Critical Advances in Ambient Air Operation of Nonaqueous Rechargeable Li-Air Batteries

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Abstract
Over the past few years, great attention has been given to nonaqueous lithium–air batteries owing to their ultrahigh theoretical energy density when compared with other energy storage systems. Most of the research interest, however, is dedicated to batteries operating in pure or dry oxygen atmospheres, while Li–air batteries that operate in ambient air still face big challenges. The biggest challenges are H2O and CO2 that exist in ambient air, which can not only form byproducts with discharge products (Li2O2), but also react with the electrolyte and the Li anode. To this end, recent progress in understanding the chemical and electrochemical reactions of Li–air batteries in ambient air is critical for the development and application of true Li–air batteries. Oxygen-selective membranes, multifunctional catalysts, and electrolyte alternatives for ambient air operational Li–air batteries are presented and discussed comprehensively. In addition, separator modification and Li anode protection are covered. Furthermore, the challenges and directions for the future development of Li–air batteries are presented.

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Abstract

Recent years, great attention has been paid to the non-aqueous lithium-air batteries due to their ultrahigh theoretical energy density compared to other energy storage systems. Most of the research interest, however, has been dedicated to the batteries operating in pure or dry oxygen atmospheres, while Li-air batteries operated in ambient air are still a big challenge. The biggest challenges are the H₂O and CO₂ from the ambient air, which could not only form by-products with discharge products (Li₂O₂), but also react with the electrolyte and the Li anode. To this end, recent progress in understanding the chemical and electrochemical reactions of Li-air batteries in ambient air is critical for the development and application of true Li-air batteries. Oxygen selective membranes, multifunctional catalysts, and electrolyte alternatives for ambient air operational Li-air batteries are presented and discussed comprehensively. In addition, separator modification and Li anode protection are also covered in the present review. Furthermore, the challenges and directions for future development of Li-air batteries are presented.

1. Introduction

The global energy crisis in such aspects as shortages of fossil fuels and terrible climate warming issues associated with CO₂ emission has driven researchers to discover clean and sustainable energy storage systems.[1] Although lithium-ion technology has developed itself as a type of reliable energy-storage chemistry over the past two decades, the high cost and limited performance of the existing Li-ion battery technologies are seriously hindering the mass market adoption of electric vehicles (EVs) and hybrid electric vehicles (HEVs). Therefore, it is imperative to develop new alternatives that extend beyond Li-ion technology to meet the energy storage needs of future generations.[2-7] Among all the battery systems going beyond Li-ion, the non-aqueous Li-air battery has attracted enormous research attention.[8-14] It could deliver
theoretical specific energy that is almost 3-4 times that of the most advanced Li-ion batteries. Unlike most other batteries that must incorporate both the anode and cathode are incorporated inside the storage system, the cathode material (oxygen) of the nonaqueous Li-air batteries is not stored in the battery.\[^{[15-19]}\] Instead, oxygen is from the air environment and reduced by catalytic sites inside the air cathode.\[^{[20]}\] During discharge in the cathode, O\(_2\) is reduced to form Li\(_2\)O\(_2\), while the latter is oxidized to release O\(_2\) on charge.\[^{[21]}\]

The first example of a rechargeable non-aqueous Li-air battery was developed by Jiang and Abraham in 1996.\[^{[22]}\] They employed lithium metal as anode, carbonate-based polyvinylidene difluoride (PVdF) as gel electrolyte, and carbon as cathode. Later, other researchers, e.g. Bruce, Yang, Nazar, and Luntz, provided advanced theoretical direction with huge efforts and promoted the non-aqueous Li-air battery research to a new stage.\[^{[23-32]}\] Along with these advances, however, critical challenges regarding the non-aqueous Li-air battery hindered its further development. These challenges can be defined from the following aspects: low electrical energy efficiency caused by the limited catalytic activity of the catalyst, short lifetime resulting from unstable electrolyte, and safety issues because of use of Li metal as anode.\[^{[33-36]}\] Fortunately, surprising achievements have been made during the past several decades. A change of electrolyte from unstable carbonate-based to dimethyl sulfoxide (DMSO) and ether-based solvents has been used to stabilize the battery cycling.\[^{[24, 37-41]}\] Multiple kinds of catalysts, e.g. metal oxides, novel metals (alloys), carbon-based, and carbon-free materials, have been widely investigated to reduce the overpotential and improve the reversibility.\[^{[42-50]}\] Mediators (also denoted as soluble catalysts) such as lithium iodide (LiI) and 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) have been adopted to enlarge the discharge/charge capacity and prolong the cycling capability.\[^{[21, 51-55]}\] A number of review papers have focused on summarizing the latest progress on cathode materials, electrolytes, and anodes.\[^{[56-62]}\] Experimental results combined with theoretical calculations towards understanding the mechanisms of Li\(_2\)O\(_2\)
formation/decomposition either via solid surface pathways or via solution-mediated pathways have also been proposed and well-reviewed by many groups.\cite{4, 33, 63-67}

As an open system however, the most crucial point, but easily overlooked, is that most of the exciting reports on non-aqueous Li-air batteries were carried out in pure or dry oxygen within a pressure vessel. Nevertheless, the ultimate goal of the Li-air battery is a true Li-air system, which means that it is expected to operate in ambient air. No further practical application could be considered before this point is well addressed. In the last few years, the challenges for ambient operation of the non-aqueous Li-air have been demonstrated in several review papers, and a brief description of the main challenges will be presented in section 2 in this review.\cite{3, 68, 69} Geng et al. made an effort to review the challenges obstructing a practical Li-air battery in terms of the influences of CO$_2$ and H$_2$O on the Li-O$_2$ electrochemistry.\cite{70} Only a very few report, however, have proposed solutions to surmount the problems regarding the open-system Li-air batteries.\cite{3, 20, 70-73} Although Hamid et al. specifically summarized how the membrane technology can mitigate crucial challenges associated with air cathodes, lithium metal anodes, and electrolytes, a detailed review on the progress on making Li-air batteries truly work in ambient air atmosphere is still lacking.\cite{74} In this review, we will particularly focus on the development of Li-air batteries operating in ambient air, to facilitate further advances on true Li-air batteries toward their original intention. **Figure 1** provides an overview of the strategies reported in recent years to operate ambient non-aqueous Li-air batteries. We start with explaining some problems facing the Li-air battery in ambient air in section 2, including how gas gradients, e.g. moisture and CO$_2$, affect the features of the Li-air battery and how the Li anode suffers from crossover gas contaminants. Then, we will introduce strategies for cathode protection including oxygen selective membranes (OSMs) and multifunctional catalysts in section 3. In section 4, we discuss electrolyte alternatives, including solid-state membranes, gel polymer electrolytes, and hydrophobic ionic liquid electrolytes for use in non-aqueous Li-air
batteries to solve the system-wide problems. In section 5, modification of the separator will be discussed. In section 6, improvement of the Li anode is introduced, e.g. protective layers and lithiated anodes to stabilize the system. At the end of this review, the latest research trends on Li-air batteries that can work in ambient air are highlighted. It should be pointed out that we focus on non-aqueous Li-air batteries, so in this review, “Li-air” always refers to “non-aqueous Li-air” if not specified.

2. Challenges on the way towards ambient air operation

For ambient operation of non-aqueous Li-air batteries, several critical challenges regarding the open system should be taken into account: the low oxygen partial pressure in air, and gas contamination, which affects both cathode and anode electrochemistry, as well as organic solvent evaporation.

The major constituents of dry air include N$_2$ (78%), O$_2$ (21%), CO$_2$ (~0.03%), and other gases in trace amounts.[33] For organic electrolyte containing Li-air batteries, the capacity and rate capability are heavily dependent on the amount of dissolved O$_2$ in the solvent. The low O$_2$ partial pressure in air results in low current densities upon battery discharge/charge due to the limited solubility of O$_2$ in the organic electrolyte and the sluggish reduction of O$_2$ to form electrochemically active oxygen species on the air electrode. The influence of air impurities on the Li-air battery system was investigated in the past.[32, 75-78] The possible reactions involved in Li-air chemistry in both cathode and anode are listed from Equations (1) to (9):

\[
2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \quad (1)
\]
\[
4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O} \quad (2)
\]
\[
4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{LiOH} \quad (3)
\]
\[
4\text{Li} + \text{O}_2 + 2\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 \quad (4)
\]
\[ \text{2Li} + \text{2H}_2\text{O} \rightarrow \text{2LiOH} + \text{H}_2 \quad (5) \]

\[ \text{2LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \quad (6) \]

\[ \text{LiOH} + \text{H}_2\text{O} \rightarrow \text{LiOH} \cdot \text{H}_2\text{O} \quad (7) \]

\[ \text{2Li}_2\text{O}_2 + \text{2CO}_3 \rightarrow \text{2Li}_2\text{CO}_3 + \text{O}_2 \quad (8) \]

\[ \text{2Li}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} + \text{O}_2 \quad (9) \]

### 2.1 Effects of water on the Li-air battery

The moisture from air results in the most dramatic impact on the performance of non-aqueous Li-air batteries. For one hand, water contamination may change the mechanism of the non-aqueous Li-air chemistry, especially for charge processes.\(^{[78-81]}\) Luntz \textit{et al.} found that an 500 ppm water in the electrolyte could largely increase the discharge capacity compared to water addition of 12 ppm (Figure 2a).\(^{[79]}\) Guo and his coworkers observed the same trend, that discharge capacities increased with the growth of the relative humidity (RH) value, but the cycling stability and rate performances moved in the opposite direction.\(^{[78]}\) Gasteiger reported that water impurities in the electrolyte do not lead to LiOH formation, but result in toroidal Li$_2$O$_2$ crystals and larger discharge capacity (Figure 2b).\(^{[81]}\) A later study, however, observed high charge overpotentials when water was introduced into the electrolyte. This was attributed to the LiOH formation via Equation (3) and (9) on the Li$_2$O$_2$ surface, which needed to be decomposed before the oxidation of Li$_2$O$_2$. This may cause electrolyte decomposition and lead to low cycling efficiency. A rapid voltage increase in the charge potential as H$_2$O content increased was reported by Luntz and coworker.\(^{[63]}\) In contrast, Zhou \textit{et al} discovered that 120 ppm water was beneficial and could reduce the charge overpotential to only 0.24 V.\(^{[82]}\) Although the detailed mechanism of water involvement in non-aqueous Li-air electrochemistry is not clear as yet, high overpotential and a low O$_2$ evolution rate during charge processes imply that
H₂O contamination has a negative effect on the rechargeability of the Li-air battery. Based on a systematic study of tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte, Guo et al. found that Li₂O₂ forms during initial discharge and changes into Li₂CO₃ and LiOH, owing to the reactions between Li₂O₂ and CO₂ and H₂O, respectively. Water from ambient air has a negligible effect on the oxygen reduction reaction (ORR) performance, but has a much more dramatic influence on the oxygen evolution reaction (OER), since there is a negligible difference in the ORR activities between ambient air and pure oxygen. The OER peak in ambient air is at approximately 4 V, however, which refers to the decomposition of carbonates. The OER peak in pure oxygen is at 3.2 V, which is ascribed to the decomposition of Li₂O₂. For another consideration, water in air crosses over the cathode and separator to reach the anode. Li metal will be corroded by H₂O according to Equation (5). Cho et al examined the effects of water contamination on the Li-air battery. Figure 3c shows the deterioration of the lithium metal during different stages of discharge, indicating the failure of the battery. Although it remains debatable whether a trace amount of water is beneficial or detrimental to the electrochemistry of a battery, the elimination of high contents of water is critical to realize the practical non-aqueous Li-air battery.

2.2 Gas effect on the Li-air battery

Besides the influence of water, the other constituents of air also have negative effects on the Li-air battery: 1) Oxygen will penetrate into the Li anode through the air cathode and separator, causing oxidation of the Li anode (Equations (3-4)), which, at this place, is unwanted and causes fast degradation of the battery as well as safety issues. CO₂ is another constituent in air that has been reported to have an adverse influence on non-aqueous Li-air chemistry. The solubility of CO₂ in organic solvents is approximately 50 times greater than that of O₂, implying a high possibility that CO₂ is involved in battery reactions. Li anode and its
discharge species, e.g. LiO\(_2\), Li\(_2\)O\(_2\), or LiOH, gradually react with CO\(_2\) to form Li\(_2\)CO\(_3\), according to Equations (4-6). Li\(_2\)CO\(_3\) is a wide band-gap insulator and electrochemically irreversible, which will result in a high oxidation potential during charging (> 4 V).\([89][90]\) Additionally, Li\(_2\)CO\(_3\) is a more chemically stable compound than Li\(_2\)O\(_2\). The chemical stability difference will always promote conversion of Li\(_2\)O\(_2\) into Li\(_2\)CO\(_3\) in the presence of CO\(_2\) in a Li-air battery.\([31, 32]\) Therefore, CO\(_2\) in ambient air clearly causes low coulombic efficiency and degrades the cycle life of Li-air batteries. In recent years, some catalysts have been reported to be able to reversibly catalyze the reaction between Li and CO\(_2\),\([91-93]\) although the studies on Li-CO\(_2\) batteries fed by CO\(_2\) atmosphere are not within the scope of this review, and only those advances that relate to reversible Li\(_2\)CO\(_3\) formation/decomposition in Li-air batteries will be discussed. (3) N\(_2\) is much more inert than water and CO\(_2\).\([94]\) Although Lutz \textit{et al.} found that N\(_2\) slowly reacts with an unprotected Li anode, there have been no detailed studies yet showing that N\(_2\) interferes with the Li-air electrochemistry.\([3]\) To realize a Li-air battery technology that would be capable of feasible operation under ambient conditions, it is critical to elucidate the side effects of the unwanted gas contamination (H\(_2\)O, CO\(_2\)) from the air.

2.3 Electrolyte evaporation effect on Li-air battery

Besides gas contamination, the regular drop in the electrolyte level drop during cell cycling is another critical factor that seriously interferes with the Li-air battery performance. Huang and Faghri developed a two dimensional (2D) physical model to stimulate the electrolyte level in a Li-air battery.\([95]\) The battery to be modelled had a typical coin cell structure and contained an air chamber. The interaction between the battery and its surroundings was therefore considered with reference to the incorporated air chamber. The solvent vapor and oxygen diffusion in this chamber were included. Simulation results showed that the highest evaporation rate appeared at the beginning of the battery discharge and decreased when the partial pressure of the solvent in the air chamber reached its saturation level. It was claimed from another simulation study
that the evaporation of the electrolyte is proportional to the oxygen flow rate passing through the battery as well as proportional to the exposed surface area of the oxygen electrode.\textsuperscript{[96]} The loss of electrolyte stops the electrochemical reaction in the dry pores in the cathode because of the lack of a three-phase boundary (which requires O\textsubscript{2}, electrolyte, and carbon). In general, electrolytes with higher boiling points are preferred because of their low evaporation rates. Such electrolytes typically have high viscosities and low ionic conductivities, however, which will result in higher Ohmic resistance and mass transfer overpotentials.\textsuperscript{[97]} More simulation studies on organic solvents were performed to find ideal ones meeting the requirements of an open battery system.\textsuperscript{[68, 98-100]} Commonly used organic solvents, e.g. dimethyl ether (DME) or DMSO, are more or less volatile solvents. An oxygen selective membrane between the cathode and the ambient environment could be a feasible approach to control the evaporation rate of the electrolyte for ambient Li-air batteries.

3. Cathode modification

3.1 Oxygen selective membrane

Employing an oxygen selective membrane is an alternative method to keep the unwanted molecules (H\textsubscript{2}O, CO\textsubscript{2}) from air out of the battery and to mitigate the electrolyte evaporation at the same time. As discussed in Section 2, H\textsubscript{2}O and CO\textsubscript{2} from the ambient air could alter the discharge products into LiOH and Li\textsubscript{2}CO\textsubscript{3}, which would affect the performance of Li-air batteries. The selectivity lies in higher solubility and/or diffusivity of the selected molecules (as O\textsubscript{2}) than for the rejected molecules (as H\textsubscript{2}O and CO\textsubscript{2}). Therefore, undesired reaction and discharge products could be prevented by using OSMs. Studies have suggested the effectiveness of suitable membranes to address some terrible challenges and advance the performance of air cathodes. OSMs can be used either on the inner side or the outer side of the air cathode, or integrated with the cathode materials. Typically, an ideal OSM for Li-air
batteries should have the following desirable properties: 1) High O\textsubscript{2} permeability; 2) No water vapor permeability; 3) No electrolyte solvent permeability; and 4) No carbon dioxide (CO\textsubscript{2}) permeability.\textsuperscript{[71]} However, H\textsubscript{2}O molecules have higher diffusivity and smaller kinetic diameter than O\textsubscript{2} molecules, so the separation and selection of pure O\textsubscript{2} molecules from H\textsubscript{2}O and CO\textsubscript{2} is not easy.\textsuperscript{[101]} In spite of this, remarkable progress has been made in the past several years on ambient operational Li-air batteries by using oxygen selective membranes. Table 1 lists some typical achievements for non-aqueous Li-air batteries using oxygen selective membranes.

Basic materials for OSMs can be classified into three groups:\textsuperscript{[36, 71, 102-105]} 1) Polysiloxanes, silicone oils, fluorinated polysiloxanes, polydimethylsiloxane, and fluorinated polysiloxane copolymers with alkyl methacrylates; 2) Fluorinated hydrocarbons, polyethers (e.g., Krytox 1506), polyperfloroalkyl oxides, polyperfloroalkyl amines, Melinex 301H (ML), high density polyethylene, low-density polyethylene, polytetrafluoroethylene (PTFE), polyaniline (PANI), and perfluoropolyether (PFPE); and 3) Metal organic frameworks (MOFs). Traditional OSMs are typically a porous substrate with silicone oil infiltration. The latter has a thickness of several hundred micrometers. The interface area between air cathode and the OSMs is limited to several square centimeters. OSMs typically have an O\textsubscript{2}/H\textsubscript{2}O separation factor of 1.5-3.6. The O\textsubscript{2} permeation is 2×10\textsuperscript{-7} to 1.5×10\textsuperscript{-6} mol m\textsuperscript{-2} s\textsuperscript{-1} Pa\textsuperscript{-1} at room temperature. Silicone oil is a promising material for O\textsubscript{2}-selective liquid from water barrier. Silicone oil has been used as an O\textsubscript{2} carrier in bioreactors. O\textsubscript{2} solubility in silicone oil is approximately 6 mmol dm\textsuperscript{-3}, 20-fold higher than that of oxygen in water.\textsuperscript{[106]} In addition, silicone oil is non-volatile and stable, and will benefit for long-term battery operation in ambient air.\textsuperscript{[101]}

The first example of using OSM in Li-air batteries in ambient air (20-30% relative humidity (RH)) was reported by Zhang and coworker.\textsuperscript{[101]} The membrane allows O\textsubscript{2} to permeate through while blocking H\textsubscript{2}O. The authors claimed that silicone oil of high viscosity presented satisfied
performances. The immobilized silicone oil was infiltrated in the porous PTFE as OSM. Li/air batteries lasted for 16.3 days when operated in ambient air (at 20\% RH). It showed a specific capacity of 789 mA h g\(^{-1}\)\text{carbon} and a specific energy of 2182 W h kg\(^{-1}\)\text{carbon}. The reference Li/air battery cathode used a commercial, porous PTFE diffusion membrane as the moisture barrier. It only cycled 5.5 days, with a specific capacity of 267 mA h g\(^{-1}\)\text{carbon} and a specific energy of 704 Wh kg\(^{-1}\)\text{carbon}. As shown in Figure 3a, the OSM with high O\(_2\) permeability could prevent water erosion and prohibited the side discharge product of Li\(_2\)CO\(_3\) in ambient air, leading to increased specific capacity from 267 to 789 mA h g\(^{-1}\)\text{carbon}.\(^{[103]}\)

Amici et al proposed an OSM by attaching silicone oil onto poly(vinylidene fluoride co-hexafluoropropylene) (PVdF-HFP) with high hydrophobicity.\(^{[107]}\) The discharge-charge profiles with and without OSM show similar behavior at the first cycle of the Li-air battery, both with a coulombic efficiency of 88\% (Figure 3b). However, a noticeable difference starts to appear at OCV after 10 days. The Li/air battery coupled with the OSM still maintains a 2.5V discharge potential and a nearly same capacity, while the one without OSM protection only presents 25\% capacity of the initial value. They claimed that the OSM could also prevent the Li anode from corrosion because of the moisture entrance during the air uptake in discharge. Crowther and coworkers developed a rather thin silicone rubber O\(_2\)-selective membrane (83 \(\mu\)m thickness) which includes polysiloxane and methacrylate-polysiloxane copolymers.\(^{[108]}\) Membrane of this kind exhibits high O\(_2\) solubility, retards moisture diffusion from the atmosphere and minimizes the organic solvent evaporation. A thin semicosil-based silicone rubber OSM was used to protect Ketjen Black EC600G cathode. The Li/air battery demonstrated a capacity of 570 mA h g\(^{-1}\) at a relatively high current density of 0.2 mA g\(^{-1}\) even though the RH is as high as 42.9\%. The battery without protection faded quickly with a capacity of only 151 mA h g\(^{-1}\) (Figure 3c). The significant increase in performances was attributed to increased O\(_2\) transmission through the thinner Semicosil-based silicone rubber membrane. The
authors emphasized that the Li-air batteries with thinner O₂-selective membranes exhibited higher specific capacities.

Apart from the above mentioned OSMs, Melinex® 301H with a thickness of 25 μm was employed as an oxygen-selective polymer membrane by Zhang et al. The introduced heat-sealable polymer membrane acts as oxygen diffusion material and as a moisture barrier, and even could minimize the electrolyte evaporation for Li-air batteries (Figure 4a). Li-air batteries with this OSM protection cycled for more than one month with an oxygen partial pressure of 0.21 atm and RH of ~20%. The specific energy was 362 Wh kg⁻¹ when the weight is based on the total battery including its packing. Later, this polymer membrane was used to regulate O₂ and H₂O flow in pouch-type Li-air battery. With the same RH of ~20% and functionalized graphene sheets as cathode, the Li-air battery delivered a discharge capacity exceeding 5000 mAhg⁻¹ when the current density was 0.1 mA cm⁻² (Figure 4b). Unfortunately, the current densities in their studies were limited to 0.05 and 0.1 mA cm⁻². By attaching a Teflon-coated fiberglass cloth (TCFC) membrane (McMaster Carr) to a pouch cell as OSM, Crowther et al. found that only approximately 2% of the electrolyte evaporates out of the pouch over 40 days under ambient conditions. This is an acceptable loss for a primary Li-air battery (Figure 4c).

Conventional OSMs are usually attached near the exterior surface of the cathode as an independent layer. The thickness of OSM is large and the contact between OSM and the cathode material is limited. Such design leads to poor rate performance during discharge process due to a limited amount of O₂ supply. To circumvent this problem, Zhu and coworkers directly coated silicone-oil film into a carbon nano-particle coated Li₁.₃Al₀.₃Ti₁.₇(PO₄)₃ (LATP) cathode. The infiltration of silicone oil enabled intimate connection with the cathode triple-phase boundaries (TPBs). The thickness of the OSM was 50 nm (Figure 5a). The discharge capacity exhibited
was 11697 mAh g⁻¹ (Figure 5b) in ambient air, which is several times higher than that of the lithium-air battery based on a conventional OSM. Moreover, the recharge process presents an obvious lower voltage plateau (about 3.8V) than that of a reference battery without OSM (merely 27% recharged). The OSM blocks H₂O and CO₂ from reaching reaction sites to form LiOH and Li₂CO₃. When the Li-air battery without the silicone-oil film cycled in ambient air (~50% RH), it only maintained 20 times with the energy efficiency decreased from 62% to 47% with a limited capacity of 1000 mA h gcarbon⁻¹ at a current density of 0.3 mA cm⁻² (Figure 5c) associated with the formation of LiOH and Li₂CO₃. On the contrary, the OSM protected Li-air battery showed almost no capacity loss after 100 cycles under the same operating conditions with the formation of Li₂O₂ (Figure 5d). It was also claimed that optimization of the OSM thickness is critical for the electrochemical performance, since the silicone-oil film can be easily broken by product growth if too thin, whereas a very thick film results in increased polarization for oxygen ingress through the films. Although the benefit of OSMs with silicone oil as a waterproof protective film is remarkable, it has limited oxygen selectivity toward H₂O. Organic nanosponges are newly found to be able to selectively capture a wide range of molecules. It was reported that a novel OSM could be achieved by incorporating dextrin-nanosponge into a poly(vinylidene fluoride co-hexafluoropropylene) (PVdF-HFP) matrix. The dextrin-nanosponge in the polymer matrix could increase the O₂ permeability to six-fold and reduce increase H₂O permeability to more than half, with respect to the same polymer matrix with silicone oil. When incorporated into a pouch type Li-air cell in air with 17% RH, this OSM insured approximately 145 cycles with a fixed capacity of 100 mAh g⁻¹ and it corresponds to about 1450 h of cell operation.

To date, although the benefit of OSMs with silicone oil as a waterproof protective film is remarkable, unfortunately, the selectivity of such OSMs toward CO₂ was not demonstrated. Few so-called oxygen selective membranes can allow O₂ to pass through while isolating
moisture and CO₂. Metal-organic frameworks (MOFs) contain both organic and inorganic moieties in crystalline lattices. Tailorable pore size combined with tunable sorption behavior in MOFs has made them promising candidates as membranes for gas separation applications.[113] MOFs were discovered to be a novel class of oxygen selective membranes that could be used in the field of Li-air battery by Cao et al.[102] Polydopamine-coated MOFs crystals of CAU-1-NH₂ was adopted into a PMMA (polymethylmethacrylate) matrix (Figure 6a-b). Li-air battery with such membrane delivered a discharge capacity of 1480 mA h g⁻¹ and a cycle life up to 66 times at a current density of 450 mA g⁻¹ with a fixed capacity of 450 mA h g⁻¹ which was much better than that without MMM (Figure 6c). They explained the substantial enhancement that the functional group –NH₂ in the MOF, –OH in the polydopamine molecule, and the –CQO in the PMMA would preferably interact with the CO₂ molecule. Then the amount of CO₂ molecule entering the cell is decreased. Besides, the PMMA polymer with high hydrophobicity prevents the intrusion of moisture into the battery. This discovery presents a strategy to realize a multifunctional OSM system and provides a new avenue for developing ambient Li-air batteries. Similar to the structure of MOF, zeolite molecular sieves have been studied for application in separation membranes because of their well-defined, regular pore structure and thermal as well as chemical stability.[114, 115] Zeolite molecular sieves have shown potential in current Li-O₂ batteries due to the advantage of zeolite in selectively absorbing moisture rather than O₂ from the air feed.[9, 45, 116] A trade-off between the O₂ diffusivity and O₂/H₂O selectivity exists in OSMs. Much reduced O₂ diffusivity will minimize the solvent evaporation, although it would cause serious oxygen polarization if the diffusion rate is too slow. So far no membrane has shown complete effectiveness in blocking the contaminants into the cell when ambient air is used as an oxygen source. Thinner membranes with high O₂ selectivity are highly in demand in order to meet the high power demand of practical applications.
Besides these specifically introduced OSMs, some graphene membranes have been reported to serve as efficient oxygen selective membranes for ambient air Li-air batteries, due to their hydrophobic nature as well as their micropores for rapid oxygen diffusion.\textsuperscript{[117-119]} Graphene, as is well known, has already been intensively studied as a promising cathode material for Li-air batteries, due to its high conductivity, large surface area and excellent catalytic ability towards the ORR and OER.\textsuperscript{[120-122]} Ozcan \textit{et al.} reported a flexible graphene paper, and it showed electrochemical stability as a cathode in a lithium air battery when cycled in ambient air.\textsuperscript{[119]} More interestingly, a graphene based moisture resistive membrane was fabricated as cathode for ambient Li-air batteries (\textbf{Figure 7a}).\textsuperscript{[117]} Surprisingly, such three-dimensional (3D) highly tortuous membranes showed remarkable oxygen/moisture selectivity to ensure efficient oxygen diffusion while retarding the ingress of moisture. By conducting water and oxygen permeability tests on such graphene membranes, they found that oxygen diffuses much faster from the beginning than moisture and reaches equilibrium with the atmosphere in about 5 h (\textbf{Figure 7b}). Furthermore, its 3D interconnected conducting structure facilitates the electron transfer that favors Li$_2$O$_2$ formation. When cycled with a fixed capacity of 1425 mAh g$^{-1}$ in ambient air, the Li-air battery with the graphene cathode containing Li-air battery displayed strong stability for up to 100 cycles with the charge potential only at 3.8 V with a rather high current density of 2.8A g$^{-1}$ (\textbf{Figure 7c}). This performance evenly matched that of another reported Li-O$_2$ battery based on 3D hierarchical porous graphene cathode that was operated under pure O$_2$.\textsuperscript{[118, 119]}

Other materials with hydrophobic properties as well have been used as water barriers in ambient Li-air batteries. Highly hydrophobic materials favor oxygen transportation but block water penetration. Zhang and coworkers pointed out that an appropriate cathode structure with a good balance between hydrophobic and hydrophilic properties could be used to develop better Li-air batteries.\textsuperscript{[123]} Highly conductive polyaniline (PANI) can act as a waterproof membrane.\textsuperscript{[124]} When attached to the air cathode, it blocks the entrance of moisture, minimizes the electrolyte
evaporation, and therefore protects the Li anode. Polytetrafluoroethylene (PTFE) treated carbon paper enhance its hydrophobicity. It prevented moisture permeation and kept the electrolyte inside of the ambient Li-air battery.\textsuperscript{[125]} It was discovered that by increasing the hydrophobicity of the carbon paper could help improve the discharge capacity. Li-air battery with a 30% PTFE treated waterproof carbon paper could get the maximum specific capacity of 2367.7mAh g\textsuperscript{-1}.

### 3.2 Multifunctional catalyst

Employing bifunctional electro-catalysts has been verified to facilitate the oxygen redox reactions for Li-air batteries in practical conditions in the absence of OSM.\textsuperscript{[126-134]} After substituting Fe on some of the Mn sites in MnO\textsubscript{x}, the Mn\textsubscript{1.8}Fe\textsubscript{0.2}O\textsubscript{3} cathode containing Li-air battery showed only 25% capacity loss after 10 cycles in ambient air.\textsuperscript{[127]} A Pd nanolayer was reported to have been deposited \textit{in situ} on Ni foam via a galvanic exchange method. The excellent catalytic activity of the Pd nanolayer enables the Li-air battery to substantially maintain its energy deliver during the transition from “O\textsubscript{2}” to “air”.\textsuperscript{[128]} Dandelion-like NiCo\textsubscript{2}O\textsubscript{4} hollow microspheres in a Li-air battery presented a reversible capacity of 8019 mAh g\textsuperscript{-1} at the current density of 300 mA g\textsuperscript{-1} with stable cycling performance for at least 40 cycles in ambient air. This excellent performance was attributed to the dandelion hollow structure, together with the abundant oxygen vacancies on the NiCo\textsubscript{2}O\textsubscript{4} catalyst, which would enhance the ORR and OER processes.\textsuperscript{[129]} Furthermore, an N-doped carbon cathode with MoFeNi and MoC nanoparticles embedded was prepared for an ambient Li-air battery. It displayed a cycling performance of more than 25 stable cycles with a limited capacity of 1000 mA h g\textsuperscript{-1} at a current density of 100 mA g\textsuperscript{-1} when operated in ambient air atmosphere.\textsuperscript{[130]} Through forming Co-N bonds, bifunctional catalyst consisting of Co\textsubscript{3}O\textsubscript{4} with nitrogen-doped hollow carbon nanospheres could deliver a capacity of 3325 mAh g\textsuperscript{-1} and a 27 discharge/charge
cycles at the current density of 100 mA g\(^{-1}\) when operated in O\(_2\) and Ar (20% of O\(_2\) in volume).\(^{[131]}\)

A novel double-catalyst system of Co-salen/MCNTs@MnO\(_2\), where MCNTs are multi-walled carbon nanotubes was proposed to prolong the cycle life of Li-air batteries in dry air (21% O\(_2\)). It showed comparable performance to that in pure O\(_2\). Co\(^{II}\)-salen in the electrolyte works as a mobile O\(_2^–\) carrier and accelerates Li\(_2\)O\(_2\) formation with the following reaction: (Co\(^{III}\)-salen)\(_2\)-O\(_2\)\(^{2–}\) + 2Li\(^+\) + 2e\(^–\) → 2Co\(^{II}\)-salen + Li\(_2\)O\(_2\) (Figure 8a). A Li-air battery with 5 mM Co\(^{III}\)-salen delivered a large capacity of ~13050 mAh g\(^{-1}\) in dry air, which is similar to that in pure O\(_2\) (Figure 8b). A stable 300 cycles at 500 mA g\(^{-1}\) (0.15 mA cm\(^{-2}\)) with limited capacity of 1000 mAhg\(^{-1}\) was achieved in the same atmosphere (Figure 8c). A large scale prototype Li-air battery (12 cm × 8 cm) delivered reversible capacity of 500 mAh at 5 mA·g\(^{-1}\) (Figure 8d), which means that there are potential applications of the Li-air battery in air with the two-catalyst system. The advantage of such a combination is that the 2-3 nm δ-MnO\(_2\) on MCNTs catalyzes Li\(_2\)O\(_2\) decomposition during charge and suppresses side reactions. On the other hand, this reaction pathway overcomes the pure O\(_2\) limitation. No superoxide (O\(_2^–\) or LiO\(_2\)) will be formed as intermediate, which avoids organic electrolyte attack from oxide species.\(^{[135]}\)

To further facilitate the operation of ambient Li-air batteries, a promising strategy is to pursue a suitable catalyst that could efficiently accelerate the decomposition of the side products, e.g. Li\(_2\)CO\(_3\) and LiOH, while being capable of functioning at a suitable potential close to that of the active OER of the Li\(_2\)O\(_2\). For example, Zhou and coworkers proposed a “water catalysis” mechanism by employing Ru/MnO\(_2\)/SP, where SP is Super P, as catalyst and DMSO-based electrolyte with a ppm-level of water (Figure 9a).\(^{[82]}\) During discharging, Li\(_2\)O\(_2\) was generated as the primary discharge product. At the same time, H\(_2\)O from the electrolyte reacts with the Li\(_2\)O\(_2\) and was converted into LiOH. MnO\(_2\) allows for water regeneration in the cathode. In the
sequential charging process, LiOH is directly oxidized to produce H$_2$O by Ru catalyst at low charge potentials. As illustrated for the whole process, H$_2$O is not consumed at all and could be circulated to act as a soluble catalyst. The authors pointed out that the decomposition of the side product LiOH is heavily determined by the catalyst, such as Ru nanoparticles supported on Super P (Ru/SP). The H$_2$O level in the electrolyte greatly influences the charge characteristics (Figure 9b). The charge potential plateau is significantly reduced to 3.2 V when the water level is 120 ppm, from 3.65 V for the dried electrolyte. The charge potential plateau is shortened, however, and increased when the level of water in the electrolyte is increased to 281 ppm. The same group further systematically investigated the reaction mechanism of a catalyst-free Li-air battery with additional water in 1 M LiTFSI/TEGDME electrolyte, where LiTFSI is lithium bis(trifluoromethanesulfonyl)imide.$^{[64]}$ The charge potential plateau drops from 4.3V with dry electrolyte to 3.5V with additional water (0.5%). It keeps a 3.5V flat charge plateau when the water content increases from 0.5% to 30% (Figure 10a). The O-O stretching mode of peroxide species in the Raman spectra from wet electrodes after discharge in a higher frequency region becomes more and more obvious than the peak of Li$_2$O$_2$ with the increasing water content (Figure 10b). The fitting results showed the presence of the adsorbed hydroperoxide anion (HO$_2^-$) (Figure 10c). These Raman results provided convincing evidence that the added water alters the intermediate of ORR from offensive superoxide species (O$_2^-$) into moderate hydroperoxide (HO$_2^-$), showing the first experimental evidence of HO$_2^-$ species in the Li-air battery system. Gas evolution investigated by differential electrochemical mass spectroscopy (DEMS) proved that the charging process is highly reversible. Their discoveries in this study largely reduced the gap between Li-O$_2$ and ambient Li-air batteries.

Redox mediators (RMs) are a new kind of soluble additive to the electrolyte that can remarkably mitigate the charge polarization in Li-air batteries. Their reduced form, RM$^{\text{red}}$, is first oxidized directly at the oxygen cathode to give M$^{\text{ox}}$, which then, in turn, oxidizes the Li$_2$O$_2$ and itself is
reduced to its $\text{RM}^{\text{red}}$ state. It acts as an electron-hole transfer agent between the solid electrode material and $\text{Li}_2\text{O}_2$. Thus, the charge overpotential is highly determined by the reversible redox pair: $\text{RM}^{\text{red}} \rightarrow \text{M}^{\text{ox}} + e^-$.[21, 51] With this approach, the capacity can be significantly increased, and the overpotential of the charge process in a Li-air battery can be greatly reduced.[26, 52, 136] It is also possible to recharge the battery at high rates, and the peroxide can be oxidized without direct contact with the air cathode. At present, RMs such as tetrathiafuvalene(TTF), lithium iodide (LiI), ion phthalocyanine (FePc), 2.2.6.6-tetramethylpiperidyloxyl (TEMPO), and 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) have been confirmed to effectively benefit Li-air batteries.[21, 51, 103, 137-140] For instance, Grey and coworkers reported the redox mediator LiI in Li-O$_2$ battery. The battery could tolerate large amounts of water. At the same time, it express an extremely high efficiency and a rather low overpotential.[140] Unlike the above-mentioned water induced reactions in Li-air batteries, their battery operation involved the reversible formation and decomposition of LiOH, rather than $\text{Li}_2\text{O}_2$. It featured a rather low voltage gap of only $\approx 0.2 \text{ V}$ when cycled at 1A/g$\text{carbon}$ with a capacity limitation of 1000 mAh g$^{-1}$. Little overpotential increase were observed after 2000 cycles (Figure 11a). A mechanism involving both electrochemical and chemical reactions during discharge/charge was proposed (Figure 11b). It is much more complicated when the reactions occur in the presence of $\text{O}_2$, $\text{H}_2\text{O}$, and $\text{I}^-$, so further mechanistic studies are still needed to gain a clear understanding of the whole redox process. In spite of this, their work has inspired researchers to find ways to remove unwelcome species, which can advance Li-air batteries for real practical applications.

NiO nanosheets were reported to be able to catalyze $\text{Li}_2\text{CO}_3$ decomposition,[141] which advanced the Li-O$_2$ battery containing them to 40 cycles at a fixed capacity of 500 mAhg$^{-1}$. Hong et al. incorporated nanoporous NiO plates into a carbon nanotube (CNT) electrode. The NiO catalyst promoted oxidation of side products such as carbonate and carboxylate species, which remarkably enhanced the oxidation efficiency of the OER process in a Li-O$_2$ battery and
significantly improved the cyclability to more than 70 cycles. A NiO-free CNT electrode was tested to distinguish the effect of NiO from the results, but a thicker passivation layer on the cathode precluded electron transfer, inducing poor cyclability.\footnote{91} Inspired by the remarkable catalytic ability of NiO toward carbonate species, an ambient Li-air battery based on a RuO$_2$ nanoparticle-decorated NiO nanosheet cathode was developed.\footnote{91, 92} A two-step process was employed to fabricate the NiO nanosheet electrode decorated with RuO$_2$ nanoparticle. (Figure 12a). RuO$_2$ acts as the ORR/OER catalyst, and promotes the decomposition of LiOH formed via the reaction between Li$_2$O$_2$ and H$_2$O. NiO nanosheets oxidize the side products like carbonates and carboxylates. Its high surface area improves the utilization of RuO$_2$ nanocatalyst. The present cathode enabled the Li-air battery a 200 cycle life (800h) in ambient air (0.21atm) operation at 500mA g$^{-1}$ capacity limitation and at a current density of 250mA g$^{-1}$ with an average discharge and charge plateau of 2.8V and 4.02V, respectively (Figure 12b).

Recently, Zeng and coworkers reported V$_2$O$_5$-NiO nanowires as electrode for Li-Air batteries with a specific capacity of 6600 mAh g$^{-1}$ in ambient air.\footnote{126} It was found that the V$_2$O$_5$-NiO nanowires could effectively decompose Li$_2$O$_2$, Li$_2$CO$_3$, and LiOH, which enable Li-air battery cycling 200 times at current density of 250 mA g$^{-1}$ in ambient air.

To develop flexible and wearable electronic devices, interpenetrative hierarchical N-doped carbon nanotubes on the surface of stainless-steel mesh (N-CNTs@SS) were synthesized as self-supporting, flexible electrode (Figure 13).\footnote{142} It could enable constantly lit of the light-emitting diode (LED) display screen when the cable-type battery were either twisted or bent into different shapes (Figure 13a). In addition, the discharge plots and capacity of the Li-air batteries showed almost no significant change with different shapes or even after thousands of repeated bending and stretching (Figure 13b and c). The open-circuit voltage remained nearly the same when bending from 0$^\circ$ to 180$^\circ$ (Figure 13d). The super-hydrophobic N-CNTs@SS cathode could effectively protect the Li anode from H$_2$O corrosion (Figure 13e). Only little
LiOH was formed when cycled at a RH of 43%. Therefore, this flexible Li-air battery could stable cycle for 121 times with a fixed capacity of 1000 mAh g$^{-1}$ at a current density of 500 mA g$^{-1}$ under air (Figure 13g).

4. Electrolyte alternatives

Li-ion conductive ceramics and gel polymers as well as hydrophobic ionic liquid electrolytes have been considered as potential electrolyte alternatives to solve the critical challenges facing Li-air batteries with an open system. For example, all solid state electrolyte and gel polymer electrolyte could prevent the leakage and evaporate of electrolyte in an open system. Compared with organic electrolyte, ionic liquid electrolytes have high hydrophobicity against water when used in an open system. And the details would be discussed in this section. Table 2 summarizes some recent advances based on electrolyte alternatives to improve the performance of Li-air batteries.

4.1 All solid state electrolyte

Li-Air batteries with solid-state electrolyte possess the following advantages:\cite{143} 1) O$_2$ transportation through the empty pores in air cathodes is easy, whereas the O$_2$ should only dissolve in the electrolyte before reaching the cathode with liquid electrolyte. This enhances the kinetics of the reactions that occur at the cathode. 2) The solid-state electrolyte acts as inter layer to isolate the Li anode from O$_2$, CO$_2$, and H$_2$O in the air, thereby significantly increasing the lifetime of the battery. 3) The leakage and evaporation of the organic liquid electrolyte is restrained. 4) The solid-state electrolyte serve as a physical barrier to avoid short circuiting caused by Li dendrites during long-term operation.
The solid electrolytes designed for lithium air batteries should own high lithium ion conductivity, and more importantly, should be stable in atmosphere. Ceramic solid membranes, such as sodium superionic conductor (NASICON)-type lithium aluminum titanium phosphate (LATP) ceramics and NASICON-type lithium aluminum germanium phosphate (LAGP), have attracted the greatest research attention among the solid electrolyte materials.\cite{98, 143-148} LATP was initially introduced to work as a separator and Li protective membrane for hybrid electrolytes in Li-O$_2$ batteries. To date, there have been an abundance of studies on LATP that were performed to improve the performance of ambient Li-air batteries. In the early stage, however, LATP was directly connected with the solid-state cathode in Li-air batteries.\cite{116, 149} For example, Zhou et al. reported a Li metal-organic electrolyte|LATP|carbon cathode battery configuration. Unfortunately, the discharge capacity was lower than 1000 mA h g$_{\text{carbon}}^{-1}$ due to the restricted number of active sites between the solid-state electrolyte and the cathode.\cite{116, 149} Then, they updated the cathode by mixing the carbon nanotubes with LATP solid electrolyte particles to reduce the interfacial resistance (Figure 14a). A polymer membrane made up of polyethylene oxide with lithium bis(trifluoromethanesulfonyl)azanide (LITFSA) was introduced to avoid direct contact between the lithium metal anode and the solid electrolyte. Although the air cathode design in this report showed good potential for solid-state Li-air batteries that could operate in ambient air, the capacity and the rate capability were still far from satisfactory because of the large interfacial resistance between the polymer membrane and lithium anode.\cite{116} Later, a solid-state air cathode, consisting of Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ and carbon black, was introduced into Li-air batteries intended to work in an ambient air environment (RH =70\% ) by Chen and coworker.\cite{150} The energy deliver of the proposed solid-state Li-air battery was much higher than that of the organic electrolyte supported Li-air battery. This is ascribed to the sufficient O$_2$ transport via the solid air cathode, overcoming the O$_2$ transport limit. Zhou used a powdery composite electrode composed of a LATP solid electrolyte, electronically conductive multi-walled CNTs (MWCNT) and a nanosized catalyst for a solid-state Li-air
battery. Kichambare et al. synthesized a cathode with nitrogen-doped carbon and LAGP to improve the performance of their rechargeable solid-state Li-O₂ battery and superior performance was achieved. Liu et al. fabricated a LAGP electrolyte membrane and a single-walled CNT (SWCNT)/LAGP composite as air cathode. The Li-air battery sustained 10 cycles with a fixed capacity of 1000 mAh g⁻¹ at a current density of 400 mA g⁻¹ in ambient air (Figure 14b).

It has been reported that electrochemical reactions involved in the Li-O₂ batteries depend largely on the thickness of the LATP electrolyte layer. Based on the above principle, Zhao et al. proposed an ultra-thin LATP electrolyte layer integrated with a carbon coated cathode. The thickness of the layer was reduced from 600 µm to 36 µm. A possible inside-out growth process of Li₂O₂ on the solid state cathode was proposed (Figure 14c). X-ray diffraction (XRD) and FTIR characterizations verified that LATP is stable enough for Li-air battery operation. Inspired by the benefits of the oxygen selective membrane (OSM) illustrated in section 3.1, the same group introduced an OSM to use in conjunction with a porous carbon cathode which was covered by a dense LATP membrane. Silicone-oil film (50 nm thickness) was directly coated on the pores of the LATP to block moisture and CO₂ from reaching the reaction sites instead of using as an independent membrane. The integrated structure only had a thickness of 19 µm (Figure 15). The porous structure of the LATP enlarged the specific surface area of the OSM, facilitating O₂ transfer and reducing the O₂ transport distance from the membrane to the reaction sites. With such a novel design, the Li-air battery could be operated in ambient air (~50% RH) at a fixed capacity of 5000 mA h g⁻¹ for 50 cycles (125 days). When the current density was as high as 2.0 mA cm⁻², a discharge/charge capacity of approximately 2500 mA h g⁻¹ could still be maintained.
Besides LAGP and LATP, amorphous LiNbO$_3$ material with low grain boundary resistance showed high Li-ion diffusivity. A hybrid quasi-solid-state electrolyte (HQSSE) combining a polymer electrolyte with an amorphous LiNbO$_3$ ceramic was proposed, and a stable interface between the solid-state electrolyte and the cathode electrode was obtained.$^{[152]}$ The Li cycling performance of the resultant battery was tested at 3 mA cm$^{-2}$, and the linear sweep voltammetry (LSV) results showed that the HQSSE significantly outperformed the battery with liquid electrolyte. The HQSSE-based solid-state Li-O$_2$ battery showed a rather stable cycle performance for more than 100 cycles.

In addition to the above-mentioned Li-conducting membranes, a lithium phosphorous oxynitride (LiPON) layer was reported as protective interlayer for separating aluminium-doped lithium lanthanum titanate (A-TTO) from the Li metal anode.$^{[153]}$ The Li-air battery with the LiPON membrane as solid electrolyte sustained 20 cycles in air atmosphere. X-ray photoelectron spectroscopy (XPS) revealed that the LiPON/A-TTO effectively suppressed the electrolyte decomposition on the surface of the Li anode.$^{[154]}$ This positive effect was ascribed to the successful prevention of O$_2$ crossover to the anode and contamination with CO$_2$ and H$_2$O. Kim and coworkers designed a gelled quasi-solid-state electrolyte, in which SiO$_2$ acted as gellant and functioned as a binder to hold the liquid electrolyte.$^{[155]}$ Experimental and theoretical findings both suggested that the organic-inorganic hybrid matrix with the gelled structure could play a critical role in diminishing the evaporation of electrolyte, which would be of benefit to a Li-air battery working in the open environment.

### 4.2 Gel-Polymer electrolyte

As an alternative approach, high Li$^+$ conductivity gel polymer electrolyte (GPE) has been proposed as a promising electrolyte candidate for Li-air batteries working in ambient
atmosphere. The use of GPE instead of liquid electrolyte has proved to be a potential strategy for solving some of the problems resulting from liquid electrolyte in Li-air batteries. It could avoid the leakage and high vapor pressure of the liquid solvent in an open system, and could effectively protect the Li anode from environmental contaminants in ambient atmosphere. The gel polymer electrolyte is based on liquid electrolyte. The GPE is a transition state between liquid electrolyte and solid state electrolyte. A polymer is used as a matrix to absorb liquid components. In previous research on LIBs, many host materials of GPE have been studied, such as poly(acrylonitrile) (PAN), poly(ethyleneoxide) (PEO), poly(methylmethacrylate) (PMMA), poly(vinylidene) (PVDF), thermoplastic polyurethane (TPU), and poly(vinylidene fluoride-co-hexafluoropropylene). Typically, the GPE is placed in close contact with the lithium metal and the liquid electrolyte. In this case, it ensures close contact of the coating film with the Li metal. Wu and his coworkers provided strong evidence that by coating a gel polymer membrane on lithium metal, the penetration of aqueous electrolyte can be effectively hindered while the Li$^+$ transfer was still ensured.

The first successful example using a polymer electrolyte in a Li-air battery was reported by Abraham and Jiang. They combined a Li metal anode, an organic polymer electrolyte and a porous air cathode. A specific energy between 250-350 Wh/kg was delivered, based on the capacity and voltage of the cell and the weight of the electrodes and electrolyte. Qualitative analysis and Raman spectrometry measurements identified the discharge product as Li$_2$O$_2$. This pioneering work was carried out under oxygen atmosphere, but it showed the great potential of polymer electrolyte-containing Li-air batteries. Another example was proposed by Zhou et al. Nanofumed SiO$_2$ doped in a composite of GPE, polypropylene (PP)-supported poly(methyl methacrylate) (PMMA) blended with poly(styrene) (PSt) was used for an Li-air battery to work in ambient atmosphere (RH=5%). By using the composite gel polymer electrolyte, lithium metal as anode, and Super P as carbon cathode, the Li-air batteries sustained
25 cycles with a capacity limitation of 1000 mAh g\(^{-1}\) (Figure 16a), which was more stable than liquid electrolyte in ambient air (8 cycles) (Figure 16b). Moreover, a lifespan of more than 100 was achieved by the use of GPE with a fixed discharge capacity of 500 mAh g\(^{-1}\), in air atmosphere (RH=5%) (Figure 16c). The swelling of polyether (TEGDME) in the GPE alleviates the corrosion of lithium metal from H\(_2\)O contamination, which consequently facilitates the anode stability during cycling and improves the battery cycling performance. Zou et al. developed a highly crosslinked quasi-solid electrolyte by the use of the hydrogen bonds between TPU and SiO\(_2\) aerogel.\(^{[159]}\) The Li-O\(_2\) battery with TPU-based electrolyte demonstrated better cycling stability for over 30 cycles at a RH of 50% compared with the Li-O\(_2\) batteries with conventional liquid electrolyte (Figure 16d-f). The Li-O\(_2\) battery with TPU-based electrolyte also worked much longer than the conventional liquid electrolyte battery (Figure 16g).

Wang et al reported a gel polymer electrolyte blended from cellulose acetate (CA) and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)).\(^{[163]}\) When employed as electrolyte and separator in a Li-air battery, it ensures superior rate capability and enhances retention of the cycling capacity for up to 40 cycles with a fixed discharge capacity of 500 mAh g\(^{-1}\) (Figure 17a), whereas the Li-air battery with liquid electrolyte could only sustain less than 30 cycles (Figure 17b). The Li anode protected by the GPE showed a slightly shiny silver color after 20 cycles (Figure 17c), whereas a thick, black film was observed on the surface of Li taken from the pure liquid electrolyte battery (Figure 17d). XRD analysis showed that there was almost no signal of LiOH from the protected Li anode. It was claimed that the better cycling performance of the GPE battery benefited from the membrane, which prevented the trace oxygen crossover from the cathode side to the anode side. A free-standing gel polymer electrolyte with poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as matrix was investigated and plasticized with TEGDME for use in lithium air batteries.\(^{[164]}\) This report
provided strong evidence that the TEGDME gel polymer electrolyte could lower the amount of oxygen transportation in the TEGDME and subsequently weaken the corrosion effect on the Li anode of oxygen crossover from the cathode. A protective membrane composed of a similar material was also reported by Ishihara and co-workers.[165] The rate capability of Li-air batteries could be greatly increased when a PVdF-HFP membrane was applied. In addition to the PVDF-HFP for gel polymer electrolyte, Park et al also introduced Al$_2$O$_3$ particles into the protective layer to improve the mechanical strength of the membrane.[166] A GPE-containing lithium-ion oxygen battery was reported by Hassoun et al.[167] The PVDF-based gel polymer membrane swelled in 1M LiTFSI/TEGDME electrolyte and enabled improvement of the battery performance. Cycling tests combined with electrochemical impedance spectroscopy (EIS) measurements indicated that the gel polymer membrane could partially avoid, at least during the first stage of the test, the direct reaction of oxygen with the anode, thus leading to higher stability of the anode/electrolyte interface.

To further restrain the electrolyte degradation, Li dendrite formation, and parasitic reactions caused by H$_2$O and CO$_2$ in ambient air during Li-air battery operation, Zhang and Zhou replaced the easily decomposable liquid electrolyte with the solid-ion conductor Li$_{1.35}$Ti$_{1.75}$Al$_{0.25}$P$_{2.7}$Si$_{0.3}$O$_{12}$ (LTAP), while the conventional solid air cathode was replaced by a crosslinked network gel cathode (CNG) consisting of SWCNTs and ionic liquid.[168] The solid-ion conductor acted as both a catholyte and a Li protective material, whereas the gel cathode placed in direct contact with the solid catholyte to form a close and durable gel/solid interface. The electrochemical results showed that this novel battery design could sustain reversible discharge-charge behavior over 100 cycles (Figure 18a), for over 78 days, and by introducing the moisture and CO$_2$ in ambient air into the electrochemical reaction. XRD measurements at terminal discharge and charge points indicated that the battery featured reversible Li$_2$CO$_3$ formation and decomposition when operating in ambient air for a long period of time (Figure
The discharge process involved the initial formation of Li$_2$O$_2$, which then reacted with H$_2$O to form LiOH, and eventually reacted with CO$_2$ to produce Li$_2$CO$_3$. Fourier transform infrared (FTIR) and gas chromatography (GC) analysis provided evidence that the recharging process is complicated, including the partial decomposition of Li$_2$O$_2$ and LiOH and the extensive decomposition of Li$_2$CO$_3$. The authors claimed that it was important to introduce a highly efficient OER catalyst into the flexible gel cathode to promote the oxidative decomposition of Li$_2$CO$_3$ containing resultants.

To meet the requirements of flexible use, a fiber-shaped lithium air battery was developed.\[169\] A gel electrolyte precursor was first covered on the lithium wire to form a layer, followed by wrapping the gel with an aligned carbon nanotube sheet which functions as an air electrode. The whole assembly was finally packed in a punched heat-shrinkable tube (Figure 19a). In this system, the gel electrolyte acted not only as a good ion conductor, but also as an effective Li anode protector to prevent side reactions in air. When tested in ambient air (RH = 5%), the fiber-shaped battery demonstrated comparable rate capability to the case in pure O$_2$ (Figure 19b). More significantly, it showed no specific decay or terminal voltage change over 100 cycles at a high current density of 1400 mA g$^{-1}$ with a fixed capacity of 500 mA g$^{-1}$ (Figure 19c).\[169\] Inspired by the advantage of GPE and the fact that a redox mediator can significantly reduce the overpotential, Kim and co-workers designed a novel GPE consisting of poly(vinylidene fluoride) (PVDF), the redox mediator p-benzoquinone (pBQ) and the liquid electrolyte LiTFSI/TEGDME. This creative strategy led to an improvement in the cyclability from 2 to over 30 cycles, and a reduced charge voltage from around 4.2 V to around 3.3 V.\[170\] By introducing 0.05 M LiI into a GPE, Xia et al. developed a Li-air battery that can stably cycle 400 times in ambient air (RH = 15%) with a fixed discharge capacity of 1000 mA h g$_{rGO}^{-1}$, where rGO is reduced graphene oxide, and a current density of 1000 mA g$_{rGO}^{-1}$. The GPE with high hydrophobicity significantly alleviates the anode passivation caused by air contaminants. The
lithium chip cycled in the GPE-based Li-air battery continued to shine with a metallic luster, while that in the liquid electrolyte turned white and was partially pulverized. $I_2/I_2^-$ conversion in GPE electrolyte serves as a redox mediator to accelerate the $\text{Li}_2\text{O}_2$ decomposition in a low overpotential. Their battery outperformed most of those in the previous reports on Li-air batteries operated in pure $\text{O}_2$ or the ambient air.

In addition to directly synthesizing the GPE, some polymeric additives such as PEO and PVDF can be added to the liquid electrolyte to stabilize the Li anode. For example, Akbulut et al. investigated different GPEs with varying amounts of polymeric additives (such as PEO and PVDF) introduced into TEGDME/LiPF$_6$ in Li-air batteries. Enhanced stability of the cyclability was observed by adding these additives, and PVDF showed a better effect than PEO as additive. Systematic electrochemical impedance spectroscopy (EIS) measurements before and after cycling demonstrated that the electrolyte additives facilitated the formation of a better Li anode passivation layer, which is responsible for the enhanced cycling stability.

4.3 Ionic liquid electrolyte

Ionic liquid (IL) is used as alternative electrolyte in ambient Li-air batteries because of its excellent non-volatility, high hydrophobicity against water, high thermal stability, broad electrochemical window, and chemical stability against $\text{O}_2^-$ radicals. Among them, the unique hydrophobicity of the IL plays an important role in the construction of stable discharge products at the interface between the cathode and the $\text{O}_2$, enabling possible a Li-$\text{O}_2$ battery for use in humid oxygen conditions. Zhou et al. tested the water content of tetr glyme (G4) and IL-based electrolytes after being kept for 1, 2, 4, and 7 days in a humid atmosphere (RH=51%) (Figure 20). They found that the H$_2$O content of the G4-based electrolyte showed a rapid increase during the 7 days period. The H$_2$O content increased to around 10000 ppm after 1 day,
and it finally reached about 35000 ppm after 7 days.\textsuperscript{[177]} The excessive content of H\textsubscript{2}O in the liquid electrolyte would trigger the dissolution of LiOH•H\textsubscript{2}O, which leads to a poor battery reversibility. This finding was also well matched with the discovery of O’Dwyer, who also confirmed the increase in the H\textsubscript{2}O content in DMSO-based electrolyte.\textsuperscript{[178]} In a sharp contrast, the H\textsubscript{2}O value of the IL-based electrolyte increased much more slowly. It nearly reached an equilibrium at about 7300 ppm and changed little after that, reflecting the superiority of the hydrophobic IL-based electrolyte over the liquid electrolyte in enabling the Li-air battery to reversibly cycle in an atmosphere with relatively high humidity.

Zhang reported a cross-linked network gel (CNG) air electrode consisting of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) ([C\textsubscript{2}C\textsubscript{1}im][NTf\textsubscript{2}]) and single-walled carbon nanotubes (SWCNTs) (Figure 20b and 20c).\textsuperscript{[179]} Excellent water stability was achieved by incorporating the ILs into the tricontinuous cathode passages where electron, ions, and oxygen flow. After immersing the CNG in deionized water for one week, there was no weight increase, but rather a slight decrease, because about half of the Li salt in the CNG dissolved into the water. The lithium-air cell delivered a discharge capacity of 10200 mAh g\textsuperscript{-1} in ambient air (RH = 50\%), although it showed some scattering in the charge plots (Figure 20d). The XRD pattern of the cathode revealed the Li\textsubscript{2}O\textsubscript{2} formation with a weak signal and LiOH with a strong signal after discharge. Therefore, the authors speculated that even through the hydrophobic IL showed water stability, there were still some water molecules that permeated into the cathode. A Li\textsubscript{2}CO\textsubscript{3} signal other than Li\textsubscript{2}O\textsubscript{2} was detected by XRD in the unstable region of the charge potential, suggesting cathode contamination by CO\textsubscript{2} from the air. Thus, the insulating property and irreversibility of Li\textsubscript{2}CO\textsubscript{3} may have partially contributed to the unstable charge potential.

Later, the same group integrated a hydrophobic ionic liquid (IL)-based electrolyte and a cathode composed of electrolytic manganese dioxide (e-MnO\textsubscript{2}) and ruthenium oxide (RuO\textsubscript{2}) supported on Super P (carbon black).\textsuperscript{[177]} Possible discharge routes for the IL based Li-O\textsubscript{2} battery under
different humidity conditions were proposed. In the case of a low RH, O$_2^-$ forms as an intermediate, resulting in low discharge potentials. A high RH with higher water content, however, will result in the direction of a reaction between O$_2$ and H$_2$O to produce LiOH, resulting in a high discharge potential. The discharge/charge curves operated at different RH values (Figure 21a) are consistent with the speculated pathways. With the protection of commercial lithium superionic conductor (LISICON) film on Li metal and the IL electrolyte, the battery sustained 218 cycles. The discharge potential was as high as 2.94 V and the charge potential was 3.34 V in humid atmosphere (RH =51%) (Figure 21b). Even though the IL had the ability to resist moisture from air, it still showed some instability in Li-air batteries. For instance, ILs with imidazolium-based cations are unstable against peroxide radical attack.[180] By employing detailed electrochemical mass spectrometry (DEMS), Das and co-workers found that the extent of rechargeability of a Li-O$_2$ battery is highly dependent on the kind of the cations and anions of the ILs,[181] since both anions and cations in ILs have been reported to affect the moisture sorption.[182] Water vapor could be adsorbed on the electrolyte and reach an equilibrium content, which significantly degrades the ORR and OER in a Li-air battery. Based on this principle, it is possible that, by adjusting the molecular design of an ionic liquid, e.g. the anion and cation, the inherent equilibrium moisture content of the battery could be controlled. Bis(trifluoromethanesulfonyl)amide$^-$ (TFSA) is a relatively hydrophobic anion, while the phosphonium based group [P$_6$6614]$^+$ is a hydrophobic cation. Thomas et al. combined the advantages of both and optimized the ratio of a more hydrophobic anion (TFSA) and a phosphonium-based hydrophobic IL.[72] Surprisingly, the equilibrium moisture content in the IL electrolyte was decreased to less than 1wt% when the RH was high up to 90%, with a ratio of 1:4 between the anion and the ionic liquid. Furthermore, the designed hydrophobic electrolyte supported the reversible discharge and charge of a battery to 5 cycles in O$_2$ with a RH of 28%. Because of the low conductivity of such electrolytes resulting from its high viscosity, however, a Li-air battery with this IL electrolyte can only work at low current density.
In addition, further consideration of the protection of Li metal at a high relative humidity is in demand for eventual implementation of an ambient Li-air battery. To improve this, a solid-state electrolyte consisting a super-hydrophobic quasi-solid membrane and a Li\(^+\)-conducting IL was developed for long-life cycling Li-air batteries operated at the RH of 45\%.\[^{183}\] The membrane was made up of a homogeneous coating of silicon dioxide (SiO\(_2\)) on a nonwoven fabric (Figure 21c). Super-hydrophobic SiO\(_2\) nanoparticles served as a cross-linked matrix and showed high porosity. An H\(_2\)O permeation experiment showed that negligible H\(_2\)O passed through for at least 7 days, indicating its robust prevention of H\(_2\)O crossover to the Li anode of the Li-air battery in humid atmosphere operation. For Li-air battery testing, the authors incorporated the super-hydrophobic membrane into a hydrophobic IL-based electrolyte. The terminal discharge and charge voltages remained constant for 150 cycles with almost no increase in the overpotential when tested with a fixed capacity of 1000 mAh\(^{-1}\) at a current density of 500 mA g\(^{-1}\), and more importantly, in humid atmosphere (45% RH). This report provides new insight into the surface decoration with super-hydrophobic materials in the solid state for safe and long-term Li-air batteries.

5. Separator modification

Although the solid and polymer membranes aforementioned exhibit potential ability towards stabilizing the Li-air battery, they tend to be attacked by superoxide radicals.\[^{184, 185}\] The separator is the main component material of batteries which electrically isolates the two electrodes (anode and cathode). Separators used in conventional Li-O\(_2\) batteries are commonly used porous membranes (e.g. glass fibers, GF) that cannot block the O\(_2\) crossover, discharge intermediates, H\(_2\)O (from air and derived from electrolyte decomposition), and even electrolyte. The Li source will be consumed via the parasitic reactions induced by the above-mentioned materials, and thus accelerate the Li-air battery cycle fading. Pursuing novel separators or
modifications on the conventional ones are therefore considered to be feasible strategies to reduce the hazards of the H$_2$O and O$_2$ from the air cathode.$^{[82, 186]}$

For example, Choi and co-workers proposed a water- and oxygen-impermeable separator made from poreless polyurethane (PU).$^{[187]}$ The poreless PU separator prevents H$_2$O and O$_2$ from approaching the Li surface. The high electrolyte uptake of the PU separator accelerates Li ion diffusion through the interchain space. The Li metal interface is well protected to ensure the battery a 200 cycle lifespan with a fixed capacity of 600 mAh g$^{-1}$. The absence of the diffraction peak of LiOH in the XRD spectrum of the cycled anode as well as the nearly shiny surface of the cycled Li anode strongly certify that the Li anode can be well isolated from attack of water and other contaminants compared with the common polymeric polyethylene (PE) separator (Figure 22). In addition, the PU separator efficiently blocks the parasitic reaction between the redox mediator and oxygen. Kim et al. fabricated anodized aluminium oxide (AAO) membranes for Li-air batteries as model nanoporous separators.$^{[188]}$ The uniform and nanoscopic pores in the AAO suppress the surface roughening of the metallic Li anode and benefit the formation of a stable and homogenous solid-electrolyte interphase (SEI) layer. A dense and uniform SEI layer was reported to effectively stabilize the Li anode against the air contaminants.$^{[186]}$

Nafion®, a 3D-structured polytetrafluoroethylene backbone, is widely used for fuel cell membranes. The sulfonic groups on the side chains of perfluoronated vinyl ethers enable its high cation conductivity.$^{[189]}$ Lithium-exchanged Nafion membrane has been reported to effectively reject polysulfide anions from the Li anode and confine the polysulfide on the cathode side, improving the stability of lithium-sulfur batteries.$^{[190]}$ Lithium-exchanged Nafion has been verified to maintain chemical stability in the presence of commercial Li$_2$O$_2$, showing its potential use in Li-air battery membranes.$^{[191]}$ By placing a Li$^+$ conducting Nafion membrane between two glass fiber separators, Qin et al. observed an effective suppression of self-
discharge in a Li-air battery compared with the one without Nafion membrane. This was because the dissolved oxygen easily passed through the porous glass fiber separator, leading to self-discharge of the battery.\textsuperscript{[192]} Their observations suggest the validity of using Li\textsuperscript{+} conducting Nafion membrane as the O\textsubscript{2} isolation membrane in Li-air batteries. Very recently, a stable reinforced bifunctional separator made of Li-exchanged Nafion ionomer and commercial tissue was proposed for the Li-air battery by Xu et al.\textsuperscript{[193]} First, the lithium sheet was coated with commercial tissue composed of plant fibers, followed by dropping the Nafion solution onto the surface of the tissue to form a film adhering to metallic lithium. The tissue helped realize an even distribution of Nafion solution on the upper surface of lithium. Lithiated Nafion showed stability against O\textsubscript{2} due to the chemical reaction between lithiated Nafion and KO\textsubscript{2} studied by FTIR spectroscopy. The Li-O\textsubscript{2} battery containing this separator/anode protective layer exhibited excellent anodic reversibility for 300 cycles and the cathodic lifetime was up to 106 cycles. The discharge by-products on both of the Li anodes was confirmed to be LiOH by XRD. Less LiOH was generated on the coated lithium anode surface, indicating that the Li-Nafion/tissue separator inhibited the side reactions and lithium consumption during cycling of the Li-O\textsubscript{2} battery. Although the battery performance was measured in oxygen atmosphere, the protective strategy proposed in this report still could be extended to the Li-air battery to eliminate the gas contamination.

6. Li anode modification

The Li anode, when coupled with oxygen as the cathode, is prone to be attacked by H\textsubscript{2}O, CO\textsubscript{2}, and O\textsubscript{2} which cross over from cathode to the anode. To eliminate the side reactions, approaches involving a protective layer on the Li anode and utilizing anode alternatives have been adopted to greatly benefit the stability of the battery anode. Table 3 lists the recent advances on the modification of the Li anode.
6.1 Protective layer on anode

Apart from the above-mentioned progress on electrolytes and separators, significant achievements have been made on the lithium anode itself by coating a protective layer on it.\cite{83, 194, 195} A poly(ethylene oxide) (PEO) thin layer on the anode with a thickness of 30 µm improved the cycling performance of a Li-air battery from 54 cycles to 64 cycles.\cite{83} As discussed in the former part, redox mediator (RM) could remarkably mitigate the charge overpotential, although it could diffuse through the separator to the Li anode and be chemically reduced there. It could be described as a self-discharge of the electrochemically oxidized RM.\cite{196} To make full use of the RM advantages in Li-air batteries, the reduction of RM at the Li anode should be addressed. Kim and co-workers devoted much effort to designing a protective layer coating on Li anode to stabilize the Li-air batteries in the presence of a RM.\cite{194, 197} One example is an Al$_2$O$_3$/PVdF-HFP protective layer. The battery with the protected Li anode showed a 0.71 V charge overpotential with slight potential plateau change from the 1$^{st}$ to the 10$^{th}$ cycle (Figure 23a). 91.3% capacity retention with a 98.4% coulombic efficiency at the 60$^{th}$ cycle was delivered (Figure 23b). Electrochemical characterization, in conjunction with SEM and XPS analyses show that the anode protective layer restrains the oxidation reaction between the RM and the Li anode, enhancing the cycling stability. The idea to combine the effects of an RM-containing electrolyte and an anode protective layer promises a good strategy to develop Li-air batteries further.\cite{194}

Another example was reported by Zhang and co-worker that involved using a composite protective film directly formed via \textit{in-situ} reactions of electrolyte containing fluoroethylene carbonate (FEC) on the anode.\cite{195} The formation mechanism of the protective film from FEC is shown in Figure 24. The FEC first decomposes into C-F groups and Li$_2$CO$_3$, and the former
goes through polymerization to form C-F polymer, while the latter becomes the first component of the protective film. Then, some of the C-F polymer decomposes to polyene compound and HF while some of them directly act as a component of the protective film. The released HF could also react with the Li$^+$ and e$^-$ to form LiF at the Li metal surface. This LiF becomes another part of the protective film. The protective film consists of Li$_2$CO$_3$, LiF, polyene, and a C-F bond-containing compound. In the presence of the protective film, a rather weak peak of LiOH was detected from XRD measurements on the Li metal after cycling compared with the anode without protection, indicating that the parasitic reactions were effectively suppressed by the protective film on the Li anode/electrolyte interfaces. Visco et al. demonstrated that protected lithium electrodes (PLEs) from the PolyPlus Battery Company were capable of preventing a lithium core from the reaction with moisture in ambient air.$^{[198]}$

Although the protective films mentioned above significantly hinder the corrosion caused by water and oxygen on Li metal, they introduce some side effects as well, e.g. high interface resistance of the battery and a sacrifice of power density.$^{[199]}$ Alternatively, Walker et al. reported that a stable protective solid-electrolyte-interphase (SEI) film could help the Li anode to resist the O$_2$ crossing over from the cathode without any addition of an extra protective layer.$^{[200]}$ By employing a salt, lithium nitrate (LiNO$_3$), and N, N-dimethylacetamide (DMA) solvent, a stable SEI film can be formed on the Li anode according to Equation (10).$^{[198, 201]}

$$2\text{Li} + \text{LiNO}_3 \rightarrow \text{Li}_2\text{O} + \text{LiNO}_2$$

(10)

A Li-O$_2$ battery with this electrolyte cycled for more than 2000 h (> 80 cycles) at a current density of 0.1 mA cm$^{-2}$ in pure O$_2$. Linear sweep voltammograms indicated that LiNO$_3$/DMA in the electrolyte effectively hinders the multiple oxidation reactions caused by LITFSI/DMA (Figure 25a). When this cell was cycled at 0.1 mA cm$^{-2}$ (Figure 25b), it demonstrated low overpotentials (∼10 mV) for plating and stripping Li in the LiNO$_3$/DMA electrolyte with little
drift in the voltage profile. This result was obtained in pure O\textsubscript{2} atmosphere rather than ambient air. Nevertheless, their discovery eliminates the need for protective layers on the anode with a ceramic or polymer membrane, which also provides some inspirations for designing a stable anode for ambient Li-air batteries.

Very recently, Asadi and co-workers reported that a lithium-air battery with a Li\textsubscript{2}CO\textsubscript{3}/C anode-protection coating could cycle in a simulated air atmosphere for up to 700 numbers.\cite{174} The coating layer was achieved on a lithium anode in a lithium-CO\textsubscript{2} cell after ten discharge/charge cycles (Figure 26a-c). It allows only lithium cations to pass through, and then protect the anode from corrosion by the components of the simulated air. In addition, Li\textsubscript{2}CO\textsubscript{3} could not react with H\textsubscript{2}O water as it was thermodynamically unfavorable under ambient conditions. Li-air battery cycled up to 700 cycles (Figure 26d). The Raman spectra confirmed only Li\textsubscript{2}O\textsubscript{2} after discharge (Figure 26e). The DEMS results also demonstrate the reversible formation and removal of Li\textsubscript{2}O\textsubscript{2} as the main product (Figure 26f). The electron/oxygen ratio was 2.07 and 2.04 for the charge reaction and the discharge reaction, respectively.

### 6.2 Anode alternatives

Another approach to improve the battery cycling performance is to employ a different negative electrode. Several anode materials have been studied as anode alternatives for Li-air batteries, such as Si, Sn, and Al-carbon.\cite{192, 202-206} They work with alloying-dealloying reactions. Recently, several researchers proposed “lithium-ion/air battery” configurations. A lithiated silicon/tin-carbon composite is used to replace the bare Li to stabilize the system.\cite{167, 202, 205-209} A solid electrolyte interphase (SEI) film could be built on the Si/Sn surface. It served as a barrier, and suppressed crossover-related side reactions on the anode. The first report was from Hassoun and co-worker, who substituted a lithiated silicon-carbon composite for Li metal, with
their battery denoted as a “lithium ion, silicon-oxygen battery”.[206] The battery combines two reversible electrode electrochemical processes (Equation (11)).

\[
xO_2 + 2\text{Li}_x\text{Si} \xrightleftharpoons{\text{discharge}}{\text{charge}} \text{xLi}_2\text{O}_2 + 2\text{Si}
\]  

(11)

**Figure 27a** shows the typical discharge/charge profiles of the lithiated-silicon (L-Si)/carbon-oxygen battery. Based on their design, the theoretical energy density of the complete (anode and cathode) Li\text{$_x$}Si-O\text{$_2$} battery here is estimated to be 980 Wh kg\textsuperscript{-1}. Later, the same group combined nanostructured Li\text{$_x$}Sn-C with ionic liquid electrolyte in a lithium-ion/oxygen battery.[207] Unfortunately, their batteries all suffered from progressive decay of the battery working voltage. The reason was because oxygen crossover through the electrolyte degraded the Li metal anode. As a similar, but more advanced design, Zhou et al. developed a long-life lithium-ion oxygen battery based on commercial silicon particles as anode.[205] In addition, fluoroethylene carbonate (FEC) was introduced to optimize the SEI film. FEC stabilized lithiated-silicon (F-L-Si) anodes could reduce the discharge/charge potential gap to only 0.40 V (Figure 27b). The cycling profiles almost remain the same except for a slight increase of the discharge/charge overpotentials during the initial 30 cycles. It is known that the silicon electrode is easy to suffer from large volume expansion during Li\textsuperscript{+} insertion in lithium ion batteries, so it is hard to form a stable and strong enough SEI on the surface of a Si electrode. Large volume expansion and cracks in the anode during cycling will cause poor resistance against O\textsubscript{2} crossover. SEI cracking and the new SEI film formation will cause the electrochemical impedance increase. The uniquely durable SEI film on F-L-Si anodes can remain intact during the cycle and then efficiently impede O\textsubscript{2} crossover, and the lithium-ion oxygen batteries with long life was achieved (Figure 27c). An Li\text{$_x$}Al-C composite electrode was reported as an alternative anode for Li-air batteries.[203] Surprisingly, when operated in ambient air with a RH of 40%, the Li\text{$_x$}Al-C anode displayed a reproducible discharge-charge voltage profile. There was no sign of capacity deterioration after 20 cycles at a current density of 100
mA g$^{-1}$ and a fixed capacity of 1000 mAh g$^{-1}$ (Figure 28). The author attributed this enhancement to the formation of a uniform SEI layer on the carbon electrode, alleviating air-attack on the anode. However, there are disadvantages and challenges for using anode alternatives. First, these anode alternatives possess lower specific capacities than Li metal, which would decrease the energy density of Li-air batteries. In addition, these anode alternatives have higher negative electrochemical potential than Li metal, which would also decreased discharge plateau and energy density of the Li-air batteries. Furthermore, these anode alternatives also suffer from oxygen crossover similar to Li metal.$^{[192,205]}$

Although the aforementioned strategies retard the unwanted molecules diffusing into the cathode and alleviate the corrosion of Li anode to some extent, they are still far from satisfactory for making the Li-air battery a practical energy storage system. It remains a high priority to develop reliable and cost-effective approach for lithium anode protection. It seems that remarkable progress in improving the cycling efficiency of the Li anode has been made by replacing the bare Li anode with anode alternatives, but the anode preparation method inevitably requires a complex treatment process. More importantly, it reduces the inherent energy density of the battery compared with the Li-air battery offered by bare Li. Attempts to use Li metal as an anode in a Li-air battery with an open system still has a long way to go.

7. Summary and perspectives

Experimental investigations and theoretical calculations have shown that the non-aqueous Li-air battery is the most promising energy storage technology. But most of the current Li-air batteries are restricted to the use of pure oxygen. Critical issues related to the open system seriously hinder its practical operation. Contaminations in ambient air such as H$_2$O and CO$_2$ are detrimental to both air cathodes and Li metal anodes. Evaporation and leakage of organic liquid
electrolyte easily cause battery decay and safety problems. Since the ultimate goal of non-aqueous Li-air batteries is to operate in ambient air condition, researchers from all over the world have carried out various investigations to address the issues of Li-air batteries in open systems. As discussed above, the electrochemical performances of Li-air batteries in ambient system, such as cycle life and coulombic efficiency, could be readily enhanced through using OSMs, multifunctional catalyst, electrolyte alternatives, separator modification, and anode modification.

Cathodes with oxygen selective membranes have been demonstrated to be an efficient option allowing for ambient operation of Li-air batteries. Besides functioning as a moisture and CO₂ barrier, the OSMs significantly decrease the evaporation rate of organic solvents. High O₂ permeability materials tend to also have high CO₂ permeability, therefore, most OSMs studied so far, only serves as good waterproofing, but poor CO₂ barriers. A novel MOF- containing OSM proposed by Cao et al, possesses the advantages of high O₂ permeability, superior CO₂ capture capability, and excellent hydrophobicity. Intimately integrating OSM materials such as silicone oil with porous cathodes may provide a new avenue to favor rapid oxygen flux and develop real Li-air batteries. Although the OSMs act well as moisture and CO₂ barriers, low O₂ permeability and flux for OSMs would lead to a low flow rate and limit the power density of Li-air batteries. Taking the weight and volume of the OSM into account, the practical specific energy and energy density in use will be inevitably less than theoretical ones. Therefore, target research directed to solve the technical and system problems of Li-O₂ are definitely needed. In the long run, novel OSM materials with high O₂ permeability and low density are expected to enable high rate performance of the Li-air battery in ambient systems. In addition to the development of OSMs to hinder unwanted molecules, some multifunctional cathode materials, e.g. redox mediators and some robust catalysts (especially for the OER), are able to effectively facilitate the decomposition of the side products, e.g. LiOH, under an atmosphere with high
humidity. Other approaches, such as adjusting the hydrophobic property of the cathode by using highly efficient novel metal catalysts, also show improvement for ambient operation of Li-air batteries.

Apart from the cathode side, the electrolyte plays an even more critical role in operating Li-air batteries in ambient air. Solid-state electrolyte avoids the evaporation of organic liquid solvent. They show no permeability of humidity and CO$_2$, and thus prevent direct reaction between the Li anode and H$_2$O/CO$_2$ in air. The LATP and LAGP based Li-ion conductive membranes studied initially were in direct contact with the anode and cathode, which causes large interfacial charge transfer resistance. Such resistance tends to induce overpotential and poor rate performance of the battery. Integrating LATP or LAGP powder with the cathode material has been proven to increase the contact surface area between the cathode materials and the conducting membrane. To further enlarge the interfacial contact, gel polymer membranes with high conductivity, flexibility, and good processability have shown superior battery performance. Hydrophobic ionic liquid has demonstrated its value as an alternative electrolyte in ambient Li-air batteries because of its excellent non-volatility and high hydrophobicity against water. To resist moisture, protect the Li anode, and eventually realize a long lifetime Li-air battery in ambient air, integrating LATP/LAGP powder or gel polymer or ionic liquid electrolyte directly with efficient catalytic material might be a promising approach to form 3D Li$^+$, oxygen, and electron conducting networks in the cathode. An integrated Li-air battery would be expected to be an ideal configuration in the future.

Separators ensure Li transportation, but at the same time, suppress the crossover of moisture and oxygen from the cathode to the Li anode. Note that solid-state electrolyte also serves as a separator in a Li-air battery. Up to the present, unfortunately, much less attention has been paid
to studying the separator except for solid-state electrolytes. Designing a robust separator to suppress the crossover effect will be very important to realize long-term Li-air batteries.

The Li metal anode has been a historic problem all Li-based battery systems are sharing. It becomes even tougher for the Li-air battery as it is rather vulnerable to moisture, oxygen, and CO₂. A variety of strategies have been proposed to block the side reactions. Developing a protective film or introducing a stable protective SEI film have been identified to significantly obstruct the corrosion by moisture and oxygen crossover on the Li metal to some extent. Silicon/Tin alloy anode materials showed improved stability, but they inevitably require complex treatment processes, and in particular, they reduce the inherent energy density as was expected. It is hard to achieve a completely satisfactory solution to ensure that the Li anode is adequate for long-term Li-air batteries.

As a system expected to present extremely high theoretical specific energy, the Li-air battery operated in an open system definitely deserves great research attention. However, there are significant challenges for the design and scale-up of Li-air batteries in ambient air. For example, the Li-air batteries need to be properly sealed to accommodate the volume change (about 30 %) of the battery when Li metal fully converted to Li₂O₂. In addition, the cathode should have sufficient space to accommodate the large Li₂O₂ discharge products without blocking the gas and electrolyte flow paths. Furthermore, gas flow fields with minimize volume and weight are required to increase the specific energy and energy density of the Li-air batteries. Finally, it is highly desired to develop OSMs with very reasonable thickness to overcome the oxygen diffusion issue associated with increased battery size. It is not yet clear if the Li-air battery will eventually become a commercial product. Despite the difficulties, however, we will always need energy storage devices that afford higher energy storage capacity than ever before. Hence, more fundamental studies to solve the systemic problems in term of cathode modification,
including a feasible oxygen selective membrane, advanced cathode/catalyst design, alternative electrolytes stable in ambient air, and Li anode protective membranes without large energy sacrifice are urgently needed.

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Figure 1. An overview of approaches towards ambient operation of non-aqueous Li-air batteries.
Figure 2. (a) Discharge/charge cycles of Li-air cells with 12, 500, and 5000 ppm H₂O in the electrolyte. Reproduced with permission.\textsuperscript{[79]} Copyright 2014, Springer. (b) Comparison between discharge capacities (1\textsuperscript{st} cycle) of Li-O₂ cells with 0.1 M LiClO₄ in dimethoxyethane (DME) using H₂O-free (---) or H₂O contaminated oxygen (100 kPa\textsubscript{abs}), in which water was introduced by means of a small leak between the cell and ambient air (---) in the “Leaker Cell” or by connecting a water reservoir to produce H₂O-saturated O₂ inside the cell (···) in the “Water Vapor Cell”. Reproduced with permission.\textsuperscript{[81]} Copyright 2012, The Electrochemical Society. (c) Photographs of lithium metal anodes after the 1\textsuperscript{st} to the 6\textsuperscript{th} discharge. Reproduced with permission.\textsuperscript{[84]} Copyright 2014, Elsevier.
Figure 3. (a) Schematic illustration of the working mechanism of a redox mediator (RM) with (i) and without (ii) low density polyethylene (LDPE) film in our Li-air battery operated in ambient air. Reproduced with permission.\textsuperscript{[103]} Copyright 2018, Wiley-VCH. (b) The first two discharge/charge cycles of Li-air cells with or without the membrane with a current density of 0.05 mA cm\(^{-2}\), voltage range of 2.25-4.40 V, and a limited time for discharge and charge of 20 h in flowing air with 17 % RH. Reproduced with permission.\textsuperscript{[107]} Copyright 2016, Springer. (c) Room temperature discharge performance of Li-air batteries with and without Semicosil\textsuperscript{®}-based O\(_2\)-selective 83 \(\mu\)m silicone rubber membrane coated directly onto cathode. The current density was 0.2 mA cm\(^{-2}\), and RH was 42.9%. Reproduced with permission.\textsuperscript{[108]} Copyright 2011, Elsevier.
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Figure 7. (a) Schematic illustration of a Li-air battery with a Li metal anode, separator, and 3D graphene moisture-resistive membrane cathode. (b) Moisture and oxygen diffusion through the 3D graphene membrane vs. ambient concentration as a function of time. (c) Galvanostatic cycling of a Li-air battery with a 3D graphene membrane cathode and limited capacity of 1425 mAh g$^{-1}$ at a current density of 2.8A g$^{-1}$ in ambient air. Reproduced with permission.$^{[117]}$ Copyright 2017, Springer.
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pretreatment, (c) Magnified spectral profiles of the outlined region in (b). Reproduced with permission.[64] Copyright 2017, Wiley-VCH.

Figure 1. (a) Discharge/charge curves for Li-O₂ batteries using reduced graphene oxide (rGO) and a 0.05 M LiI/0.25 M LiTFSI/DME electrolyte with a fixed capacity of 1000 mAh g⁻¹ carbon. (b) Schematic mechanisms for the formation and removal of LiOH in iodide redox-mediated Li-O₂ batteries in the presence of water. The electron/LiOH molar ratios during discharge and charge are both equal to 1. Reproduced with permission.[140] Copyright 2015, American Association for the Advancement of Science, 2015.

Figure 12. (a) Schematic illustration of the fabrication process for the RuO₂ nanoparticle-decorated NiO nanosheet electrode. (b) Cycling stability of a Li-air battery fitted with the
RuO$_2$/NiO cathode in ambient air at 250 mA g$_{\text{RuO}_2}^{-1}$ with a fixed capacity of 500 mA h g$_{\text{RuO}_2}^{-1}$. Reproduced with permission.$^{76}$ Copyright 2016, The Royal Society of Chemistry, 2016.

Figure 13. (a) Cable-type flexible Li-air battery powering a commercial red light-emitting diode (LED) display screen under various bent and twisted conditions, (b) the corresponding discharge curves, (c) charge/discharge curves of the cable-type, flexible, Li-air battery after thousands of rounds of bending. (d) Open-circuit voltage of the flexible Li-air battery during a continuous bending process from 0° to 180°, XRD patterns of the Li metal anodes after cycling at an RH of 43% in Li-air batteries assembled with (e) a hydrophilic carbon cathode and (f) the super-hydrophobic N-CNTs@SS cathode. The insets are SEM images of corresponding Li metal anodes after cycling. (g) Cycling performance of the cable-type flexible Li-air battery with N-CNTs@SS cathode. Reproduced with permission.$^{[142]}$ Copyright 2018, Wiley-VCH.
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Figure 17. Discharge-charge profiles of Li-air batteries at a fixed capacity of 500 mAh g\(^{-1}\) with (a) GPE and (b) liquid electrolyte. Photographs of the Li anodes disassembled after 20 test cycles from the (c) GPE battery and (d) the battery with liquid electrolyte. Reproduced with permission.\cite{163} Copyright 2015, Elsevier.

Figure 18. (a) Discharge/charge curves of the Li-air cell with Li salt-modified CNG under a capacity limitation of 2,000 mAh g\(_{SWNT}\)^{-1} for 100 cycles, with the cut-off voltages were set at 2 V for discharge and 5 V for charging. The tests were performed in ambient air. (b) Discharge/charge performance and XRD analysis of Li-air batteries in ambient air. The inset shows the corresponding XRD patterns of the CNG air electrode in its pristine state (XRD 1), and after it was discharged to 2 V (XRD 2) and then recharged to 5 V (XRD 3). Reproduced with permission.\cite{168} Copyright 2013, Springer.
Figure 19. (a) Schematic illustration of the fabrication of the fiber-shaped Li-air battery, (b) comparison of rate capability of the fiber-shaped Li-air battery at different current densities in air and oxygen, (c) charge and discharge profiles of the fiber-shaped Li-air battery at current density of 1400 mA g\(^{-1}\) in air. Reproduced with permission.\(^{[169]}\) Copyright 2016, Wiley-VCH.
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Figure 21. (a) Initial 3 cycles of the discharge-charge profiles of the glyme-based Li-O₂ battery at a RH of ~5% at 500 mA g⁻¹. (b) Discharge-charge profiles of IL-based Li-O₂ batteries in O₂ atmosphere with varied RHs at 500 mA g⁻¹. The Li-O₂ batteries were fabricated with a configuration of (MnO₂/RuO₂/SP)/electrolyte/LiFePO₄. Reproduced with permission.[177] Copyright 2016, Wiley-VCH. (c) Schematic illustration of a Li-air battery operating in humid atmosphere with a super-hydrophobic quasi-solid electrolyte (SHQSE). Reproduced with permission.[183] Copyright 2017, Wiley-VCH.

Figure 22. XRD spectra and color changes of the Li metals from cells with (a) PE and (b) PU separators at different cycle numbers. Reproduced with permission.[187] Copyright 2016, Wiley-VCH.
Figure 23. Charge/discharge profiles at the first, third, fifth, and tenth cycles of (a) CPL-coated Li electrodes (cell B). (b) Cycling stabilities of both cells at a discharge depth of 1000 mA h g$^{-1}$ carbon and a current density of 0.2 mA cm$^{-2}$ (250 mA g$^{-1}$ carbon). Reproduced with permission.$^{[194]}$ Copyright 2016, Wiley-VCH.
Figure 2. The proposed formation mechanism of the protective film on Li anode with FEC electrolyte. Reproduced with permission.© Copyright 2015, Wiley-VCH.

Figure 25. (a) Linear sweep voltammograms on carbon paper electrodes (scan rate = 0.05 mV/s, 1 atm O2, room temperature, OCV: 10 min.). (Inset) Galvanostatic cycling at 0.1 mA/cm² of a Li-O2 cell in 0.5 M LiTFSI/DMA at 30 °C. (b) Galvanostatic cycling of a three-electrode cell utilizing a Super P carbon (CSP) cathode, a Li anode, a lithium reference electrode, and 1 M LiNO3/DMA electrolyte. The cell was cycled at room temperature under 1 atm O2 at a rate of 0.1 mA/cm², with a dwell at OCV between each half cycle. Discharge was limited to 1 mAh/cm², and charge was limited to 3.8 V. Reproduced with permission.© Copyright 2013, American Chemical Society.
Figure 26. (a) SEM image of the protected anode surface (scale bar, 1 μm), with enlargement in the inset. (b) Raman spectrum of the protected anode, excited by a 785-nm laser. (c) XPS spectra of the protected anode surface in the Li 1s and C 1s regions. (d) The discharge-charge voltage profiles over 700 cycles. (e) Raman spectra of the cathode after the first and after the 250th discharge-charge cycle, compared to pristine MoS$_2$ and a 200-hour-aged sample. (f) DEMS profiles of the cell during the first charging process, after the cell was discharged to 500 mAh g$^{-1}$. The inset shows the number of moles of oxygen detected by DEMS, before (red line) and after (black line) discharge in the first cycle. Reproduced with permission.[174] Copyright 2018, Springer.
Figure 27. (a) Voltage profile of the first galvanostatic cycle of the lithiated-silicon/carbon-oxygen cell. (b) Selected discharge-charge profiles of Li-ion O₂ batteries with F-L-Si anodes. (c) SEI film evolution of L-Si and F-L-Si anodes in Li-ion O₂ batteries during a discharge-charge cycle and their resistance towards the O₂ crossover effect on Si anode. Reproduced with permission.[205] Copyright 2016, The Royal Society of Chemistry.

Figure 28. Voltage profiles of the Li-air battery with a Li anode (a) and with a LiₓAl-C anode (b) cycled at a current density of 100 mA g⁻¹ and at a fixed capacity of 1000 mAh g⁻¹. Reproduced with permission.[203] Copyright 2015, The Royal Society of Chemistry.
Table 1. Comparison of OSMs, performances, and operating parameters between the non-aqueous Li-air batteries with OSMs employed externally or inside the cathodes. RH: relative humidity.

<table>
<thead>
<tr>
<th>Material of OSM</th>
<th>Function</th>
<th>Electrolyte</th>
<th>Capacity (mAh g⁻¹)</th>
<th>Cycle life</th>
<th>Current density (mA cm⁻²)</th>
<th>Voltage range (V)</th>
<th>RH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicone oil</td>
<td>O₂ selective membrane</td>
<td>LATP solid electrolyte</td>
<td>1000</td>
<td>100</td>
<td>2 mA cm⁻²</td>
<td>&gt;2.53 V</td>
<td>in air</td>
<td>[98]</td>
</tr>
<tr>
<td>Low-density polyethylene</td>
<td>Moisture-resistive</td>
<td>Gel electrolyte with LiI</td>
<td>1000</td>
<td>610</td>
<td>2000</td>
<td>2.5 V</td>
<td>5%</td>
<td>[103]</td>
</tr>
<tr>
<td>CAU-1-NH₂@PD and PMMA PVdF-HFP and silicone oil</td>
<td>O₂ selective membrane</td>
<td>1M LiClO₄/DMSO (fixed)</td>
<td>450</td>
<td>66</td>
<td>450 mA g⁻¹</td>
<td>&gt;2 V</td>
<td>30% in air</td>
<td>[102]</td>
</tr>
<tr>
<td>Teflon coated fiberglass cloth Polyaniline membrane Polysiloxane/Silicones (Silicone rubber)</td>
<td>O₂ selective membrane</td>
<td>1.5 M LiBF₄/PC:DMC:MOB</td>
<td>~5000</td>
<td>discharge</td>
<td>--</td>
<td>0.1 mA cm⁻²</td>
<td>&gt;2 V</td>
<td>20% in air</td>
</tr>
<tr>
<td>Melinex 301H polymer Polysiloxane/methacrylate-polysiloxane (Silicone rubber)</td>
<td>O₂ selective membrane</td>
<td>1M LiTFSI/Triglyme</td>
<td>570</td>
<td>discharge</td>
<td>--</td>
<td>0.2 mA cm⁻²</td>
<td>&gt;1.5V</td>
<td>42.9% in air</td>
</tr>
<tr>
<td>Silicalite zeolite and PTFE Silicone oil</td>
<td>O₂ selective membrane</td>
<td>1M LiTFSI/EC/PC</td>
<td>789</td>
<td>discharge</td>
<td>--</td>
<td>0.05 mA cm⁻²</td>
<td>&gt;2V</td>
<td>20-30% in air</td>
</tr>
</tbody>
</table>
Table 2. Electrochemical performances of Li-air batteries with different electrolytes and operation parameters.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Solvent/Li salt</th>
<th>Capacity (mAh g⁻¹)</th>
<th>Cycle</th>
<th>Voltage range (V)</th>
<th>Current density</th>
<th>RH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPON/B₂O₃/LA-GP solid-state electrolyte</td>
<td>1M LiTFSI/TEGDME</td>
<td>1000</td>
<td>52</td>
<td>2.4-3.3</td>
<td>0.2 mA cm⁻²</td>
<td>O₂</td>
<td>[2]</td>
</tr>
<tr>
<td>LiPON/LA-LTAP solid-state electrolyte</td>
<td>75 μAh</td>
<td>1000</td>
<td>--</td>
<td>2.91V</td>
<td>0.125 mA cm⁻²</td>
<td>humid O₂</td>
<td>[2]</td>
</tr>
<tr>
<td>LiNbO₃/quasi-solid-state electrolyte</td>
<td>--</td>
<td>1000</td>
<td>100</td>
<td>~2.6-4.5</td>
<td>dry O₂</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>LiPON/Al-lithium lanthanum titanate (A-LLTO)</td>
<td>1M LiTFSI/TEGDME</td>
<td>1000</td>
<td>20</td>
<td>~2.4-4.2</td>
<td>0.1 mA cm⁻²</td>
<td>20% in air</td>
<td>[1]</td>
</tr>
<tr>
<td>LiPON/Al-lithium lanthanum titanate (A-LLTO)</td>
<td>1M LiTFSI/TEGDME</td>
<td>1000</td>
<td>128</td>
<td>2.4-5</td>
<td>0.1 mA cm⁻²</td>
<td>O₂</td>
<td>[1]</td>
</tr>
<tr>
<td>Material Description</td>
<td>LiTFSI Concentration</td>
<td>Molar Ratio</td>
<td>Cycles</td>
<td>Oxidation Potential</td>
<td>Oxidation Current Density</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------</td>
<td>-------------</td>
<td>--------</td>
<td>---------------------</td>
<td>--------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>LTAP quasi-solid state</td>
<td>1M LiTFSI/PEGDME</td>
<td>1000</td>
<td>10</td>
<td>2.6-4.2</td>
<td>0.24 mA cm⁻²</td>
<td>Pure O₂ [2]</td>
<td></td>
</tr>
<tr>
<td>Li⁺ₓ₋ₓAlₓ(Ge,Ti)₂₋ₓSi₇P₃O₁₂</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.0 µA cm⁻²</td>
<td>99.9% O₂ [1]</td>
<td></td>
</tr>
<tr>
<td>LATP solid-state electrolyte</td>
<td>0.9M LiTFSI in TEGDME</td>
<td>500</td>
<td>15</td>
<td>2-4.5</td>
<td>100 mA g⁻¹</td>
<td>70% humidity O₂ [2]</td>
<td></td>
</tr>
<tr>
<td>Porous LATP with silicone oil</td>
<td>EC/DMC</td>
<td>5000</td>
<td>50</td>
<td>2.4-4 (125 days)</td>
<td>0.3 mA cm⁻²</td>
<td>50% ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>Ultra-thin LATP electrolyte layer</td>
<td>EC/DMC</td>
<td>1000</td>
<td>100</td>
<td>2 V</td>
<td>0.15 mA cm⁻²</td>
<td>O₂ [2]</td>
<td></td>
</tr>
<tr>
<td>LATP solid state electrolyte</td>
<td>0.9M LiTFSI/TEGDME</td>
<td>500</td>
<td>10</td>
<td>2-4.5</td>
<td>100 mA g⁻¹</td>
<td>70% ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>LAGP solid state electrolyte</td>
<td>--</td>
<td>1000</td>
<td>10</td>
<td>2-5</td>
<td>400 mA g⁻¹</td>
<td>Ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>PEO-solid polymer electrolyte</td>
<td>glyme</td>
<td>200</td>
<td>40</td>
<td>2.2</td>
<td>0.2 mA cm⁻²</td>
<td>Dry O₂ [2]</td>
<td></td>
</tr>
<tr>
<td>LTAP Gel cathode/electrolyte</td>
<td>EC</td>
<td>2000</td>
<td>100</td>
<td>2-5 (78 days)</td>
<td>200 mA g⁻¹</td>
<td>Ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PVDF)/p-benzoquinone (pBQ) gel polymer electrolyte</td>
<td>LiTFSI/TEGDME</td>
<td>500</td>
<td>35</td>
<td>2.3-4.5</td>
<td>0.05 mA cm⁻²</td>
<td>O₂ [1]</td>
<td></td>
</tr>
<tr>
<td>PEO/PVDF</td>
<td>LiPF₆/TEGDME</td>
<td>4488 to 2992</td>
<td>20</td>
<td>2.15-4.25</td>
<td>0.1 mA cm⁻²</td>
<td>Ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>PMMA/PSt/SiO₂/PP gel polymer membrane</td>
<td>1M LiTFSI/TEGDME</td>
<td>500</td>
<td>100</td>
<td>&gt;2</td>
<td>200 mA g⁻¹</td>
<td>Dry air [1]</td>
<td></td>
</tr>
<tr>
<td>Gel polymer electrolyte</td>
<td>TEGDME/LiTFSI</td>
<td>500</td>
<td>6</td>
<td>1.2-4</td>
<td>0.1 mA cm⁻²</td>
<td>O₂ [1]</td>
<td></td>
</tr>
<tr>
<td>Hydrophobic ionic liquid</td>
<td>TEGDME</td>
<td>1000</td>
<td>218</td>
<td>2.94-3.54</td>
<td>500 mA g⁻¹</td>
<td>51% ambient air [1]</td>
<td></td>
</tr>
<tr>
<td>Modified Anode</td>
<td>Li Anode</td>
<td>Electrolyte</td>
<td>Capacity (mAh g(^{-1}))</td>
<td>Cycle</td>
<td>Voltage range (V)</td>
<td>Current density</td>
<td>RH</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------</td>
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<td>--------------------</td>
</tr>
<tr>
<td>Li(_2)CO(_3)/C</td>
<td>EMIM-BF(_4)/DMSO</td>
<td>500</td>
<td>700</td>
<td>500 mA g(^{-1})</td>
<td>Air-like atmosphere</td>
<td>O(_2)</td>
<td>[174]</td>
</tr>
<tr>
<td>Al(_2)O(_3)/PVdF-HFP composite protective layer</td>
<td>1M LiClO(_4)/TEGMDE</td>
<td>1000</td>
<td>60 cycles</td>
<td>&lt;4.3</td>
<td>250 mA g(^{-1})</td>
<td>O(_2)</td>
<td>[194]</td>
</tr>
<tr>
<td>Composite protective layer</td>
<td>--</td>
<td>--</td>
<td>400</td>
<td>3-4.2</td>
<td>1 mA cm(^{-2})</td>
<td></td>
<td>[197]</td>
</tr>
<tr>
<td>Artificial Protection Film</td>
<td>1M LiTFSI/TEGMDE</td>
<td>1000</td>
<td>40 cycles</td>
<td>&gt;2V</td>
<td>300 mA g(^{-1})</td>
<td>O(_2)</td>
<td>[195]</td>
</tr>
<tr>
<td>(PVdF-HFP) protective layer</td>
<td>1M LiTFSI/TEGMDE</td>
<td>1111</td>
<td>30 cycles</td>
<td>~2-4.0</td>
<td>0.1 mA cm(^{-2})</td>
<td>O(_2)</td>
<td>[165]</td>
</tr>
<tr>
<td>Al(_2)O(_3)/PVdF-HFP</td>
<td>LiClO(_4)/C-PC</td>
<td>1000</td>
<td>80 cycles</td>
<td>2.2-4.4</td>
<td>0.1 mA cm(^{-2})</td>
<td>O(_2)</td>
<td>[166]</td>
</tr>
<tr>
<td>PEO layer</td>
<td>LiTFSI/TEGMDE</td>
<td>1000</td>
<td>64 cycles</td>
<td>2.0-4.5</td>
<td>0.1 mA cm(^{-2})</td>
<td>Ambient air</td>
<td>[83]</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical performances of Li anodes with different modification methods and operating parameters in non-aqueous Li-air batteries.
<table>
<thead>
<tr>
<th>Anode</th>
<th>Electrolyte</th>
<th>Capacity</th>
<th>Current Density</th>
<th>Voltage Range</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₅Sn-C alloy anode</td>
<td>Gel polymer electrolyte</td>
<td>500 mAh g⁻¹</td>
<td>100 mA g⁻¹</td>
<td>1.2-4 V</td>
<td>Ambient air</td>
</tr>
<tr>
<td>Li₅Si anode with stabilized SEI</td>
<td>1M LiTFSI/TEGDM</td>
<td>1000 cycles</td>
<td>100 mAg⁻¹</td>
<td>1.5-4 V</td>
<td>Ambient air</td>
</tr>
<tr>
<td>Li₅Al-C anode</td>
<td>TEGDME/LiTFSI</td>
<td>1000 cycles</td>
<td>100 mAg⁻¹</td>
<td>2.35-3.65 V</td>
<td>Ambient air</td>
</tr>
<tr>
<td>Li₅Sn-C anode</td>
<td>Ionic liquid electrolyte</td>
<td>500 cycles</td>
<td>50 mA g⁻¹</td>
<td>2.4 V</td>
<td>Ambient air</td>
</tr>
<tr>
<td>Li₅Si-C anode</td>
<td>LiCF₃SO₂/TEGDME</td>
<td>1000 cycles</td>
<td>200 mA g⁻¹</td>
<td>2-4.5 V</td>
<td>Ambient air</td>
</tr>
</tbody>
</table>
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This review addresses challenges in ambient air operation of non-aqueous Li-air batteries, and comprehensively demonstrates critical progress on the cathode in terms of oxygen selective membranes and multifunctional catalysts, electrolyte alternatives, and anode protection to advance this battery system. Perspectives for the future development of ambient air Li-air batteries are also given.

**Keywords:** Li-air battery; ambient air; oxygen selective membranes; electrolyte; Li anode

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Critical Advances in Ambient Air Operation of Non-aqueous Rechargeable Li-air Batteries
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