalysts can reduce overpotentials during charge-discharge cycles by increasing discharge voltage and decreasing charge voltage, thereby enhancing the overall round-trip efficiency of the battery[137].

Further investigations, particularly research work discussed in[138], have revealed that the growth of lithium peroxide (Li_2O_2) during discharge contributes to increased overpotential due to its insulating properties. This insulating nature of Li_2O_2 not only decreases the discharge voltage but also leads to higher charge voltages. Consequently, improving the round-trip efficiency of lithium-air batteries requires considerations beyond catalyst optimization alone. It also involves modifying the nucleation and growth processes of Li_2O_2, as well as optimizing its morphology, particle size, and distribution within the cathode. These multifaceted approaches to enhance battery performance underscore the complex interplay between materials science, electrochemistry, and battery engineering in the development of high-efficiency LABs.

4.2.3 Increasing rate capability

Improving the rate capability of LABs is a critical aspect of their development, as it directly impacts the ability of the battery to deliver and accept charge at higher currents. This enhancement requires a multifaceted approach that addresses key factors simultaneously. Firstly, the rapid diffusion of oxygen within the air cathode is crucial[139]. This involves designing cathode structures with optimized porosity and tortuosity to facilitate efficient oxygen transport throughout the electrode, even at high current densities. Equally important is ensuring high-rate transfer of both electrons and ions within the cathode. This necessitates the use of conductive materials for electron transport and the creation of pathways for swift ionic movement. However, beyond these structural considerations, the kinetics of the fundamental electrochemical reactions play a pivotal role in determining rate capability. Accelerating the rates of both the ORR during discharge and the OER during charge is of paramount importance. These reactions often serve as the rate-limiting steps in lithium-air battery operation[140].

To address this challenge, the employment of highly active catalysts becomes not important, but necessary. These catalysts work to lower the energy activation barriers for both ORR and OER, thereby increasing reaction rates and allowing the battery to operate efficiently at higher current densities. The quest for such catalysts has become a major focus of research in the field, with scientists exploring a wide range of materials including noble metals, transition metal oxides, and carbon-based materials with various dopants and structures.

4.2.4 Optimizing cycling stability

In LABs, ORR/OER catalysts are crucial for enhancing cycle ability. An effective catalyst promotes the formation of reversible Li_2O_2 during discharge while minimizing by-products from electrolyte decomposition and electrode corrosion. This catalyst also accelerates the reduction of Li_2O_2 during charging, thereby improving overall cycling performance[141]. Additionally, a stable, porous cathode enhances cycling performance by facilitating oxygen diffusion and improving electrolyte wettability, which enables rapid accumulation and decomposition of Li_2O_2 within the pores of cathode during cycling[142].

Controlling electrode material passivation and ensuring that electrode materials remain adhered to the substrate throughout cycling is essential[143]. High electrical conductivity in the cathode is also necessary for optimal battery performance. Achieving this requires an optimal ratio of electrode components, including carbon materials, catalysts, conductive agents, binders, substrates, and current collectors. Efficient ion transfer at the electrode-electrolyte interface, driven by good electrolyte wettability on the electrode, is equally important. Moreover, the cathode and its materials must maintain a durable porous structure to facilitate oxygen diffusion and transport. However, there is a trade-off between electrolyte wettability and oxygen diffusion due to the limited solubility of oxygen in organic electrolytes. Therefore, optimizing electrode materials and cathode structure is crucial to balance these factors and achieve high performance.

4.3 Enhancements in electrolyte configurations

The development of advanced electrolyte compositions plays a crucial role in enhancing the performance and longevity of LABs. Research has focused on optimizing the stability and efficiency of electrolytes to support high capacity and prolonged cycling, making LABs more practical for real-world applications.

In 2012, Jung and colleagues demonstrated that by selecting a stable electrolyte and designing an appropriate cell, LABs could operate over multiple cycles with capacity and rate values as high as 5000 mAh/g and 3 A/g, respectively[145]. For effective long-term operation, especially in atmospheric conditions, the ideal electrolyte must have several key properties: low flammability, low vapor pressure, wide electrochemical stability, high Li^+ ion transfer rates, good salt solubility, moisture tolerance, and strong compatibility with the lithium anode[146]. Although many ionic liquids meet some of these criteria, they often suffer from limitations like low Li^+ ion transfer rates, poor salt solubility, and moisture sensitivity, making them unsuitable for commercial use. Moreover, traditional nonaqueous electrolytes, such as organic carbonates, have been found vulnerable to nucleophilic attack by oxygen reduction products, further emphasizing the need for improved, more robust electrolyte solutions for LABs[147].

Numerous studies have shown that for a stable nonaqueous electrolyte, the composition should include alkyl carbonates, antioxidants, solvents like dimethoxyethane and methoxybenzene, as well as co-solvents to address operational challenges[148]. Crowther et al.[116] examined lithium tetrafluoroborate ($LiBF_4$) in various solvents, including propylene carbonate, dimethoxyethane, dimethyl carbonate, and tetraethylene glycol dimethyl ether, to assess their influence on battery performance. Crown esters, when combined with alkyl carbonates, were found to reduce viscosity, enhance ion transport, and boost discharge capacity. Low-vapor-pressure esters, such as tetraethylene glycol dimethyl ether, have also been evaluated for their suitability in aprotic LABs[149].

McCloskey et al. highlighted that discharge products like Li_2O_2/LiO_2 react with the electrolyte and carbon cathode, forming Li_2CO_3, which diminishes battery efficiency[79]. Nitriles, such as trimethylacetonitrile, and amides, like N, N-dialkyl amides, demonstrated greater stability against oxygen reduction species compared to organic carbonates and ethers, while sulfones-based electrolytes resisted superoxide anion degradation[150]. Recently, additives have been introduced to improve the interface with the anode, protect the cathode, stabilize $LiPF_6$ salt, enhance solvation, and function as antioxidants and wetting agents. These additives also reduce dendrite formation and improve the solid electrolyte interface layer, thereby preventing reactions with the lithium anode[151–153].

Most organic electrolytes studied so far have failed to fully meet the criteria for an ideal electrolyte. Researchers are now focusing on developing compound or blended electrolytes with the necessary characteristics for LAB operation under typical environmental conditions[154]. For instance, a mixture of propylene carbonate and ethylene carbonate, combined with lithium bis(trifluoromethanesulfonyl)imide, has been identified as an effective solvent system for ambient operations in aprotic LABs. Solid-state electrolytes (SSEs), made from glass-ceramics[155] or polymers, have emerged as alternatives to liquid electrolytes, although their low ionic conductivity remains a challenge.

Despite this, SSEs offer advantages such as flexibility, safety, low cost, and thin profile, making them competitive alternatives. These batteries can operate across a wide temperature range and better prevent dendrite formation[156]. These electrolytes also provide an effective barrier against the diffusion of atmospheric gases and moisture toward the Li-metal anode. Two main types of SSEs are used in LABs: (1) Li^+ ion-conducting inorganic ceramics and (2) organic polymers. Polymeric electrolytes are stable, adhere well to the Li anode, and are promising candidates for solid-state batteries[157]. Among these, polyethylene oxide-based electrolytes containing lithium salts, such as lithium trifluoromethanesulfonate, have been extensively studied[158].

The second category, Li^+ ion-conducting glass-ceramic materials, is known for its excellent Li^+ conductivity, thermal and electrochemical stability, and resistance to atmospheric gases, enabling safe operation at high temperatures. Various materials such as sulfides, oxides, and phosphates have been investigated as SSEs[158]. Compounds like Li–Al–Ge–PO_4 and Li–Al–Ti–PO_4 have been recognized as fast Li^+ ion conductors in SSLABs[159–160]. Table S3 summarizes the performance characteristics of LABs with different solid-state electrolytes, highlighting the potential of solid-state systems to address the limitations of conventional liquid electrolytes.

4.4 Li metal protection techniques in LAB systems

This section focusses on diverse approaches to mitigate challenges at the Li metal anode-electrolyte interface. The protective strategies are classified into 3 primary categories: (1) Improvement in the solid-electrolyte interface (SEI) formation. (2) Application of protective layers. (3) Optimization of barrier layers. SEI formation involves the development of a protective layer on the Li metal anode surface through reactions with additives, electrolytes, salts, or air components. The application of protective layers employs inorganic or organic materials as separators or coatings on the Li metal anode. The optimization of barrier layers focuses on developing enhanced stability through improved barrier layer design. The discussion highlights significant examples from literature, emphasizing the interplay between various protection techniques and their interactions with air constituents. This comprehensive analysis aims to provide insights into effective strategies for improving the performance and longevity of Li metal anodes in battery systems.

4.4.1 Innovative stabilization of solid electrolyte interphase (SEI)

The solid electrolyte interphase (SEI) plays a pivotal role in determining battery performance through its influence on interfacial reactions and lithium deposition/dissolution behavior. Recent mechanistic studies using advanced characterization techniques have revealed that the atomic-scale structure and composition of the SEI critically influence its protective capabilities. In-situ transmission electron microscopy observations have shown that electrochemically deposited lithium is primarily amorphous, with crystalline LiF domains present in the SEI layer. This structural heterogeneity suggests more complex interfacial interactions than previously understood, where the presence of nanoscale LiF in the SEI enhances stability through its high surface energy and ability to promote uniform Li-ion flux distribution[161].

Electrochemical impedance spectroscopy (EIS) studies have provided crucial insights into SEI formation and stability. A stable SEI layer typically exhibits consistent impedance over time, indicating minimal corrosion and maintaining low charge transfer resistance. The Nyquist plots from EIS measurements reveal characteristic features: a high-frequency semicircle representing the SEI resistance (R_{SEI}), a mid-frequency semicircle corresponding to charge transfer resistance (R_{ct}), and a low-frequency Warburg impedance reflecting Li^+ diffusion. These measurements have shown that SEI stability strongly correlates with its composition and morphology, where optimal SEI structures demonstrate minimal growth in RSEI over extended cycling.

The effectiveness of SEI protection is heavily influenced by its mechanical properties. Studies have shown that successful SEI layers must balance flexibility and mechanical strength to accommodate volume changes while maintaining protective function[162]. This understanding has led to the development of advanced SEI engineering strategies, including the incorporation of elastic components in artificial SEIs and controlled formation of nanostructured SEIs with optimized mechanical properties.

The mechanistic insights have also revealed the importance of local current density distribution in SEI formation. In 2015, Zhang et al.[163] reported the creation of a LiF-containing SEI layer by cycling a Li |

1 mol L^{-1} LiF_3SO_3 + TEGDME/FEC (5 : 1, *v*/*v*) | Li symmetric cell. The impedance spectra of LABs with this modified anode remained stable over time, suggesting that the electrochemically induced SEI effectively mitigates Li anode corrosion from the electrolyte and dissolved oxygen, which would otherwise increase resistance and lead to cell failure. Recent work has demonstrated the critical role of interfacial chemistry in SEI stability. For instance, Shen Huang and colleagues[164] demonstrated the efficacy of this approach by incorporating boric acid (BA) into a 1.0 mol/L LiTFSI/DMSO electrolyte system. This addition facilitated the formation of a continuous, dense SEI on the lithium anode surface in oxygen-rich environments. Experimental storage tests in humid air and electrolyte environments confirmed enhanced barrier properties against oxygen, moisture, and electrolyte penetration (Fig. 11a-c). As a result, the cycle life of batteries incorporating the BA additive exhibited a more than six-fold increase. Beyond operando reactions utilizing additives, in-situ SEI formation can also be achieved through pretreatment methods prior to battery assembly. Liao et al.[165] developed an innovative lithium-metal preprocessing technique involving brief immersion in a $GeCl_4$-THF solution. Remarkably, a mere five-minute treatment resulted in the formation of a germanium composite SEI characterized by a compact structure and appropriate thickness, providing exceptional protection against moisture and dissolved O_2 reaction.

Another effective approach to enhancing SEI stability involves the ex-situ synthesis of artificial SEI. Artificial solid electrolyte interphase (SEI) surpass in-situ SEIs in stability due to their controlled fabrication. In-situ SEIs, while conformally adhered, are susceptible to failure from cycling-induced volume changes. Their uncontrolled composition evolution, extreme thinness, and other inherent properties make them susceptible to dendrite penetration and expansion-related damage. Sun et al.[166] tackled these issues by developing a rigid, uniformly distributed graphene-polydopamine composite layer (GPDL) on Li anodes by drop-casting. This engineered protective interface significantly enhanced battery performance, enabling over 150 cycles with a sustained high energy efficiency of 80%. The GPDL acts as an effective barrier, preventing unwanted reactions between the Li anode, redox mediators, oxygen and moisture,

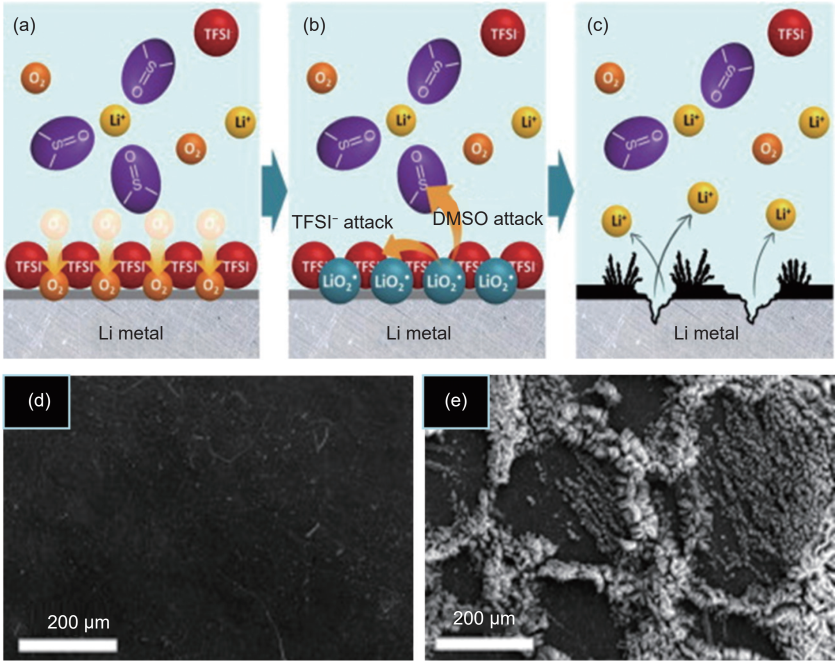


Fig. 11 O_2 crossover effects on Li anode: Degradation: (a) $TFSI^-/O_2$ adsorption; (b) LiO_2 formation; (c) mossy structure precipitation and Li^+ dissolution. (d) SEM images in LiTFSI-DMSO; (e) SEM images after 30 day in LiTFSI-DMSO-O_2[180]. (Copyright permission granted from Ref. [180])

thus contributing to the development of long-lasting, high-efficiency batteries.

Advanced characterization techniques have further revealed that successful SEI formation depends on uniform Li^+ flux distribution across the electrode surface. Based on the simplicity of solution-casting methods, Zhang et al.[167] developed a durable lithiated Nafion composite coating for Li metal using a tissue template and simple solution-casting. XRD and SEM studies showed the tissue-directed bifunctional film (TBF) that are strong mechanically and chemically protected, shielding Li from oxygen, moisture, and cycling byproducts. The TBF-coated Li anode exhibited improved cycling stability and longer battery life. Furthermore, several electrolyte additives have been proposed to aid SEI formation, including dissolved O_2, CO_2 species, trace H_2O[168], lithium nitrate[169], boric acid[170], germanium[171], polyphosphoric acid[172] and others. Incorporating compounds such as $LiNO_3$, common in Li-S energy storage systems, offers potential benefits. This substance interacts with the metal to create a defensive Li_2O barrier, shielding the anode from harmful reactions with polysulfides and preventing electrolyte decomposition[173].

These mechanistic insights have collectively contributed to the growth of more effective SEI stabilization approaches, leading to significant improvements in battery performance and longevity. The combination of fundamental understanding at the atomic scale with practical engineering solutions continues to drive innovation in this critical aspect of battery technology[174]. While significant progress has been made in understanding and controlling SEI formation and stability, several crucial challenges remain. (1) The dynamic nature of the SEI during cycling, particularly its evolution under different operating conditions and long-term structural changes, requires further investigation[175]. Advanced in-situ characterization techniques will be essential for real-time monitoring of SEI formation and degradation mechanisms[113]. (2) The relationship between local current density distributions and SEI uniformity needs deeper understanding to prevent preferential dendrite nucleation sites[176]. (3) Developing predictive models that can accurately capture the complex interplay between mechanical stress, electrochemical reactions, and interfacial dynamics remains an important goal[177].

Future research should focus on establishing clear structure-property relationships in SEI formation, developing more robust artificial SEI designs, and understanding the role of various additives in SEI stability[178]. Additionally, the integration of artificial intelligence and machine learning approaches could accelerate the discovery of optimal SEI compositions and formation protocols[179]. These advances will be crucial for realizing the full potential of lithium metal anodes in next-generation battery systems.

4.4.2 Hybrid inorganic-organic protective layers

In LABs, inorganic, organic and hybrid membranes are employed to prevent unwanted reactions between the air electrode components and the Li anode. These membranes serve two primary roles: as a separating membrane between the 2 electrodes (protected anode design)[181], or positioned at the cathode-ambient air interface (protected cathode design)[182]. The protected anode configuration requires membranes with high Li^+ ionic conduction, reducing protons transfer and preventing reactions with moisture and CO_2. In contrast, the protected cathode design necessitates membranes that offer high O_2 permeability, effective H_2O and CO_2 rejection, and low miscibility with organic electrolytes to prevent electrolyte evaporation. Visco et al. introduced inorganic solid-state electrolytes (SSEs) for protecting Li metal anodes in 2007[183]. They created a hybrid Li-O_2 system, which combines aqueous and organic components, using a NASICON-type SSE ($Li_3\ M_2(PO_4)\ _3$) known for its elevated Li ion conduction. This SSE barrier between cell regions, successfully protected the lithium electrode from water-based solutions in the air cathode section. Their system demonstrated stable discharge performance for up to 14 h.

Further research improved stability and efficiency by enhancing oxygen catalysts[184], creating protective barriers for solid electrolytes against moisture and lithium degradation[185], developing better electrolytes[186], and adjusting operating temperatures. This compartmentalized design was later applied to non-aqueous lithium-air batteries, allowing tailored optimization of electrolyte components for each electrode[187]. A specialized glass membrane serves as the separator[188], with the cathode region containing one electrolyte mixture and redox compound, while the anode area uses a different solvent and the same salt to protect the lithium surface[163]. Testing showed a clean lithium surface after cycling. Separated from components that would create unstable interfaces, the lithium electrode exhibited better cycling stability in its designated environment. Additional protection approaches, such as the solvent-in-salt approach and self-healing electrostatic shields[189], could also be integrated into this dual-compartment system[190]. Research also includes structured current collectors to accommodate lithium deposition, moisture additives for smoother lithium surfaces[168], and nanoscale engineering strategies as protective measures.

Polymer membranes have recently gained attention for Li metal anode protection due to their design flexibility and potential cost-effectiveness[191]. This research builds upon extensive polymer electrolyte work in LABs. A notable example is the nonporous polyurethane (PU) membrane, consisting of hard and soft domains. Its air-impermeable nature is evidenced by an undetectable Gurley time. The structure demonstrates superior solvent absorption capabilities and facilitates lithium-ion transport, which contributes to extended lithium metal electrode performance. Post-cycling examination (100 cycles) showed pure lithium metal composition on polyurethane-protected electrodes, contrasting with LiOH particles detected on anodes protected by porous polyethylene (PE) separators[192].

A recent investigation explored an innovative composite membrane for cathode modification in lithium-air batteries. This membrane consisted of a polydopamine-coated metal-organic framework (CAU@1-NH_2) embedded within a poly(methylmethacrylate) matrix. When incorporated at the cathode, this composite structure demonstrated enhanced cycling stability under ambient conditions[124]. The functional groups present in the membrane components exhibited a notable ability to capture CO_2, resulting in high O_2/CO_2 selectivity.

While the polyurethane (PU) separator successfully blocks H_2O and O_2 transfer, the issue of dendrites formation persists, and this is attributed to their insufficient mechanical strength. This limitation, which is common in polymeric membranes, can be addressed. One solution involves adding inorganic compounds to enhance performance. Research has demonstrated that Al_2O_3 nanoparticles can be dispersed throughout lithiated Nafion membranes, creating reinforced composite barriers[193]. Based on these properties, the protective layer behaves differently during Li plating/stripping: the Nafion layer without Al_2O_3 nanoparticles tends to pulverize, while the Nafion-based composite layer containing Al_2O_3 nanoparticles remains intact. This composite structure also effectively suppresses dendrite growth. Symmetric Li cells with the composite protective layer demonstrate improved cycling longevity compared to cells that are either unprotected or only protected by Nafion.

Various research groups have emphasized the critical nature of evaluating membrane chemical stability in the presence of reactive oxygen species within LABs. These studies conducted comparative analyses between Nafion-based and PVDF-based composite membranes. Utilizing online electrochemical mass spectrometry[181], researchers observed irreversible O_2 reduction and CO_2 evolution in PVDF-based membranes. This process will directly affect the PVDF degradation. In contrast, Nafion-based membranes exhibited more reversible O_2 reduction and evolution processes. These findings align with previous research indicating that PVDF is quite unstable against oxide radicals. NCL facilitates more reversible O_2 reduction and evolution processes.

Protected cathode structures frequently incorporate OSMs positioned between the cathode and surrounding atmosphere. These specialized membranes facilitate oxygen passage while restricting other atmospheric constituents including water vapor and carbon dioxide. As water molecules have smaller dimensions than oxygen molecules, pore size control alone proves insufficient for selective gas transport. Instead, researchers utilize nonpolar membrane materials with preferential solubility and diffusion characteristics for nonpolar oxygen, creating selectivity against polar species such as water. This approach is exemplified by implementations of low-density polyethylene (LDPE), which effectively excludes atmospheric moisture and substantially improving the cycling stability of LABs. Additionally, a porous metallic nickel (Ni) substrate infused with silicone oil has been shown to provide effective separation of O_2 from H_2O[194]. However, separating O_2 from CO_2 is more complex, as both are nonpolar molecules. Although substantial work has been done on CO_2 capture from air, particularly for carbon sequestration, there is limited research specifically focusing on O_2/CO_2 separation in the context of LABs.

In a related study, researchers evaluated a perfluoropolyether-based membrane, which effectively dehydrated ambient air and significantly mitigated DMSO evaporation. An intriguing aspect of this membrane was its selective CO_2 permeation properties, which contributed to the stabilization of the lithium metal anode. This stabilization occurred through the promotion of a protective Li_2CO_3 layer formation on the anode surface. Interestingly, despite the CO_2 permeation, no Li_2CO_3 formation was detected on the cathode side. This absence of carbonate formation on the cathode is significant, as it could potentially arise from the reaction between the discharged products, Li_2O_2 and CO_2. These findings suggest that the selective permeation of CO_2, in the absence of moisture, may enhance the stability of the lithium metal anode while simultaneously preventing the unfavorable formation of carbonates on the cathode.

4.4.3 Optimized barrier layers for superior stability

Recent research has focused on innovative approaches to protect the Li-metal anode and maintain stable battery operation in Li-O_2 cells through the integration of barrier layers. These layers serve as a critical differentiator from other sealed LABs by isolating harmful components that could trigger detrimental side reactions. The functional requirements of these barriers are location-dependent, with those positioned between electrodes designed to selectively allow Li-ion diffusion while blocking other substances[195].

Lithium-air batteries typically implement protective barriers and specialized separators that block water/oxygen penetration while facilitating lithium-ion transport. Elia and Hassoun[196] contributed to this field by developing a PVDF gel polymer membrane incorporated with ZrO_2 nanoparticles that minimized oxygen transfer and enhanced battery longevity. In related work, Shang and colleagues[197] created a moisture-resistant lithium-ion conductive material, $Li_{1.3}Al_{0.5}Nb_{0.2}Ti_{1.3}(PO_4)_3$ (LANTP), characterized by excellent ion mobility and structural strength, which achieved energy densities reaching 984 Wh/kg at current densities of 0.32 mA/cm^2 in aqueous systems.

Imanishi and colleagues[198] combined organic and inorganic barrier advantages by designing a battery incorporating a LATP glass-ceramic electrolyte and a polyethylene oxide (PEO) buffer layer, enhancing stability with both water and Li metal. A more sophisticated approach was presented by Choi et al.[199], who developed a composite membrane using surface-modified LATP particles embedded in a polymer matrix by an enhanced float-casting method (Fig. 12a). The strong bond between the polymer matrix and the surface-modified glass-ceramic particles provides the membrane with excellent airtightness. This design overcomes limitations of traditional thick ceramic layers while maintaining essential properties such as ionic conductivity and gas impermeability.

An alternative streamlined approach for barrier layer creation involves direct separator modification rather than incorporating additional interlayers. Choi et al.[192] engineered a non-porous polyurethane (PU) separator exhibiting remarkable air-blocking capabilities attributed to its tightly packed molecular structure. The distinctive architecture of PU, comprising both rigid and elastic segments, confers the separator with structural durability while preserving essential flexibility. As a result, the battery with the PU film achieved

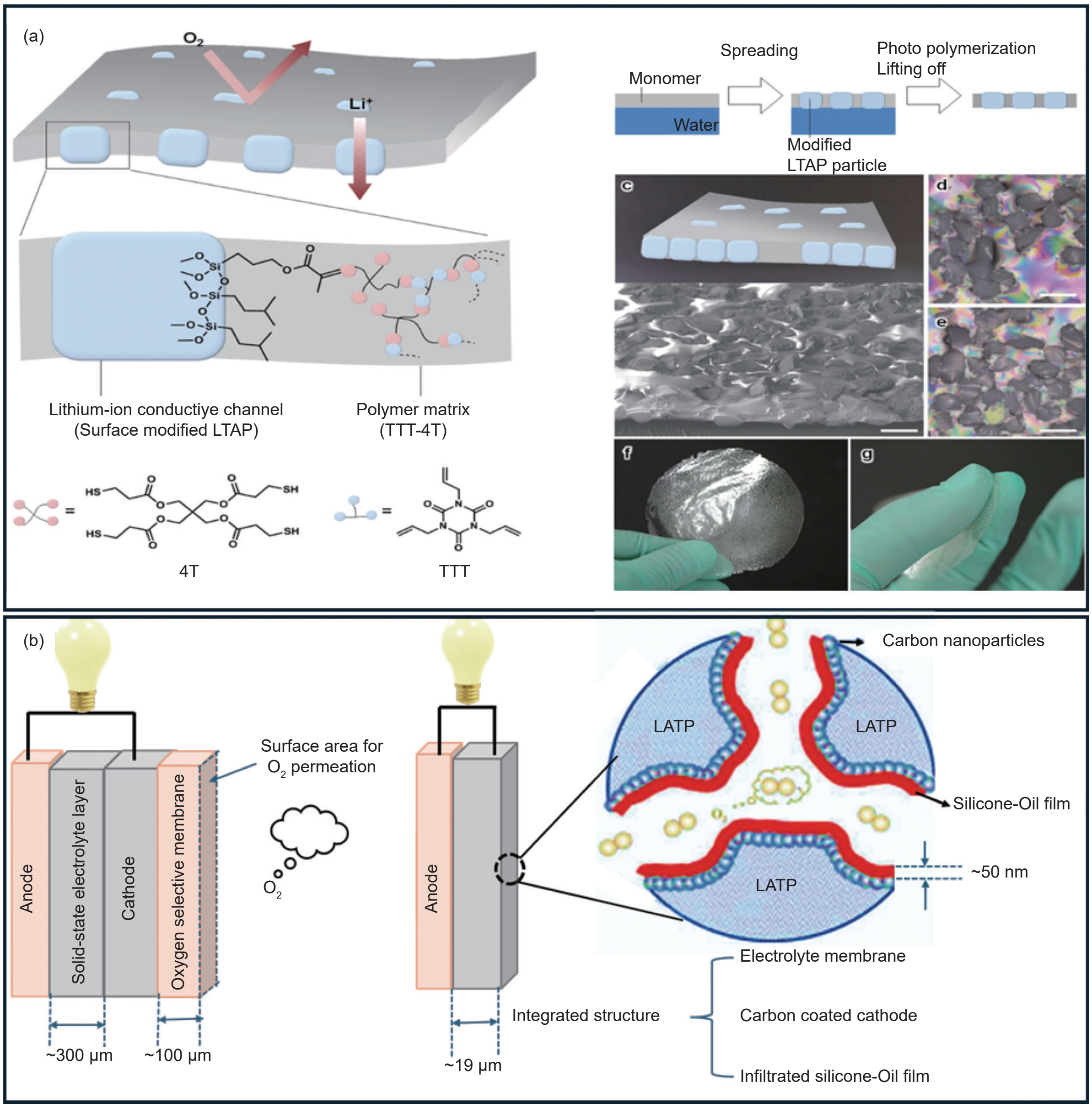


Fig. 12 (a) Composition, fabrication and morphological aspects of the composite membrane[199] (Copyright permission granted from Ref. [199]). (b) Architectures of SSLABs[201] (Reproduced from Ref. [201])

a cycle life of 110 cycles, compared to 56 cycles for the porous polyethylene separator at a current density of 200 mA/g. In another study, Yin et al.[200] developed a flexible polyimide and poly (vinylidene fluoride-co-hexafluoropropylene) (PIPV) composite separator. The PIPV membrane has excellent waterproof properties, enabling the battery with this design to deliver superior cycling stability for over 200 cycles at a current of 1 mA and a capacity of 4 mAh.

A barrier layer can also be introduced on the exterior of the air cathode or used as a packaging material to encapsulate the entire cell. This layer must exclusively permit oxygen passage, functioning as an OSM to maintain battery performance[195]. Peng et al.[125] created a protective LDPE membrane surrounding a carbon nanotube air electrode to block water penetration, which typically leads to irreversible Li_2CO_3 formation during discharge cycles. The nonpolar structure of the LDPE membrane allows selective oxygen diffusion. This membrane enabled the battery to sustain a stable discharge voltage for more than 325 cycles at a current density of 2000 mA/g under ambient air conditions (RH factor ~ 50%). Additionally, silicone oil, which has greater oxygen solubility and diffusivity than water, can be employed to produce efficient oxygen selective membranes. In 2010, Zhang et al.[122] introduced a silicone oil film that not only prevents moisture from entering but also reduces the evaporation of the liquid electrolyte. This feature enabled a non-aqueous LAB with an OSM to function in ambient conditions (RH = 20%) for 16.4 days, providing a specific capacity of 788 mAh g^{-1} at a current density of 0.05 mA/cm^2.

Following this, Zhao et al.[201] applied silicone oil in a SSLAB design, constructing both the solid electrolyte and air-cathode framework from identical LATP material where the solid electrolyte and air-cathode framework were made from the same LATP material, but with differing levels of compactness (Fig. 12b). A 50 nm-thick silicone oil membrane, created through an infiltration technique, was applied to the carbon-coated LATP surface, offering a large surface area as an OSM to block moisture and CO_2. As a result, the SLLAB with this membrane achieved consistent cycling for 50 cycles in ambient air (RH ~ 50%) while maintaining a capacity of 5000 mAh g^{-1} at a current density of 0.3 mA/cm^2.

In conclusion, LAB technology has perceived remarkable progress, particularly in protecting Li-metal anodes and cathodes, leading to significant improvements in cycling lifetimes. These advancements bring us closer to realizing the potential of this high-energy-density storage system. However, as we endeavor for practical, large-scale applications, several challenges demand our attention. These include the reactivity of protective layers, persistent dendrite formation, and the stability of gas-selective membranes in oxygen-rich environments. Additionally, the impact of atmospheric components like CO_2 and H_2O on battery materials and interfaces require further investigation. In future, research efforts should focus on addressing these fundamental issues to guide the development of more robust materials and innovative designs. By addressing these challenges, LABs could transform energy storage systems and enable sustainable solutions for applications ranging from electric vehicles to grid-scale storage.

5 Conclusion and Prospects

The comprehensive analysis presented in this review demonstrates both the remarkable potential and significant challenges facing lithium-air battery technology. LABs represent a promising frontier in energy storage, offering theoretical energy densities that far surpass current lithium-ion systems. This review has highlighted significant advancements in understanding and improving LAB functionality, particularly in lithium anode protection, solid-electrolyte interphase (SEI) layers, and oxygen reduction and evolution reactions at the cathode.

Our examination reveals that the advancement of LABs requires effective protection strategies across multiple components. The integration of oxygen-selective membranes for air constituent management, stabilized lithium metal interfaces, and optimized cathode structures has shown promising results in addressing key degradation mechanisms. Interface engineering has emerged as a critical factor, with hybrid inorganic-organic protective layers demonstrating effectiveness in preventing unwanted reactions while maintaining necessary functionality. Innovative approaches, including advanced porous cathode designs, have shown considerable promise in addressing critical challenges.

Our analysis of air constituent effects indicates that controlled management of moisture and CO_2 through advanced membrane designs can significantly enhance battery performance and stability. The detailed understanding of dendrite formation mechanisms has led to more effective lithium metal protection approaches. In cathode design, the optimization of porosity and architecture has proven crucial for balancing oxygen transport with discharge product accommodation.

Despite these advancements, significant hurdles remain on the path to practical implementation. Key issues include lithium dendrite formation, electrolyte instability, poor cathode reversibility, and the need for effective moisture and CO_2 management, especially in non-aqueous systems. Achieving consistent performance under real-world conditions continues to be a major challenge requiring further innovation.

Future research directions include enhancing the stability and performance of lithium metal anodes, exploring hybrid electrolyte systems that combine the advantages of aqueous and non-aqueous chemistries, and optimizing cathode materials to accommodate large quantities of discharge products efficiently. The integration of nanotechnology, advanced materials like metal-organic frameworks, and graphene composites may provide breakthroughs in cathode performance. Additionally, leveraging computational modeling and machine learning approaches could significantly accelerate material design and cell configuration optimization.

In conclusion, while lithium-air batteries face several challenges, continued innovation in materials science, electrochemistry, and cell design holds the promise of overcoming these obstacles. With sustained research efforts focused on material innovations and improved cell designs, LABs have the potential to revolutionize energy storage systems. Their potential applications in electric vehicles and grid-scale energy storage position them as a pivotal technology in the transition to a sustainable energy future.

Acknowledgements

The authors acknowledge Universiti Sain Malaysia for the financial support by postdoctoral fellowship scheme. The authors also acknowledge the financial assistance and facilities provided by Ministry of Higher Education Malaysia under the Fundamental Research Grant Scheme (FRGS/1/2020/TK0/USM/01/4,203. PJKIMIA.6071484), Universiti Sains Malaysia.

Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/S1872-5805(25)60976-0.

Author information

***Corresponding author:**
Abdul Latif Ahmad. E-mail: chlatif@usm.my

First author:
Humaira Rashid Khan. E-mail: humairar_khan@usm.my;
Asim Ali Yaqoob. E-mail: asimchem4@gmail.com

References

[1] Wang J, Azam W. Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries[J]. Geoscience Frontiers, 2024, 15(2): 101757.

[2] Xiaoman W, Majeed A, Vasbieva D G, et al. Natural resources abundance, economic globalization, and carbon emissions: Advancing sustainable development agenda[J]. Sustainable Development, 2021, 29(5): 1037-1048.

[3] Jilani A, Awan Z, Taqvi S, et al. Recent Advances in the Development of Li-Air Batteries, Experimental and Predictive Approaches–Prospective, Challenges, and Opportunities[J]. ChemBioEng Reviews, 2024, 11(1): 95-114.

[4] Tai H, Samandari H, Pacthod D, et al. The energy transition: A region-by-region agenda for near-term action[J]. 2022.

[5] Bi X, Jiang Y, Chen R, et al. Rechargeable zinc–air versus lithium–air battery: from fundamental promises toward technological potentials[J]. Advanced Energy Materials, 2024, 14(6): 2302388.

[6] Fazendeiro L M, Simões S G. Historical variation of IEA energy and CO_2 emission projections: implications for future energy modeling[J]. Sustainability, 2021, 13(13): 7432.

[7] Kober T, Schiffer H W, Densing M, et al. Global energy perspectives to 2060–WEC's World Energy Scenarios 2019[J]. Energy Strategy Reviews, 2020, 31: 100523.

[8] Wang J, Song C, Yuan R. CO_2 emissions from electricity generation in China during 1997–2040: The roles of energy transition and thermal power generation efficiency[J]. Science of The Total Environment, 2021, 773: 145026.

[9] Lai J, Xing Y, Chen N, et al. Electrolytes for rechargeable lithium–air batteries[J]. Angewandte Chemie International Edition, 2020, 59(8): 2974-2997.

[10] Kularatna N, Gunawardane K. Energy Storage Devices for Renewable Energy-Based Systems: Rechargeable Batteries and Supercapacitors[J]. Academic Press, 2021.

[11] Armand M, Axmann P, Bresser D, et al. Lithium-ion batteries–Current state of the art and anticipated developments[J]. Journal of Power Sources, 2020, 479: 228708.

[12] Placke T, Kloepsch R, Dühnen S. Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density[J]. Journal of Solid State Electrochemistry, 2017, 21: 1939-1964.

[13] Song M K, Park S, Alamgir F M, et al. Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives[J]. Materials Science and Engineering: R: Reports, 2011, 72(11): 203-252.

[14] Ye J, Wang C, Shao Z, et al. From Li–O_2 to Li–Air Batteries: Challenges and Progress on Oxygen-Permeable Membranes[J]. Energy & Fuels, 2024, 38(16): 15001-15024.

[15] Littauer E L, Tsai K C. Anodic behavior of lithium in aqueous electrolytes: ii. Mechanical passivation[J]. Journal of the Electrochemical Society, 1976, 123(7): 964.

[16] Abraham K, Jiang Z. A polymer electrolyte-based rechargeable lithium/oxygen battery[J]. Journal of the Electrochemical Society, 1990, 143(1): 1.

[17] Huang J, Xie Y, You Y, et al. Rational design of electrode materials for advanced supercapacitors: from lab research to commercialization[J]. Advanced Functional Materials, 2023, 33(14): 2213095.

[18] Tan P, Wei Z, Shyy W, et al. Prediction of the theoretical capacity of non-aqueous lithium-air batteries[J]. Applied Energy, 2013, 109: 275-282.

[19] Andrei P, Zheng J P, Hendrickson M, et al. Some possible approaches for improving the energy density of Li-air batteries[J]. Journal of the Electrochemical Society, 2010, 157(12): A1287.

[20] Mahadevan R, Chhabra M, Pasrich P, et al. Battery Technologies, Electric, Hybrid, and Fuel Cell Vehicles[J]. Springer, 2021: 353-393.

[21] Josepetti D M, Sousa B P, Rodrigues S A, et al. The initial stages of Li_2O_2 formation during oxygen reduction reaction in Li-O_2 batteries: The significance of Li_2O_2 in charge-transfer reactions within devices[J]. Journal of Energy Chemistry, 2024, 88: 223-231.

[22] Nzereogu P, Omah A, Ezema F, et al. Anode materials for lithium-ion batteries: A review[J]. Applied Surface Science Advances, 2022, 9: 100233.

[23] Kondori A, Esmaeilirad M, Harzandi A M, et al. A room temperature rechargeable Li_2O-based lithium-air battery enabled by a solid electrolyte[J]. Science, 2023, 379(6631): 499-505.

[24] Zhang M T, Qu H T, Zhou G M. The factors that influence the electrochemical behavior of lithium metal anodes: electron transfer and Li-ion transport[J]. New Carbon Materials, 2023, 38(4): 776-786.

[25] Song C, Ito K, Sakata O, et al. Operando structural study of non-aqueous Li–air batteries using synchrotron-based X-ray diffraction[J]. RSC advances, 2018, 8(46): 26293-26299.

[26] Liang H, Liu R, An X, et al. Bimetal-organic frameworks with coordinatively unsaturated metal sites for highly efficient Fenton-like catalysis[J]. Chemical Engineering Journal, 2021, 414: 128669.

[27] Chen K, Yang D Y, Huang G, et al. Lithium–air batteries: Air-electrochemistry and anode stabilization[J]. Accounts of Chemical Research, 2021, 54(3): 632-641.

[28] Wang J, Zheng J, Liu X. The key to improving the performance of Li–air batteries: recent progress and challenges of the catalysts[J]. Physical Chemistry Chemical Physics, 2022, 24(30): 17920-17940.

[29] Kumar B, Kumar J, Leese R, et al. A solid-state, rechargeable, long cycle life lithium–air battery[J]. Journal of The Electrochemical Society, 2009, 157(1): A50.

[30] Fan X, Zhong C, Liu J, et al. Opportunities of flexible and portable electrochemical devices for energy storage: expanding the spotlight onto semi-solid/solid electrolytes[J]. Chemical Reviews, 2022, 122(23): 17155-17239.

[31] Bachman J C, Muy S, Grimaud A, et al. Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction[J]. Chemical reviews, 2016, 116(1): 140-162.

[32] Chattopadhyay J, Pathak T S, Santos D M. Applications of polymer electrolytes in lithium-ion batteries: a review[J]. Polymers, 2023, 15(19): 3907.

[33] Xu Y J, Wang B, Wan Y, et al. Understanding the process of lithium deposition on a graphite anode for better lithium-ion batteries[J]. New Carbon Materials, 2023, 38(4): 678-697.

[34] Shao Y, Ding F, Xiao J, et al. Making Li-air batteries rechargeable: Material challenges[J]. Advanced Functional Materials, 2013, 23(8): 987-1004.

[35] Ikeuba A I, Iwuji P C, Nabuk I I, et al. Advances on lithium, magnesium, zinc, and iron-air batteries as energy delivery devices —a critical review[J]. Journal of Solid State Electrochemistry, 2024, 28(9): 2999-3025.

[36] Tao T, Zheng Z, Gao Y, et al. Understanding the role of interfaces in solid-state lithium-sulfur batteries[J]. Energy Materials, 2022, 2(200036): 10.20517.

[37] Balaish M, Peled E, Golodnitsky D, et al. Liquid-free lithium–oxygen batteries[J]. Angewandte Chemie, 2015, 127(2): 446-450.

[38] Choudhury S, Choudhury S. Lithium fluoride additives for stable cycling of lithium batteries at high current densities[J]. Rational Design of Nanostructured Polymer Electrolytes and Solid–Liquid Interphases for Lithium Batteries, 2019: 81-94.

[39] Cao R, Chen K, Liu J, et al. Li–air batteries: air stability of lithium metal anodes[J]. Science China Chemistry, 2024, 67(1): 22-136.

[40] Yu W, Xue C, Hu B, et al. Oxygen-and dendrite-resistant ultra-dry polymer electrolytes for solid-state Li–O_2 batteries[J]. Energy Storage Materials, 2020, 27: 244-251.

[41] Kundu A, Mallick S, Ghora S, et al. Advanced oxygen electrocatalyst for air-breathing electrode in Zn-air batteries[J]. ACS Applied Materials & Interfaces, 2021, 13(34): 40172-40199.

[42] Jeong Y S, Park J B, Jung H G, et al. Study on the catalytic activity of noble metal nanoparticles on reduced graphene oxide for oxygen evolution reactions in lithium–air batteries[J]. Nano letters, 2015, 15(7): 4261-4268.

[43] He B, Wang J, Liu J, et al. Super-assembly of porous Fetet$(NiFe)_{oct}O$ frameworks with stable octahedron and multistage structure for superior lithium–oxygen batteries[J]. Advanced Energy Materials, 2020, 10(21): 1904262.

[44] Liu T, Vivek J P, Zhao E W, et al. Current challenges and routes forward for nonaqueous lithium–air batteries[J]. Chemical Reviews, 2020, 120(14): 6558-6625.

[45] Li G, Li N, Peng S, et al. Highly efficient Nb_2C MXene cathode catalyst with uniform O-terminated surface for lithium–oxygen batteries[J]. Advanced Energy Materials, 2021, 11(1): 2002721.

[46] Ergen O, Ciftci N O, İbis O. Simple air blow to charge Li-air, rechargeable, solid-state batteries using nano-engineered aerogel structures[J]. Electrochemistry Communications, 2022, 142: 107379.

[47] Liu Z, Zhao N, Zhao X, et al. Combination of Li-rich layered-oxide with O_2 cathodes for high-energy Li-ion/Li-O_2 hybrid batteries[J]. Applied Physics Letters, 2022, 120(19).

[48] Huang L, Mao Y, Wang G, et al. Ru-decorated knitted Co_3O_4 nanowires as a robust carbon/binder-free catalytic cathode for lithium–oxygen batteries[J]. New Journal of Chemistry, 2016, 40(8): 6812-6818.

[49] Shao Y, Park S, Xiao J, et al. Electrocatalysts for nonaqueous lithium–air batteries: status, challenges, and perspective[J]. ACS Catalysis, 2012, 2(5): 844-857.

[50] Black R, Adams B, Nazar L F. Non-aqueous and hybrid Li-O_2 batteries[J]. Advanced Energy Materials, 2012, 2(7): 801-815.

[51] Ge X, Sumboja A, Wuu D, et al. Oxygen reduction in alkaline media: from mechanisms to recent advances of catalysts[J]. ACS Catalysis, 2015, 5(8): 4643-4667.

[52] Nepel T C, Anchieta C G, Cremasco L F, et al. In Situ Infrared Micro and Nanospectroscopy for Discharge Chemical Composition Investigation of Non-Aqueous Lithium–Air Cells[J]. Advanced Energy Materials, 2021, 11(45): 2101884.

[53] Yao X, Dong Q, Cheng Q, et al. Why do lithium–oxygen batteries fail: parasitic chemical reactions and their synergistic effect[J]. Angewandte Chemie International Edition, 2016, 55(38): 11344-11353.

[54] Hafiz H, Suzuki K, Barbiellini B, et al. Tomographic reconstruction of oxygen orbitals in lithium-rich battery materials[J]. Nature, 2021, 594(7862): 213-216.

[55] Li J Y, Du X Y, Wang X X, et al. Photo-Assisted Li-N2 Batteries with Enhanced Nitrogen Fixation and Energy Conversion[J]. Angewandte Chemie International Edition, 2024, 63(11): e202319211.

[56] Zhao Z, Pang L, Su Y, et al. Deciphering CO_2 reduction reaction mechanism in aprotic Li–CO_2 batteries using in situ vibrational spectroscopy coupled with theoretical calculations[J]. ACS Energy Letters, 2022, 7(2): 624-631.

[57] Iputera K, Huang J Y, Haw S C, et al. Revealing the absence of carbon in aprotic Li–CO_2 batteries: a mechanism study toward CO_2 reduction under a pure CO_2 environment[J]. Journal of Materials Chemistry A, 2022, 10(7): 3460-3468.

[58] Wang Y F, Ji G J, Song L N, et al. A highly reversible lithium–carbon dioxide battery based on soluble oxalate[J]. ACS Energy Letters, 2023, 8(2): 1026-1034.

[59] Zhong W, Zeng Z, Cheng S, et al. Advancements in Prelithiation Technology: Transforming Batteries from Li-Shortage to Li-Rich Systems[J]. Advanced Functional Materials, 2024, 34(2): 2307860.

[60] Andrés C M C, Pérez de la Lastra J M, et al. Superoxide anion chemistry —Its role at the core of the innate immunity[J]. International journal of molecular sciences, 2023, 24(3): 1841.

[61] Feng H, Jia M, Lin Y, et al. Unveiling the reaction mechanism and $1O_2$ suppression effect of CO_2 in Li-CO_2/O_2 battery through the reacquaintance of discharge products[J]. Energy Storage Materials, 2023, 61: 102886.

[62] Qiao Y, Yi J, Guo S, et al. Li_2CO_3-free Li–O_2/CO_2 battery with peroxide discharge product[J]. Energy & Environmental Science, 2018, 11(5): 1211-1217.

[63] Yin W, Grimaud A, Lepoivre F, et al. Chemical vs electrochemical formation of Li_2CO_3 as a discharge product in Li–O_2/CO_2 batteries by controlling the superoxide intermediate[J]. The journal of physical chemistry letters, 2017, 8(1): 214-222.

[64] Schwenke K U, Metzger M, Restle T, et al. The influence of water and protons on Li_2O_2 crystal growth in aprotic Li-O_2 cells[J]. Journal of The Electrochemical Society, 2015, 162(4): A573.

[65] Prehal C, Mondal S, Lovicar L, et al. Exclusive Solution Discharge in Li–O_2 Batteries[J]. ACS Energy Letters, 2022, 7(9): 3112-3119.

[66] Li Y, Wang X, Dong S, et al. Recent Advances in Non-Aqueous Electrolyte for Rechargeable Li–O_2 Batteries[J]. Advanced Energy Materials, 2016, 6(18): 1600751.

[67] Guo Z, Dong X, Yuan S, et al. Humidity effect on electrochemical performance of Li–O_2 batteries[J]. Journal of power sources, 2014, 264: 1-7.

[68] Cho M, Trottier J, Gagnon C, et al. The effects of moisture contamination in the Li-O_2 battery[J]. Journal of Power Sources, 2014, 268: 565-574.

[69] Shui J L, Okasinski J S, Kenesei P, et al. Reversibility of anodic lithium in rechargeable lithium–oxygen batteries[J]. Nature communications, 2013, 4(1): 2255.

[70] Huang S, Cui Z, Zhao N, et al. Influence of ambient air on cell reactions of Li-air batteries[J]. Electrochimica Acta, 2016, 191: 473-478.

[71] Zhang S S, Foster D, Read J. Discharge characteristic of a non-aqueous electrolyte Li/O_2 battery[J]. Journal of Power Sources, 2010, 195(4): 1235-1240.

[72] Read J. Characterization of the lithium/oxygen organic electrolyte battery[J]. Journal of the Electrochemical Society, 2002, 149(9): A1190.

[73] Beattie S, Manolescu D, Blair S. High-capacity lithium–air cathodes[J]. Journal of the Electrochemical Society, 2008, 156(1): A44.

[74] Kuboki T, Okuyama T, Ohsaki T, et al. Lithium-air batteries using hydrophobic room temperature ionic liquid electrolyte[J]. Journal of power sources, 2005, 146(1-2): 766-769.

[75] Torayev A, Engelke S, Su Z, et al. Probing and interpreting the porosity and tortuosity evolution of Li-O_2 cathodes on discharge through a combined experimental and theoretical approach[J]. The Journal of Physical Chemistry C, 2021, 125(9): 4955-4967.

[76] Débart A, Bao J, Armstrong G, et al. An O_2 cathode for rechargeable lithium batteries: The effect of a catalyst[J]. Journal of Power Sources, 2007, 174(2): 1177-1182.

[77] Kwak W J, Rosy, Sharon D, et al. Lithium–oxygen batteries and related systems: potential, status, and future[J]. Chemical Reviews, 2020, 120(14): 6626-6683.

[78] Oh G, Seo S, Kim W, et al. Seed layer formation on carbon electrodes to control Li_2O_2 discharge products for practical Li–O_2 batteries with high energy density and reversibility[J]. ACS Applied Materials & Interfaces, 2021, 13(11): 13200-13211.

[79] McCloskey B D, Speidel A, Scheffler R, et al. Twin problems of interfacial carbonate formation in nonaqueous Li–O_2 batteries[J]. The journal of physical chemistry letters, 2012, 3(8): 997-1001.

[80] Xu W, Hu J, Engelhard M H, et al. The stability of organic solvents and carbon electrode in nonaqueous Li-O_2 batteries[J]. Journal of Power Sources, 2012, 215: 240-247.

[81] McCloskey B D, Bethune D, Shelby R, et al. Limitations in rechargeability of Li-O_2 batteries and possible origins[J]. The journal of physical chemistry letters, 2012, 3(20): 3043-3047.

[82] McCloskey B D, Burke C M, Nichols J E, et al. Mechanistic insights for the development of Li–O_2 battery materials: addressing Li_2O_2 conductivity limitations and electrolyte and cathode instabilities[J]. Chemical Communications, 2015, 51(64): 12701-12715.

[83] Belova A I, Kwabi D G, Yashina L V, et al. Mechanism of oxygen reduction in aprotic Li–Air batteries: the role of carbon electrode surface structure[J]. The Journal of Physical Chemistry C, 2017, 121(3): 1569-1577.

[84] Urbano J L G. The Role of Graphene for Advanced Electrochemical Energy Storage Devices[J]. Universidad del País Vasco-Euskal Herriko Unibertsitatea, 2022.

[85] Itkis D M, Semenenko D A, Kataev E Y, et al. Reactivity of carbon in lithium–oxygen battery positive electrodes[J]. Nano Letters, 2013, 13(10): 4697-4701.

[86] Younesi R, Hahlin M, Björefors F, et al. Li–O_2 battery degradation by lithium peroxide (Li_2O_2): a model study[J]. Chemistry of Materials, 2013, 25(1): 77-84.

[87] Ottakam M M, Freunberger S A, Peng Z, et al. The carbon electrode in nonaqueous Li–O_2 cells[J]. Journal of the American Chemical Society, 2013, 135(1): 494-500.

[88] Xu W, Wang J, Ding F, et al. Lithium metal anodes for rechargeable batteries[J]. Energy & Environmental Science, 2014, 7(2): 513-537.

[89] Lu Y, Chen J. Prospects of organic electrode materials for practical lithium batteries[J]. Nature Reviews Chemistry, 2020, 4(3): 127-142.

[90] Li X, Wang Y, Lv L, et al. Electroactive organics as promising anode materials for rechargeable lithium ion and sodium ion batteries[J]. Energy Materials, 2022, 2(3): 200014.

[91] Sun M, Liu T, Yuan Y, et al. Visualizing lithium dendrite formation within solid-state electrolytes[J]. ACS Energy Letters, 2021, 6(2): 451-458.

[92] Selis L A, Seminario J M. Dendrite formation in silicon anodes of lithium-ion batteries[J]. RSC Advances, 2018, 8(10): 5255-5267.

[93] Kazyak E, Garcia-Mendez R, LePage W S, et al. Li penetration in ceramic solid electrolytes: operando microscopy analysis of morphology, propagation, and reversibility[J]. Matter, 2020, 2(4): 1025-1048.

[94] Zhao J, Tang Y, Dai Q, et al. In situ observation of Li deposition-induced cracking in garnet solid electrolytes[J]. Energy & Environmental Materials, 2022, 5(2): 524-532.

[95] Jeon S, Heo T, Hwang S Y, et al. Reversible disorder-order transitions in atomic crystal nucleation[J]. Science, 2021, 371(6528): 498-503.

[96] Jäckle M, Groß A. Microscopic properties of lithium, sodium, and magnesium battery anode materials related to possible dendrite growth[J]. The Journal of chemical physics, 2014, 141(17).

[97] Herbert E G, Hackney S A, Thole V, et al. Nanoindentation of high-purity vapor deposited lithium films: A mechanistic rationalization of the transition from diffusion to dislocation-mediated flow[J]. Journal of Materials Research, 2018, 33(10): 1361-1368.

[98] Yu S, Siegel D J. Grain boundary softening: a potential mechanism for lithium metal penetration through stiff solid electrolytes[J]. ACS applied materials & interfaces, 2018, 10(44): 38151-38158.

[99] Yu S, Siegel D J. Grain boundary contributions to Li-ion transport in the solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO)[J]. Chemistry of Materials, 2017, 29(22): 9639-9647.

[100] Ren Y, Shen Y, Lin Y, et al. Microstructure manipulation for enhancing the resistance of garnet-type solid electrolytes to "short circuit" by Li metal anodes[J]. ACS applied materials & interfaces, 2019, 11(6): 5928-5937.

[101] Basappa R H, Ito T, Morimura T, et al. Grain boundary modification to suppress lithium penetration through garnet-type solid electrolyte[J]. Journal of Power Sources, 2017, 363: 145-152.

[102] Tsai C L, Roddatis V, Chandran C V, et al. $Li_7La_3Zr_2O_{12}$ interface modification for Li dendrite prevention[J]. ACS applied materials & interfaces, 2016, 8(16): 10617-10626.

[103] Kasemchainan J, Zekoll S, Jolly D S, et al. Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells[J]. Nature Materials, 2019, 18(10): 1105-1111.

[104] Parejiya A, Amin R, Essehli R, et al. Electrochemical healing of dendrites in garnet-based solid electrolytes[J]. ACS Energy Letters, 2020, 5(11): 3368-3373.

[105] Fu J, Yu P, Zhang N, et al. In situ formation of a bifunctional interlayer enabled by a conversion reaction to initiatively prevent lithium dendrites in a garnet solid electrolyte[J]. Energy & Environmental Science, 2019, 12(4): 1404-1412.

[106] Wu B, Wang S, Lochala J, et al. The role of the solid electrolyte interphase layer in preventing Li dendrite growth in solid-state batteries[J]. Energy & Environmental Science, 2018, 11(7):

1803-1810.

[107] Song Y, Yang L, Zhao W, et al. Revealing the short-circuiting mechanism of garnet-based solid-state electrolyte[J]. Advanced Energy Materials, 2019, 9(21): 1900671.

[108] Han F, Yue J, Zhu X, et al. Suppressing Li dendrite formation in Li$_2$S-P$_2$S$_5$ solid electrolyte by LiI incorporation[J]. Advanced Energy Materials, 2018, 8(18): 1703644.

[109] Huo H, Liang J, Zhao N, et al. Dynamics of the garnet/Li interface for dendrite-free solid-state batteries[J]. ACS Energy Letters, 2020, 5(7): 2156-2164.

[110] Aguesse F, Manalastas W, Buannic L, et al. Investigating the dendritic growth during full cell cycling of garnet electrolyte in direct contact with Li metal[J]. ACS Applied Materials & Interfaces, 2017, 9(4): 3808-3816.

[111] Ren Y, Shen Y, Lin Y, et al. Direct observation of lithium dendrites inside garnet-type lithium-ion solid electrolyte[J]. Electrochemistry Communications, 2015, 57: 27-30.

[112] Gao B, Jalem R, Tian H K, et al. Revealing atomic-scale ionic stability and transport around grain boundaries of garnet Li7La$_3$Zr$_2$O$_{12}$ solid electrolyte[J]. Advanced Energy Materials, 2022, 12(3): 2102151.

[113] Han F, Westover A S, Yue J, et al. High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes[J]. Nature Energy, 2019, 4(3): 187-196.

[114] Farooqui U, Ahmad A, Hamid N. Challenges and potential advantages of membranes in lithium air batteries: A review[J]. Renewable and Sustainable Energy Reviews, 2017, 77: 1114-1129.

[115] Muthiah P, Hsu S H, Sigmund W. Coaxially electrospun PVDF−teflon AF and teflon AF−PVDF Core−sheath nanofiber mats with superhydrophobic properties[J]. Langmuir, 2010, 26(15): 12483-12487.

[116] Crowther O, Keeny D, Moureau D M, et al. Electrolyte optimization for the primary lithium metal air battery using an oxygen selective membrane[J]. Journal of Power Sources, 2012, 202: 347-351.

[117] Dias A, Freire M, Coutinho J A, et al. Solubility of oxygen in liquid perfluorocarbons[J]. Fluid Phase Equilibria, 2004, 222: 325-330.

[118] Laoire C O, Mukerjee S, Abraham K, et al. Elucidating the mechanism of oxygen reduction for lithium-air battery applications[J]. The Journal of Physical Chemistry C, 2009, 113(46): 20127-20134.

[119] Kwon H J, Lee H C, Ko J, et al. Effects of oxygen partial pressure on Li-air battery performance[J]. Journal of Power Sources, 2017, 364: 280-287.

[120] Liu L, Guo H, Fu L, et al. Critical advances in ambient air operation of nonaqueous rechargeable li–air batteries[J]. Small, 2021, 17(9): 1903854.

[121] Amici J, Alidoost M, Francia C, et al. O$_2$ selective membranes based on a dextrin-nanosponge (NS) in a PVDF-HFP polymer matrix for Li–air cells[J]. Chemical Communications, 2016, 52(94): 13683-13686.

[122] Zhang J, Xu W, Liu W. Oxygen-selective immobilized liquid membranes for operation of lithium-air batteries in ambient air[J]. Journal of power sources, 2010, 195(21): 7438-7444.

[123] Zou X, Liao K, Wang D, et al. Water-proof, electrolyte-nonvolatile, and flexible Li-air batteries via O$_2$-permeable silica-aerogel-reinforced polydimethylsiloxane external membranes[J]. Energy Storage Materials, 2020, 27: 297-306.

[124] Cao L, Lv F, Liu Y, et al. A high performance O$_2$ selective membrane based on CAU-1-NH$_2$@ polydopamine and the PMMA polymer for Li–air batteries[J]. Chemical Communications, 2015, 51(21): 4364-4367.

[125] Wang L, Pan J, Zhang Y, et al. A Li–air battery with ultralong cycle life in ambient air[J]. Advanced Materials, 2018, 30(3): 1704378.

[126] Amici J, Francia C, Zeng J, et al. Protective PVDF-HFP-based membranes for air de-hydration at the cathode of the rechargeable Li–air cell[J]. Journal of Applied Electrochemistry, 2016, 46: 617-626.

[127] Xie M, Huang Z, Lin X, et al. Oxygen selective membrane based on perfluoropolyether for Li-Air battery with long cycle life[J]. Energy Storage Materials, 2019, 20: 307-314.

[128] Kishi M, Nagatsuka K, Toda T. Effect of membrane hydrophobicity and thickness on energy-efficient dissolved oxygen removal from algal culture[J]. Frontiers in Bioengineering and Biotechnology, 2020, 8: 1-10.

[129] Deng X, Ma L, Wang, et al. Recent Progress in Materials Design and Fabrication Techniques for Membrane Electrode Assembly in Proton Exchange Membrane Fuel Cells[J]. Catalysts, 2025, 15(1): 74.

[130] Wang C, Park M J, Yu H, et al. Recent advances of nanocomposite membranes using layer-by-layer assembly[J]. Journal of Membrane Science, 2022, 661: 120926.

[131] Wang Y, Wei G. Recent Trends in Polymer Membranes: Fabrication Technique, Characterization, Functionalization, and Applications in Environmental Science (Part I)[J]. Polymers, 2024, 16(20): 2889.

[132] Yang S, He P, Zhou H. Research progresses on materials and electrode design towards key challenges of Li-air batteries[J]. Energy Storage Materials, 2018, 13: 29-48.

[133] Monaco S, Soavi F, Mastragostino M. Role of oxygen mass transport in rechargeable Li/O$_2$ batteries operating with ionic liquids[J]. The Journal of Physical Chemistry Letters, 2013, 4(9): 1379-1382.

[134] Ryan E M, Ferris K, Tartakovsky A, et al. Computational modeling of transport limitations in Li-air batteries[J]. ECS Transactions, 2013, 45(29): 123.

[135] Akhtar N, Akhtar W. Prospects, challenges, and latest developments in lithium–air batteries[J]. International Journal of Energy Research, 2015, 39(3): 303-316.

[136] Dai A, Li Q, Liu T, et al. Fundamental Understanding of Water-Induced Mechanisms in Li–O$_2$ Batteries: Recent Developments

and Perspectives[J]. Advanced Materials, 2019, 31(31): 1805602.

[137] Zhang Y L, Goh K, Zhao L, et al. Advanced non-noble materials in bifunctional catalysts for ORR and OER toward aqueous metal–air batteries[J]. Nanoscale, 2020, 12(42): 21534-21559.

[138] Viswanathan V, Thygesen K S, Hummelshøj J, et al. Electrical conductivity in Li_2O_2 and its role in determining capacity limitations in non-aqueous Li-O_2 batteries[J]. The Journal of chemical physics, 2011, 135(21).

[139] Xu S, Yao Y, Guo Y, et al. Textile inspired lithium–oxygen battery cathode with decoupled oxygen and electrolyte pathways[J]. Advanced Materials, 2018, 30(4): 1704907.

[140] Wu X, Tang C, Cheng Y, et al. Bifunctional catalysts for reversible oxygen evolution reaction and oxygen reduction reaction[J]. Chemistry–A European Journal, 2020, 26(18): 3906-3929.

[141] Tkacheva A. Redox Mediators and Electrolytes for High-Performance Li-O_2 Batteries[J]. University of Technology Sydney (Australia), 2021.

[142] Song H, Xu S, Li Y, et al. Hierarchically porous, ultrathick, “breathable" wood-derived cathode for lithium-oxygen batteries[J]. Advanced Energy Materials, 2018, 8(4): 1701203.

[143] Li L, Liu W, Dong H, et al. Surface and interface engineering of nanoarrays toward advanced electrodes and electrochemical energy storage devices[J]. Advanced Materials, 2021, 33(13): 2004959.

[144] Ma Z, Yuan X, Li L, et al. A review of cathode materials and structures for rechargeable lithium–air batteries[J]. Energy & Environmental Science, 2015, 8(8): 2144-2198.

[145] Jung H G, Hassoun J, Park J B, et al. An improved high-performance lithium–air battery[J]. Nature Chemistry, 2012, 4(7): 579-585.

[146] Wu Z, Tian Y, Chen H, et al. Evolving aprotic Li–air batteries[J]. Chemical Society Reviews, 2022, 51(18): 8045-8101.

[147] Nimon V Y, Visco S J, De Jonghe L C, et al. Modeling and experimental study of porous carbon cathodes in Li-O_2 cells with non-aqueous electrolyte[J]. ECS Electrochemistry Letters, 2013, 2(4): A33.

[148] Hernández G, Mogensen R, Younesi R, et al. Fluorine-free electrolytes for lithium and sodium batteries[J]. Batteries & Supercaps, 2022, 5(6): e202100373.

[149] Siekierski M, Piszcz M, Żukowska G. Electrolytes for metal-air batteries. In Designing Electrolytes for Lithium-Ion and Post-Lithium Batteries[J]. Jenny Stanford Publishing, 2021: 215-229.

[150] Zhang L L, Wang Z L, Xu D, et al. The development and challenges of rechargeable non-aqueous lithium–air batteries[J]. International Journal of Smart and Nano Materials, 2013, 4(1): 27-46.

[151] Ma X, Zhang D, Wen J, et al. Sustainable Electrolytes: Design Principles and Recent Advances[J]. Chemistry–A European Journal, 2024: e202400332.

[152] Gao K, Sun L, Wang K, et al. Non-aqueous liquid electrolytes in lithium metal battery: components and modification[J]. Materials Today Energy, 2023: 101413.

[153] Peng Q, Liu Z, Chen S, et al. Developing multifunctional amide additive by rational molecular design for high-performance Li metal batteries[J]. Nano Energy, 2023, 113: 108547.

[154] Wang L, Ye Y, Chen N, et al. Development and challenges of functional electrolytes for high-performance lithium–sulfur batteries[J]. Advanced Functional Materials, 2018, 28(38): 1800919.

[155] Yu X, Manthiram A. A review of composite polymer-ceramic electrolytes for lithium batteries[J]. Energy Storage Materials, 2021, 34: 282-300.

[156] Yang T, Wang C, Zhang W, et al. A critical review on composite solid electrolytes for lithium batteries: Design strategies and interface engineering[J]. Journal of Energy Chemistry, 2023, 84: 189-209.

[157] Ding P, Lin Z, Guo X, et al. Polymer electrolytes and interfaces in solid-state lithium metal batteries[J]. Materials Today, 2021, 51: 449-474.

[158] Wu J, Shen L, Zhang Z, et al. All-solid-state lithium batteries with sulfide electrolytes and oxide cathodes[J]. Electrochemical Energy Reviews, 2021, 4: 101-135.

[159] Pogosova M A, Krasnikova I V, Sanin A O, et al. Complex investigation of water impact on Li-Ion conductivity of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$—Electrochemical, chemical, structural, and morphological aspects[J]. Chemistry of Materials, 2020, 32(9): 3723-3732.

[160] Tolganbek N, Yerkinbekova Y, Khairullin A, et al. Enhancing purity and ionic conductivity of NASICON-typed $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid electrolyte[J]. Ceramics International, 2021, 47(13): 18188-18195.

[161] Xia Q, Liu H, Zhao X S. Surface engineering of anode materials for improving sodium-ion storage performance[J]. Journal of Materials Chemistry A, 2022, 10(8): 3889-3904.

[162] Cheng E J, Sharafi A, Sakamoto J. Intergranular Li metal propagation through polycrystalline $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ ceramic electrolyte[J]. Electrochimica Acta, 2017, 223: 85-91.

[163] Liu Q C, Xu J J, Yuan S, et al. Artificial protection film on lithium metal anode toward long-cycle-life lithium–oxygen batteries[J]. Advanced Materials, 2015, 27(35): 5241-5247.

[164] Huang Z, Ren J, Zhang W, et al. Protecting the Li-metal anode in a Li–O_2 battery by using boric acid as an SEI-forming additive[J]. Advanced Materials, 2018, 30(39): 1803270.

[165] Liao K, Wu S, Mu X, et al. Developing a "Water-Defendable" and "Dendrite-Free" lithium-metal anode using a simple and promising GeCl4 pretreatment method[J]. Advanced Materials, 2018, 30(36): 1705711.

[166] Kwak W J, Park S J, Jung H G, et al. Optimized concentration of redox mediator and surface protection of Li metal for maintenance of high energy efficiency in Li–O_2 batteries[J]. Advanced Energy Materials, 2018, 8(9): 1702258.

[167] Xu J J, Liu Q C, Yu Y, et al. In situ construction of stable tissue-

directed/reinforced bifunctional separator/protection film on lithium anode for lithium–oxygen batteries[J]. Advanced Materials, 2017, 29(24): 1606552.

[168] Qian J, Xu W, Bhattacharya, et al. Dendrite-free Li deposition using trace-amounts of water as an electrolyte additive[J]. Nano Energy, 2015, 15: 135-144.

[169] Giordani V, Walker W, Bryantsev V S, et al. Synergistic effect of oxygen and $LiNO_3$ on the interfacial stability of lithium metal in a Li/O_2 battery[J]. Journal of The Electrochemical Society, 2013, 160(9): A1544.

[170] Zhuang D, Huang X, Chen Z, et al. The synergistic effect of Cu_2O and boric acid forming solid electrolyte interphase layer to restrain the dendritic growth[J]. Journal of Power Sources, 2020, 458: 228055.

[171] Crompton K R, Hladky M. Analysis of germanium nanoparticle composites with an aluminum current collector toward Li-ion battery anodes with high capacity and broad potential stability range[J]. ACS Applied Energy Materials, 2021, 4(6): 5511-5532.

[172] Cui C, Zhang R, Fu C, et al. An armor-like artificial solid electrolyte interphase layer for high performance lithium-sulfur batteries[J]. Applied Materials Today, 2021, 24: 101108.

[173] Wulandari T, Fawcett D, Majumder S B. Lithium-based batteries, history, current status, challenges, and future perspectives[J]. Battery Energy, 2023, 2(6): 20230030.

[174] Wang X, Zeng W, Hong L, et al. Stress-driven lithium dendrite growth mechanism and dendrite mitigation by electroplating on soft substrates[J]. Nature Energy, 2018, 3(3): 227-235.

[175] Liu Y, Ju Z, Zhang B, et al. Visualizing the sensitive lithium with atomic precision: cryogenic electron microscopy for batteries[J]. Accounts of Chemical Research, 2021, 54(9): 2088-2099.

[176] Bucci G, Christensen J. Modeling of lithium electrodeposition at the lithium/ceramic electrolyte interface: the role of interfacial resistance and surface defects[J]. Journal of Power Sources, 2019, 441: 227186.

[177] Bistri D, Di Leo C V. A continuum electro-chemo-mechanical gradient theory coupled with damage: Application to Li-metal filament growth in all-solid-state batteries[J]. Journal of the Mechanics and Physics of Solids, 2023, 174: 105252.

[178] Fan W, Gou J, Huang Y, et al. "Peapod-like" Fiber Network: A Universal Strategy for Composite Solid Electrolytes to Inhibit Lithium Dendrite Growth in Solid-State Lithium Metal Batteries[J]. Nano Letters, 2024, 24(29): 9050-9057.

[179] Fu C, Venturi V, Kim J, et al. Universal chemo-mechanical design rules for solid-ion conductors to prevent dendrite formation in lithium metal batteries[J]. Nature Materials, 2020, 19(7): 758-766.

[180] Lee H, Lee D J, Lee J N, et al. Chemical aspect of oxygen dissolved in a dimethyl sulfoxide-based electrolyte on lithium metal[J]. Electrochimica Acta, 2014, 123: 419-425.

[181] Lim H S, Kwak W J, Chae S, et al. Stable solid electrolyte interphase layer formed by electrochemical pretreatment of gel polymer coating on Li metal anode for lithium–oxygen batteries[J]. ACS Energy Letters, 2021, 6(9): 3321-3331.

[182] Wen X, Zhu X, Wu Y, et al. A hydrophobic membrane to enable lithium-air batteries to operate in ambient air with a long cycle life[J]. Electrochimica Acta, 2022, 421: 140517.

[183] Visco S J, Katz B D, Nimon Y S, et al. Protected active metal electrode and battery cell structures with non-aqueous interlayer architecture[J]. Google Patents, 2007.

[184] Li L, Manthiram A. Dual-electrolyte lithium–air batteries: influence of catalyst, temperature, and solid-electrolyte conductivity on the efficiency and power density[J]. Journal of Materials Chemistry A, 2013, 1(16): 5121-5127.

[185] Liu Y, Li Y, Huang X, et al. Copper hexacyanoferrate solid-state electrolyte protection layer on Zn metal anode for high-performance aqueous zinc-ion batteries[J]. Small, 2022, 18(38): 2203061.

[186] Li L, Zhao X, Fu Y, et al. Polyprotic acid catholyte for high capacity dual-electrolyte Li–air batteries[J]. Physical Chemistry Chemical Physics, 2012, 14(37): 12737-12740.

[187] Zhang H, Lv X, Tian W, et al. One-pot fabrication of N, S co-doped carbon with 3D hierarchically porous frameworks and high electron/ion transfer rate for lithium-ion batteries[J]. Chemical Engineering Science, 2021, 234: 116453.

[188] Kwak W J, Jung H G, Aurbach D, et al. Optimized bicompartment two solution cells for effective and stable operation of $Li–O_2$ batteries[J]. Advanced Energy Materials, 2017, 7(21): 1701232.

[189] Suo L, Hu Y S, Li H, et al. New class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries[J]. Nature communications, 2013, 4(1): 1481.

[190] Ding F, Xu W, Graff G L, et al. Dendrite-free lithium deposition via self-healing electrostatic shield mechanism[J]. Journal of the American Chemical Society, 2013, 135(11): 4450-4456.

[191] Wang T, Liu X, Huang S, et al. Development of Polymer-based Artificial Solid Electrolyte Interphase for Safer Li-Metal Batteries: Challenges, Strategies and Prospects[J]. Nano Energy, 2024: 109970.

[192] Kim B G, Kim J S, Min J, et al. A moisture-and oxygen-impermeable separator for aprotic $Li-O_2$ batteries[J]. Advanced Functional Materials, 2016, 26(11): 1747-1756.

[193] Kwak W J, Park J, Nguyen T, et al. A dendrite-and oxygen-proof protective layer for lithium metal in lithium–oxygen batteries[J]. Journal of Materials Chemistry A, 2019, 7(8): 3857-3862.

[194] Prado L H. Fabrication and characterization of superhydrophobic and slippery liquid infused porous surfaces (SLIPS) for corrosion protection of stainless steel[J]. Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), 2022.

[195] Crowther O, Salomon M. Oxygen selective membranes for Li-air (O_2) batteries[J]. Membranes, 2012, 2(2): 216-227.

[196] Elia G A, Hassoun J. A gel polymer membrane for lithium-ion oxygen battery[J]. Solid State Ionics, 2016, 287: 22-27.

[197] Nemori H, Shang X, Minami H, et al. Aqueous lithium-air batteries with a lithium-ion conducting solid electrolyte $Li_{1.3}Al_{0.5}Nb_{0.2}Ti_{1.3}(PO_4)_3$[J]. Solid State Ionics, 2018, 317: 136-

141.

[198] Zhang T, Imanishi N, Shimonishi Y, et al. A novel high energy density rechargeable lithium/air battery[J]. Chemical Communications, 2010, 46(10): 1661-1663.

[199] Choi W, Kim M, Park J O, et al. Ion-channel aligned gas-blocking membrane for lithium-air batteries[J]. Scientific Reports, 2017, 7(1): 12037.

[200] Yin Y B, Yang X Y, Chang Z W, et al. A water-/fireproof flexible lithium–oxygen battery achieved by synergy of novel architecture and multifunctional separator[J]. Advanced Materials, 2018, 30(1): 1703791.

[201] Zhu X, Zhao T, Wei Z, et al. A high-rate and long cycle life solid-state lithium–air battery[J]. Energy & Environmental Science, 2015, 8(12): 3745-3754.

锂空气电池的研究进展、挑战与展望

Humaira Rashid Khan[1], Abdul Latif Ahmad[1,*], Asim Ali Yaqoob[2]

（1. School of Chemical Engineering, Universiti Sains Malaysia, Engineering campus, Seri Ampangan, 14300 Nibong Tebal,
Seberang Perai Selatan, Pulau Penang, Malaysia;
2. City of Oxford College, Oxpens Rd, Oxford OX1 1SA, United Kingdom）

摘　要： 为实现2050年净零排放目标，能源生产系统亟需彻底转型，而先进电池技术将在推动下游行业向可持续能源转型中发挥关键作用。锂空气电池（LABs）因其超高的理论能量密度，远超传统锂离子电池，成为一种极具吸引力的“超越锂离子”技术选项。然而，LABs在实际应用中面临诸多挑战，包括电解质不稳定性、不可逆电极反应、循环性能差以及倍率性能低等问题。本文综述了LAB系统近期研究进展，重点介绍了电解质稳定化、电极改性和界面工程等创新方法，以应对上述挑战。文章评估了当前解决这些问题的策略，并指出了未来研究的重点方向，以推动LAB技术克服相应障碍。目前已取得的进展表明，实现具有与汽油相当比能量的实用型LABs已成为可能，这将有望革新电动交通领域。

关键词： 锂空气电池；水性与非水性电解质；枝晶形成；副反应；复合隔膜

中图分类号： 127.1$^+$1　　**文献标识码：** A

通讯作者：Abdul Latif Ahmad. E-mail: chlatif@usm.my
第一作者：Humaira Rashid Khan. E-mail: humairar_khan@usm.my;
Asim Ali Yaqoob. E-mail: asimchem4@gmail.com

本文的电子版全文由Elsevier出版社在ScienceDirect上出版（https://www.sciencedirect.com/journal/new-carbon-materials/）