



Advances and challenges in lithium-air batteries



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HIGHLIGHTS

- The overall picture about the present lithium-air batteries is reviewed.
- The challenges of battery's electrolyte and electrodes are emphasized.
- Several possible research directions for performance improvements are highlighted.

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ABSTRACT

Rechargeable lithium-air batteries have ultra-high theoretical capacities and energy densities, allowing them to be considered as one of the most promising power sources for next-generation electric vehicles. The technology has been honed in various ways over the years, but it still experiences critical issues that need to be addressed in order to make it commercially viable. For instance, its practical capacity, round-trip efficiency, and cycling life are among the factors that need to be improved. In this review, the developments of this type of battery are presented. In particular, the system levels of design that encompass the optimization of the battery's electrolyte and electrodes are discussed. More importantly, this report provides perspectives on achieving the desired battery performance to meet the demands of commercial viability.

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Abbreviations and acronyms

AAO	anodized aluminum oxide	ORR	oxygen reduction reaction
CNT	carbon nanotube	PC	propylene carbonate
CPL	composite protective layer	PVDF	polyvinylidene fluoride
DEGDME	diethylene glycol dimethyl ether	PVDF-HFP	poly(vinylidene fluoride-co-hexafluoropropene)
DEMS	differential electrochemical mass spectrometry	RH	relative humidity
DFT	density functional theory	RM	redox mediator
DMA	N,N-dimethylacetamide	RTIL	room temperature ionic liquid
DME	dimethoxyethane	SEI	solid-electrolyte interface
DMSO	dimethyl sulfoxide	SEM	scanning electron microscope
EC	ethylene carbonate	SPE	solid polymer electrolyte
ETPTA	ethoxylated trimethylolpropane triacrylate	TEGDME	tetraethylene glycol dimethyl ether
EV	electric vehicles	TEM	transmission electron microscope
FePc	iron phthalocyanine	TEMPO	2,2,6,6-tetramethylpiperidinyloxy
HMPA	hexamethylphosphoramide	TPFPB	tris(pentafluorophenyl) borane
LAGP	lithium aluminum germanium phosphate	TTF	tetrathiafulvalene
LATP	lithium aluminum titanium phosphate	VC	Vulcan carbon
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide	XPS	X-ray photoelectron spectroscopy
OER	oxygen evolution reaction	XRD	X-ray diffraction

1. Introduction

Global warming and finite oil reserves are two issues that exert tremendous pressure on the traditional vehicle industry. Radically different from the conventional gasoline-fuelled vehicles, electric vehicles (EV), which are powered by rechargeable batteries, not only relieve the pressure on gasoline usage but perhaps more importantly, eradicate pollution generated from exhausts, lending hopes to the vehicle industry. To date, one of the most promising candidates for such power sources is the lithium-ion battery [1–3]. It has demonstrated a reasonable energy density (theoretical value: $\sim 400 \text{ W h kg}^{-1}$), which is much higher than that of conventional lead-acid batteries ($30\text{--}40 \text{ W h kg}^{-1}$) and nickel-cadmium batteries ($40\text{--}60 \text{ W h kg}^{-1}$) [4]. As a result, lithium-ion batteries have been used as the power source for electric vehicles with achieving a driving distance of $\sim 400 \text{ km}$ per charge [5]. Despite the progress accomplished to date, however, the specific energy densities of lithium-ion batteries are still far inferior to that of the conventional gasoline engines ($\sim 13,000 \text{ W h kg}^{-1}$) [6]. Thus, the exploitation of new energy storage technologies for EVs is still a grand challenge.

In attempts to improve the energy density, much attention has been paid to metal-air batteries, especially lithium-air, aluminum-air, and zinc-air batteries [7]. In this type of batteries, oxygen is straight obtained from air, as opposed to storing an internal oxidizer, and the pure metal is used as the electrode instead of conventional intercalated materials. Theoretically, the energy density of metal-air batteries only relies on the metal electrode so that it can be significantly increased. Among the metal-air batteries, the lithium-air battery has garnered the most attention, predominantly because lithium is the lightest metal. This means that it has the highest theoretical capacity (3862 A h kg^{-1}), which corresponds to an energy density of $11,680 \text{ W h kg}^{-1}$ for a potential of about 3.0 V. Even based on the consideration of the entire battery system, the energy density of $\sim 1000 \text{ W h kg}^{-1}$ is still several times higher than that of lithium-ion batteries [8], showing the remarkable potential to completely replace gasoline in vehicles.

The fundamental chemistry of lithium-air batteries involves lithium dissolution and deposition on the lithium electrode (or anode) and oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on the air electrode (or cathode) [9]. Since the demonstration of a prototype rechargeable lithium-air battery by

Abraham and Jiang in 1996 [10], many advancements have been made due to worldwide attention. In terms of electrolyte used, four types of lithium-air batteries have been proposed and developed: non-aqueous, aqueous, hybrid non-aqueous/aqueous, and solid-state lithium-air batteries [4], as schematically illustrated in Fig. 1. A typical non-aqueous lithium-air battery is made up of a lithium electrode and an air electrode saturated with a non-aqueous electrolyte composed of a lithium salt dissolved in a non-aqueous solvent (Fig. 1a). The typical route in electrolytes was proposed by Abraham and co-workers [11–13], involving the reduction of oxygen to lithium superoxide (LiO_2) through a one-electron transfer as:



followed by a disproportionation reaction:



and/or another one-electron-transfer electrochemical process:



to form lithium peroxide (Li_2O_2) as the main discharge product [14–16], which is insoluble in the non-aqueous electrolyte, filling the void spaces or covering the surface areas of the porous cathode. To make the battery rechargeable, electrochemical decomposition of solid Li_2O_2 to lithium and oxygen is required. The reaction during charge is thought to be [17]:



and/or



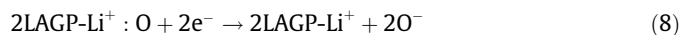
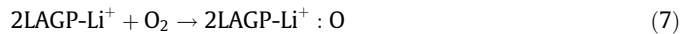
In non-aqueous lithium-air batteries, oxygen is reduced and forms solid Li_2O_2 in the porous cathode. The capacity of this battery system is therefore mainly limited by the clog of the solid product

and/or passivation of active surfaces at the porous cathode [18]. To address such problem, a new type of lithium-air batteries was proposed by Visco et al. in 2004 [19]. As schemed in Fig. 1b, an aqueous lithium-air battery is basically made up of a lithium anode and a porous air electrode with an aqueous electrolyte. To protect the lithium anode from the solvent (water), a solid-state lithium ion conducting membrane is placed on the anode [20–25]. To avoid the direct contact between the lithium and the solid electrolyte membrane and to increase the lithium ion conductivity, a hybrid non-aqueous/aqueous system has therefore been proposed [26–31], with a non-aqueous electrolyte filled in between (Fig. 1c). Different from those of non-aqueous lithium-air batteries, the reaction in basic solutions is:



Instead of forming solid Li_2O_2 , the discharge product is soluble lithium hydroxide (LiOH). However, the solubility of LiOH is limited to 5.25 M at room temperature. Otherwise, precipitates of $\text{LiOH} \cdot \text{H}_2\text{O}$ starts to form, thus limiting the specific capacity to be 130 mAh g^{-1} when considering the electrolyte (H_2O) participates in the reaction [32]. Although the solubility of LiOH can be effectively increased with the use of lithium acetate salts [21,22], the specific energy of an aqueous lithium-air battery is, therefore, lower than that of a non-aqueous lithium-air battery when considering whole reactants [32,33]. In the charge process, oxygen evolves at the air electrode and lithium deposits on the lithium electrode with the help of electrocatalysts [34].

The above-mentioned three types of lithium-air batteries are based on liquid electrolytes, which may cause the leakage and safety issues. A remedy is to develop a solid-state lithium-air battery without using any liquid electrolytes, as schemed in Fig. 1d. Till now, many solid-state lithium ion conducting materials have been developed, and some types have been tested in lithium-air batteries, such as polymers, glass-ceramics, and single-crystalline silicon [35]. Among them, NASICON-type glass-ceramics, including lithium aluminum titanium phosphate (LATP, $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$) and lithium aluminum germanium phosphate (LAGP, $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$), have been deeply studied. It is proposed that LAGP possesses an inherent characteristic to absorb oxygen molecules, followed by the reduction of oxygen to superoxide and peroxide molecules as [36]:



Similar to non-aqueous lithium-air batteries, the discharge product in solid-state lithium-air batteries is solid Li_2O_2 , and the charge process is the electrochemical decomposition of Li_2O_2 .

Although different types of lithium-air batteries involve different reaction mechanisms and materials, they also share some important features. For instance, the reactions of non-aqueous and solid-state lithium-air batteries are the formation and decomposition of solid product Li_2O_2 ; while in aqueous and hybrid systems, the product is in the dissolved phase (LiOH). Solid-state electrolyte membranes are crucial components for aqueous, hybrid, solid-state, and even non-aqueous lithium-air batteries [37,38], which not only transport lithium ions but also protect the lithium anode. During the past years, dozens of reviews have been published focused on the technical issues and challenges in one or several types of lithium-air batteries, such as assessment of electrolytes, materials and structures of the air electrodes, and improved understanding of reaction mechanisms [39–57]. However, the developments of battery components toward the practi-

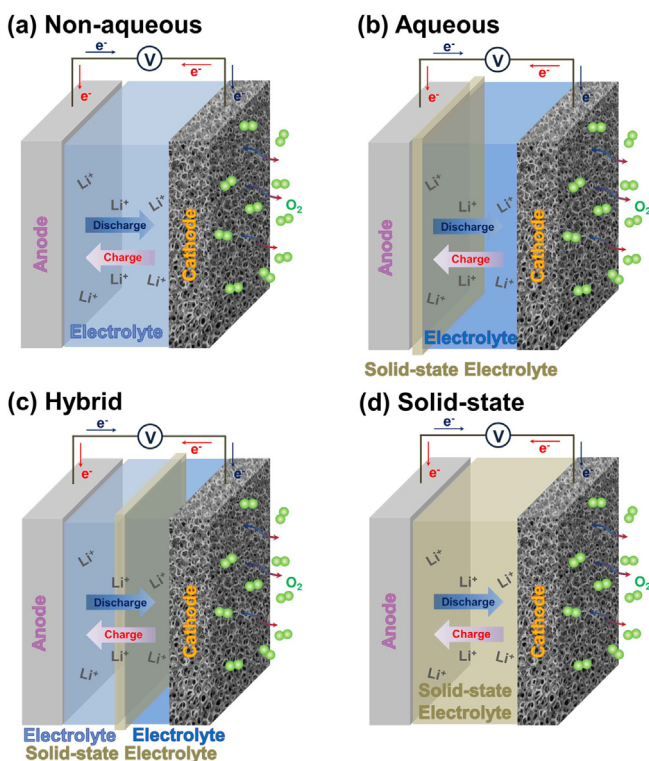


Fig. 1. Schematic configurations of lithium-air batteries.

cal applications, covering four types of batteries, have not been systematically reviewed. In this article, we focus on the advances and challenges that encompass the optimization of the battery's electrolyte and electrodes. The remaining part of this paper is organized as follows: Section 2 summarizes different types of electrolytes in lithium-air batteries, including non-aqueous, solid-state, and aqueous electrolytes; Section 3 introduces the challenges of the air electrode, including the structure design, the reaction kinetics, the long-term stability, and the operation in ambient air; and Section 4 reviews the lithium electrode, including contaminations from oxygen and water crossover, suppression of lithium dendrite, and alternative materials of lithium metal. In Section 5, future research directions of lithium-air batteries are highlighted.

2. Electrolytes

In lithium-air batteries, electrolytes are used to transport lithium ions, dissolve oxygen gas and transport it to the reaction sites (non-aqueous and aqueous electrolytes), and protect the lithium anode (aqueous, hybrid, and solid-state lithium-air batteries). For aqueous electrolytes, the solvent (H_2O) also acts as a reactant and participates in the electrochemical process. Therefore, the electrolyte is often considered the most critical component in the battery system. Focused on the electrolytes applied in lithium-air batteries, developments and remaining challenges, covering the scope of non-aqueous, aqueous, and solid-state electrolytes, are summarized and discussed in this section.

2.1. Non-aqueous electrolytes

An ideal non-aqueous electrolyte should have high ionic conductivity, good chemical and electrochemical stability, high boiling point (or low vapor pressure), and high oxygen solubility [45]. Meanwhile, to effectively transport oxygen, the high oxygen solubility and diffusivity are also required. Even with tremendous efforts, the stability issues of both solvent and lithium salt are still big challenges for non-aqueous electrolytes. In addition, functional additives in electrolytes, which may lead to a significant improvement in the battery performance, have drawn great interests in research.

2.1.1. Stability issues

In the early stage, carbonate-based liquid electrolyte solvents that are widely used in lithium-ion batteries, such as propylene carbonate (PC) and ethylene carbonate (EC), were applied in non-aqueous lithium-air batteries [58–65], but the cycling performance was surprisingly poor. Later studies showed that in carbonated-based solvents, the discharge products are lithium carbonate and alkylcarbonate, rather than Li_2O_2 [66,67]. The main reason is that the reduction of O_2 involves the formation on superoxide (O_2^-), which is a strong reducing agent and causes the decomposition of carbonate-based solvents to form carbonate species [65]. Consequently, these products are responsible for the poor reversibility. More importantly, the cycle performance is associated with the decomposition of solvents rather than the reversible formation and decomposition of Li_2O_2 , resulting in a poor cycling life.

The failure of carbonate-based solvents leads to the search of other stable solvents. Ether-based solvents have been tried, mainly due to their relatively high stability with respect to superoxide radicals and oxidation potentials [68–72]. Among them, dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME) have been deeply studied. DME is seen as a good candidate for non-aqueous lithium-air batteries, in which Li_2O_2 is the dominant discharge product [73–77]. TEGDME has been considered as another choice, which is now widely used in the research of non-aqueous

lithium-air batteries, and improved cycling life has been achieved [78–85]. However, the decomposition of DME during discharge and the oxidization of DME at high potentials by Li_2O_2 have also been reported [71,75]. Although TEGDME is relatively stable to superoxide attack [86], its instability at high potential (e.g., >4.3 V) is also an issue [87]. Another promising solvent is dimethyl sulfoxide (DMSO), which is shown to be relatively stable in the superoxide environment [88]. However, the instability of DMSO in lithium-air batteries has also been reported [89–92]. During the oxygen reduction on carbon electrodes, the solvent undergoes oxidation with reactive oxygen species [93] and lithium oxides to form side-products such as LiOH, dimethyl sulfone, Li_2SO_3 and Li_2SO_4 [91]. In addition, the chemical reaction between DMSO and Li_2O_2 could decompose DMSO to $DMSO_2$ and form LiOH [92]. These side products greatly affect the reversibility.

Room temperature ionic liquids (RTILs) have various advantages over conventional non-aqueous solvents, especially the wide electrochemical window, making them the promising stable candidates for non-aqueous lithium-air batteries [94–105]. For instance, Elia et al. reported that the RTIL-based electrolyte could enable a stable electrode-electrolyte interface and a highly reversible cycling behavior, leading to an enhanced round-trip efficiency of 82% [106]. Adams et al. synthesized a new lithium-ether-derived chelate ionic liquid, which is not only stable to metallic lithium but also much more inherently stable to superoxide-initiated hydrogen abstraction than DME [107]. Even with such striking features, the high viscosity of most RTILs [108] is a big issue, which leads to large transport resistance [109,110]. In addition, many RTILs have low lithium salt solubility and low conductivity [111], limiting the available discharge current density.

To search suitable solvents for non-aqueous lithium-air batteries, several other types of solvents have also been investigated, such as acetonitrile [12], N-methylpyrrolidone [112], methoxybenzene [113], amide-based [114,115], and sulfone-based [116–118]. In addition, reaction mechanisms in mixture solvents and their performance in the battery have also been studied [119–121]. To achieve a non-aqueous lithium-air battery with good reversibility and long cycle life, further investigations in identifying the decomposition mechanisms and searching new non-aqueous solvents are still challenges.

In addition to the solvent, the lithium salt also plays a significant role in the electrolyte system. An ideal lithium salt should not only have high solubility in the solvent to support ion transport but also be inert to the solvent and other battery components, especially to the oxygen reduction intermediates [46]. The salts that have been mostly employed in non-aqueous lithium-air batteries include $LiPF_6$, $LiClO_4$, $LiCF_3SO_3$, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Veith et al. investigated the influence of different lithium salts on the discharge chemistry in non-aqueous lithium-air batteries, and found that $LiClO_4$ appears to be the least reactive lithium salt [122]. Du et al. reported that in tri(ethylene glycol)-substituted trimethylsilane-based electrolyte, the decomposition of $LiPF_6$ triggers the decomposition of the solvent; while the same reactions are not observed when LiTFSI and $LiCF_3SO_3$ are used as the lithium salts [123]. Thus, the stability of the electrolyte strongly depends on the compatibility of lithium salts with solvent. Kang et al. reported a new kind of electrolyte system, in which $LiNO_3$ was dissolved in DME [124]. The interaction between the ionic solvate and active sites of carbon during the discharge process resulted in the formation of Pyridinic structure, which caused the deactivation of the carbon electrode. Compared with traditional LiTFSI/DME, the application of $LiNO_3$ leads to complete elimination of CO_2 during the charge cycle. Using the same lithium salt in DMSO electrolyte, Sun et al. showed that the charge overpotential is lower than that using $LiClO_4$ /DMSO electrolyte, illustrating the striking feature of $LiNO_3$ [125].

Lepoivre et al. reported a design for an electrochemical test battery that integrates a pressure sensor to monitor the pressure changes during charge/discharge, quantifying the parasitic reactions in non-aqueous lithium-air batteries based on a carbon electrode [126]. They tested various electrolytes frequently encountered in the literature, such as LiTFSI in DME, diethylene glycol dimethyl ether (DEGDME) and TEGDME, LiNO_3 in N,N-dimethylacetamide (DMA), and LiClO_4 in DMSO. The amount of parasitic reactions is deduced from the ratio between the experimental and theoretical gas evolution rates, based on the assumption that a rate of $2e^-/\text{mol}$ of gas would only involve oxygen. The first discharge is closer to the theoretical value ($2e^-/\text{mol}$ of gas) than the subsequent ones, suggesting a progressive chemical deviation from the expected reaction with cycling. In contrast, the first charge always comes with gas emissions lower than expected, indicating irreversible transformations. When reached the steady-state, 2 M LiNO_3 in DMA appears as the most efficient electrolyte among those investigated. The stability of the lithium salt and the subsequent effect on the stability of the electrolyte should therefore raise great attention. Further studies should combine both the solvent and the lithium salt as a whole electrolyte system, and investigate the influence on the electrochemical behaviors.

2.1.2. Functional additives

Due to the significant role of electrolyte in non-aqueous lithium-air batteries, selecting the optimum electrolyte is an essential prerequisite for the successful operation of batteries. Functional additives in electrolytes, which aim to improve the performance, have drawn great interests. It is worth noting that the functions of some kinds of additives seem to be “catalyst”. Due to their soluble properties and low concentrations in the electrolytes, here we focus on these additives while the solid catalysts will be discussed in the air electrode part.

The instability of electrolytes is mainly caused by the inevitable generation of superoxide (O_2^-) during the ORR process. To address this issue, Kim et al. reported a method by adding polydopamine in the ether-based electrolyte as a radical scavenger with the inspiration from the human eye, as schemed in Fig. 2a [127]. Both the batteries with and without polydopamine showed almost the same discharge voltage, but the battery with polydopamine exhibited markedly lower charge voltage due to the generation of more reversible Li_2O_2 with the lower equilibrium potential as a dominant product during the discharge process. As the side reactions were alleviated by this radical scavenging, the battery could fully retain the capacity of $600 \text{ mA h g}_{\text{carbon}}^{-1}$ over 100 cycles.

Since the ORR process in non-aqueous electrolytes accompanied by the formation of solid Li_2O_2 , traditional catalysts on the electrode surface would be gradually covered by the product. To accelerate the ORR process and improve the discharge performance, diffusive catalysts that can be repeatedly adsorbed on the growing front of Li_2O_2 are needed. Matsuda et al. investigated the effect of the addition of quinone derivatives in non-aqueous electrolytes for ORR on carbon materials and demonstrated that the Li_2O_2 formation could proceed efficiently [128]. As schemed in Fig. 2b, Q_{sem} species generally catalyze the reduction of molecular oxygen to superoxide anion radicals as:



where Q_{sem} and Q_{ox} denote the semiquinone and oxidized form of quinone. In the presence of Li^+ , the $Q_{\text{sem}}\text{Li}$ is formed by a lithium-coupled one electron reduction reaction on the electrode, and then molecular oxygen (O_2) is converted to superoxide anion radicals (O_2^-) mediated by the $Q_{\text{sem}}\text{Li}$ as:

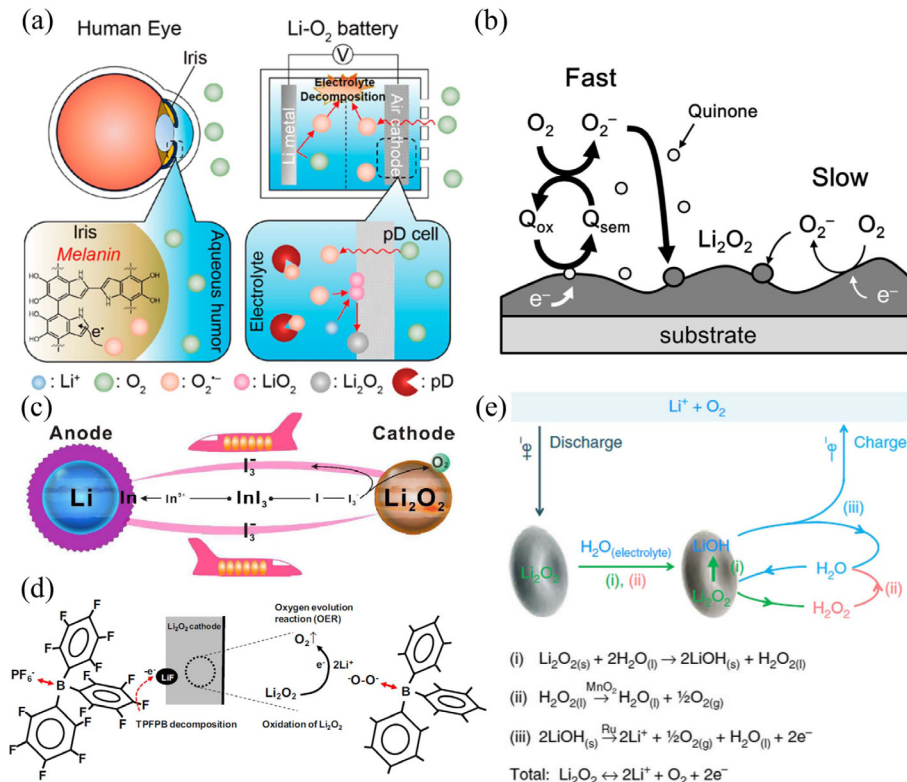


Fig. 2. Schematic illustrations of functional additives in non-aqueous electrolytes: (a) Polydopamine as a superoxide radical scavenger [127]; (b) quinone derivatives facilitate Li_2O_2 formation [128]; (c) a self-defense redox mediator [133]; (d) TPFPB on the oxidation of Li_2O_2 to O_2 during charge [134]; and (e) H_2O in the charge process [139].

The formed superoxide anion radicals on the cathode surface further react with Li^+ , resulting in continuous Li_2O_2 deposition. They also showed benzoquinone achieved an overpotential for the Li_2O_2 formation of less than 100 mV, exhibiting the best catalytic performance [128].

The large voltage polarization on charging is a significant problem in non-aqueous lithium-air batteries, due to the difficulty in transporting charge between solid Li_2O_2 and the solid electrode surface. To address this issue, a redox mediator (RM) may be helpful to facilitate the charge process: on charging, RM is oxidized to RM^+ at the air electrode surface as



which in turn oxidizes the solid Li_2O_2 and results in the regeneration of RM:



Consequently, the RM acts as an electron-hole transfer agent that permits efficient oxidation of solid Li_2O_2 , resulting in the low charge potential and long cycle life. For example, Bruce et al. introduced tetrathiafulvalene (TTF) into the DMSO electrolyte, which successfully lower the charge voltage [129]. Kang et al. reported lithium iodine (LiI) in TEGDME which enables the battery to achieve a high reversible capacity up to 900 cycles at the fixed capacity of 1000 mA h $\text{g}_{\text{carbon}}^{-1}$ with a charge voltage less than 3.5 V [130]. Goodenough et al. reported iron phthalocyanine (FePc), which acts not only as a redox mediator, but also a molecular shuttle of O_2^- species between the surface of the electronic conductor and the insulator Li_2O_2 [131]. Bergner et al. reported another kind of redox mediator, 2,2,6,6-tetramethylpiperidinyloxy (TEMPO). By using the addition of 10 mM TEMPO in the electrolyte, the charging potentials had a distinct reduction of 500 mV, and the cycle life of the battery was doubled from 25 to 50 cycles at the fixed capacity of 1000 mA h $\text{g}_{\text{carbon}}^{-1}$ [132]. Even with the improved charge performance, at the same time, undesirable reactions accompanied by the RMs were also noticed, especially the parasitic shuttle to lithium anode, resulting in a poor cycle life [132,133]. To address this issue, Zhang et al. proposed a self-defense redox mediator indium triiodide (InI_3), as schemed in Fig. 2c [133]. It can form a pre-deposited indium layer to resist the synchronous attack by the soluble I_3^- , and hence suppress the shuttle effect. The InI_3 -containing Li-O₂ battery gives ~80% round-trip efficiency and remains quite stable in a considerably prolonged cycling.

Since the formation of solid Li_2O_2 leads to a series issues, a natural thought is to dissolve the solid product. Tris(pentafluorophenyl) borane (TPFPB), as an additive in electrolytes to increase the solubility of solid Li_2O_2 , was evaluated by Choi et al. [134] and Zheng et al. [135]. The partially dissolve of solid Li_2O_2 was observed by adding TPFPB in the electrolyte. Moreover, the effectively electrochemical oxidation of Li_2O_2 to lithium and oxygen was confirmed. However, due to the electrochemical decomposition of TPFPB, the surface layer of the Li_2O_2 composed of LiF, which limited the application of this additive, as shown in Fig. 2d [134]. Very recently, Peng et al. reported a hexamethylphosphoramide (HMPA) electrolyte that can dissolve Li_2O_2 up to 0.35×10^{-3} M. Compared to the pristine ether-based batteries, the capacity, rate capability, and voltage efficiency are greatly improved [136].

Although water in electrolytes has been found to affect the morphologies of discharge products and increase the discharge capacity [137], it leads to the formation of LiOH, which was thought to be irreversible and causes a short cycling life [138]. Li et al. found that the decomposition of LiOH is strongly related to the applied catalysts, such as Ru nanoparticles supported on Super P [139]. They showed that using a trace amount of water in electrolytes

and electrolytic manganese oxide (MnO_2) can favor the transformation of the discharge product from Li_2O_2 to LiOH, as schemed in Fig. 2e, resulting in a greatly reduced the charge overpotential. The application of water in non-aqueous lithium-air batteries has also been reported by Liu et al. [140], in which combined a reduced graphene oxide electrode, the additive LiI, and the solvent DME to reversibly form and remove crystalline LiOH during discharge and charge, leading to high specific capacities, excellent round-trip efficiency (93.2%) with a voltage gap of only 0.2 V. It is noting that as lithium metal is very sensitive to even a trace amount of moisture, the effect of water on the battery behavior requires further investigations.

2.2. Solid-state electrolytes

An ideal solid-state electrolyte should have a high lithium ion conductivity, a very low diffusion coefficient for the other species (e.g., O_2 and H_2O), a high stability in the aqueous/non-aqueous electrolytes, and a high resistance towards the direction reaction with lithium metal. With the rapid development of lithium-ion batteries, a number of solid-state lithium ion conducting materials have been introduced [35]. Here we mainly focus on the solid-state electrolytes that have been applied in lithium-air batteries.

2.2.1. NASICON-type oxides

Among NASICON-type oxides, glass ceramic LATP and LAGP have been widely studied in lithium-air batteries [141]. A typical LATP plate has a thickness of 260 μm and an ionic conductivity of 3.5×10^{-4} S cm^{-1} at 25 °C [39]. Although LATP could provide a high lithium ion conductivity and neglected H^+ conductivity [142], it is unstable in direct contact with lithium metal. Thus, a buffer layer must be applied between the lithium metal and LATP plate, as schemed in Fig. 3a [143]. Consequently, the buffer layer also acts as a kind of electrolyte and thus should have high lithium ion conductivity and meanwhile be stable in contact with lithium metal. This buffer layer can be made by sputtering a thin layer of solid lithium phosphorous nitride (LiPON) on LATP [25,144]. Besides, poly(ethylene oxide) (PEO)₁₈LiTFSI was also applied as the buffer layer [143,145], which served as an effective protective interlayer to suppress the reaction between LATP and lithium metal. To further reduce the interfacial resistance between the lithium anode and the buffer layer, a nanosized BaTiO₃ ceramic filler was added to the polymer, and successfully decreased the interfacial resistance between the PEO₁₈LiTFSI and lithium from 240 to 125 Ω cm^2 by the addition of 10 wt% nanosized BaTiO₃ [20,24].

Due to the introduction of a buffer layer on LATP, the total lithium ion conductivity will inevitably decrease, leading to a large resistance for a practical lithium-air battery and resulting in low capacity and round-trip efficiency. LAGP, another kind of NASICON-type oxides [146–151], which has favorable chemical stability against lithium metal and the wide electrochemical window [152], has drawn great attention as the solid-state separator, as schemed in Fig. 3b [153]. The lithium ion conductivity of LAGP can be over 10^{-4} S cm^{-1} at 25 °C. However, the large interfacial resistance between the lithium metal and the LAGP plate is still a big issue that should be carefully addressed [154].

2.2.2. Single-crystal silicon membranes

Besides NASICON-type oxides, single-crystalline silicon membranes have been investigated as the solid-state lithium ion conducting material in a lithium-air battery [155]. Results showed that single-crystalline silicon membranes with thicknesses ranging from 2 to 20 μm demonstrate a lithium ion conductivity of 10^{-6} S cm^{-1} , while the diffusion coefficient of oxygen at room temperature is extremely low (i.e., 4×10^{-44} cm^2 s^{-1}). Hence, the silicon membrane can effectively protect the lithium anode from

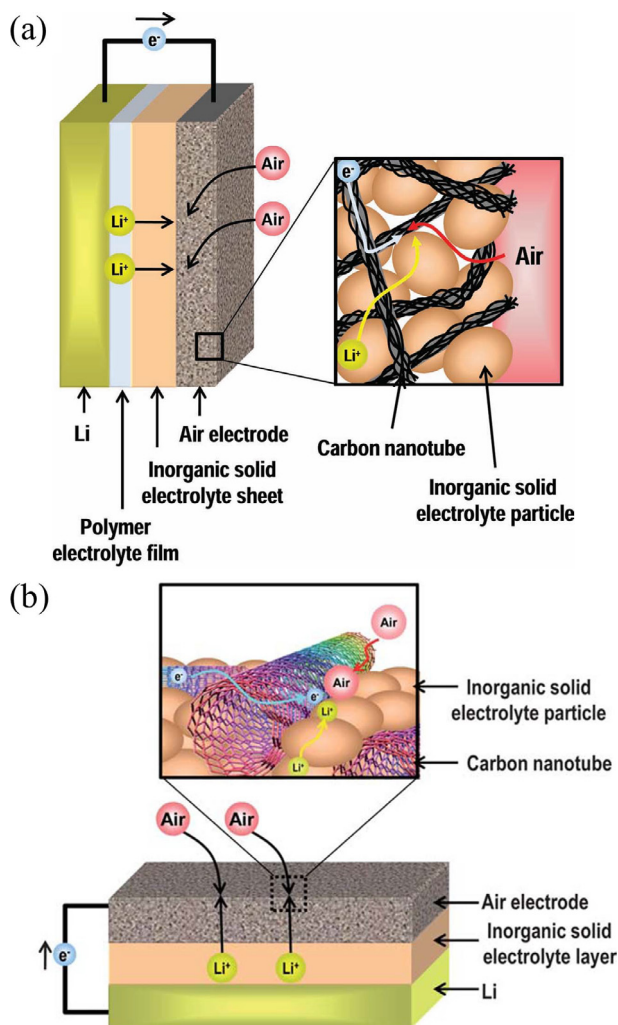


Fig. 3. Schematic of a solid-state lithium-air battery with (a) LAMP [143] and (b) LAGP [153].

the crossover of oxygen molecules and meanwhile transport lithium ions to support a reasonable current density during charge and discharge. It is worth noting that in the reported experiments, carbonate-based electrolytes were used so that the resistance increase was attributable to the formation of additional solid-electrolyte interface (SEI) layers from the reactions between the electrolyte and the silicon membrane and decomposition of the electrolyte under an oxygen atmosphere. Consequently, in stable non-aqueous electrolytes or aqueous electrolytes, the performance of such silicon membrane should be re-evaluated. In addition, the lithium ion conductivity of silicon is still low, which leads to a low obtainable power output. Hence, to modify the silicon membrane (e.g., doping) with a high conductivity is crucial for practical applications.

2.2.3. Polymer electrolytes

In addition to the solid glass ceramic and the silicon membrane, polymer electrolytes, with their special property of nontoxic, low-vapor-pressure, and non-flammable properties have attracted increasing interests [156–158]. Based on the applied materials, polymer electrolyte can be divided into three types [156]: (i) gel polymer, which is made of polymer network with liquid electrolytes; (ii) solid polymer, where the polymer host together with a lithium salt act as a solid solvent; and (iii) composite polymer,

which is developed by the integration of ceramic fillers into the organic polymer host.

Zhang et al. synthesized a hydrophobic ionic liquid-silica-polyvinylidene fluoride (PVDF)-hexafluoro propylene polymer composite electrolyte and employed it in a lithium-air battery [159]. When the battery was tested in ambient atmosphere, the compact structure and stable interface resistance were in favor of long-time durability. Lu et al. prepared a novel polymer electrolyte based on poly(carbonate-ether) and LiBF_4 [160]. The electrolyte with $\sim 17\%$ of LiBF_4 showed the ionic conductivity of $1.57 \times 10^{-3} \text{ S cm}^{-1}$. A lithium-air battery with this polymer electrolyte showed similar cycling stability to the traditional liquid electrolyte, demonstrating a new choice for fabrication of all-solid-state lithium-air batteries. Elia and Hassoun developed a gel polymer membrane by employing PVDF as polymer matrix, LiTFSI to allow increased porosity and ensure an efficient swelling process and ZrO_2 nanoparticles to improve the mechanical properties of the membrane [161]. The obtained film has a suitable conductivity of 0.4 mS cm^{-1} at 25°C , and also can mitigate oxygen crossover from the cathode to the anode side and avoid excessive increase of the interphase resistance. However, some polymer matrices (e.g., PVDF) are susceptible to a nucleophilic attack of the superoxide radical, leading to decomposition of the polymer electrolyte and poor cycling performance. To this end, Wu et al. developed lithiated perfluorinated sulfonic single-ionic conducting ionomers swollen with non-aqueous solvents and used as both the electrolyte and separator [162]. A polymer battery could be operated stably for 55 cycles under a fixed capacity of $1000 \text{ mA h g}_{\text{carbon}}^{-1}$ and a high theoretical energy density of 3900 W h kg^{-1} .

Generally, inorganic solid electrolytes (e.g., NASICON-type oxides) own high ionic conductivity and non-flammability, but display brittleness and high interface resistance to air electrodes; while gel/solid polymer electrolytes show high flexibility and low fabrication costs. To overcome the above disadvantages, a composite gel polymer electrolyte was made from ethoxylated trimethylolpropane triacrylate, 2-hydroxy-2-methyl-1-phenyl-1-propanone, Al_2O_3 nanoparticles, associated with $1 \text{ M LiCF}_3\text{SO}_3$ in TEGDME [163]. Benefitted from its high ionic conductivity and low activation energy, the terminal voltage of a battery is higher than 2.2 V after 140 cycles at 0.4 mA cm^{-2} with a capacity of $1000 \text{ mA h g}_{\text{composite}}^{-1}$. Moreover, a composite solid polymer electrolyte combining poly(methyl methacrylate-styrene) with amorphous LiNbO_3 has been designed by Zhou et al. [164], as shown in Fig. 4a. Attributed to the incorporation of high ionic conductive amorphous LiNbO_3 powder, the ionic conductivity ranges from 0.26 to 0.59 mS cm^{-1} (Fig. 4b), confirming the low crystallinity degree of the swelled membrane and attractive ionic conductivity of the composite electrolyte. With this electrolyte, a solid-state lithium-oxygen battery delivered an improved cycling life of more than 100 cycles and safety.

In comparison with glass-ceramics, the advantages of polymer composite as the solid-state electrolytes include the high lithium ion conductivity, more contact interfaces since the good flexibilities, and easy fabrication. With the increasing research interests in flexible power sources for the next-generation wearable electronic devices [165,166], further investigations on polymer composites are in great need.

2.3. Aqueous electrolytes

The oxygen electrochemical mechanism of aqueous and hybrid lithium-air batteries is similar to that of zinc-air batteries with the formation of soluble LiOH , eliminating the blockage of the porous air electrode by the discharge product in non-aqueous and solid-state lithium-air. However, two issues in aqueous electrolytes

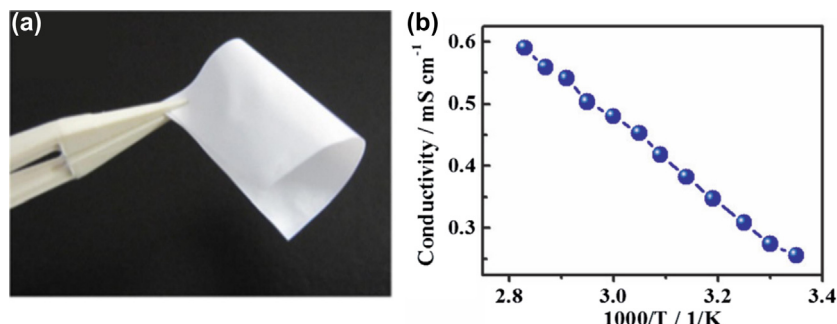


Fig. 4. (a) Photo image of a composite solid polymer electrolyte membrane; (b) arrhenius plots of the ionic conductivity versus temperature [164].

require great attention, including the energy density and the stability towards the solid-state electrolyte membrane.

2.3.1. Limited energy density

In non-aqueous lithium-air batteries, electrolytes are used to transport lithium ions and oxygen to the reaction sites. Since oxygen could be obtained from ambient air, the practical capacity and energy density depend on the utilization of the lithium anode or the porous air electrode. However, in aqueous and hybrid lithium-air batteries, the aqueous solvent, H_2O , also participates in the reaction as a reactant, as expressed in Reaction 6. The addition amount of electrolytes can inevitably decrease the specific energy density of the battery. Moreover, when the Li^+ and OH^- concentrations reach the solubility value (12.5 g of $LiOH/100$ g of H_2O), $LiOH$ will precipitate, filling the void space in the porous air electrode, as the situation in non-aqueous lithium-air batteries. To prevent this deposition, a large amount of water is required, which results in the further decrease in the theoretical energy density to only about 477 $W\ h\ kg^{-1}$ [32]. Therefore, to increase the energy density of aqueous and hybrid lithium-air batteries, other aqueous electrolytes rather than water should be applied.

The theoretical specific capacities and energy densities of different aqueous solutions are listed in Table 1 [32]. Different electrolytes could result in various energy densities, and the highest energy density could be achieved by using strong acid solutions such as HCl and $HClO_3$, due to the high solubility of discharge products. However, some other problems will be introduced when using these electrolytes, such as the instability towards the solid-state electrolytes and the air electrodes. Besides, with the increased amount of lithium salt in the electrolyte, the oxygen solubility and transfer coefficient decrease, along with the operating voltage [30,167], which may reduce the practical energy density. Consequently, when applying aqueous electrolytes with high energy densities, these above-mentioned issues need to be considered.

Table 1
Summary of specific capacities and energy densities for lithium-air batteries with some aqueous electrolytes. (Data from Ref. [32].)

Aqueous solution	Minimum amount H_2O for 1 mol of product (mol)	Specific capacity ($mA\ h\ g^{-1}$)	Energy density at OCV = 3.69 V ($W\ h\ kg^{-1}$)
$LiOH$	11.14	129.19	476.70
CH_3COOH	8.15	130.97	483.28
$HClO_3$	1.09	262.51	968.68
$HClO_4$	10.07	95.83	353.63
$HCOOH$	7.35	152.10	561.24
HNO_3	3.76	208.49	769.33
H_2SO_4	17.86	72.73	268.37
HBr	2.67	211.31	779.74
HCl	2.79	316.88	1169.29

2.3.2. Stability towards lithium ion conducting ceramics

To date, LAMP and LAGP are most applied solid-state membranes in aqueous and hybrid lithium-air batteries. The stability of LAMP in different aqueous electrolytes was tested by Imanishi et al. [21–23,168,169]. They found that LAMP is stable in aqueous $LiNO_3$ and $LiCl$, but unstable in aqueous 0.1 M HCl and 1.0 M $LiOH$ [39]. In addition, lithium ion-saturated solutions could increase the stability of LAMP in aqueous electrolytes, such as CH_3COOLi saturated $CH_3COOH-H_2O$ solution [21,23] and $LiCl$ saturated $LiOH$ solution [169]. The stability of LAGP in various acid and alkaline aqueous electrolytes was tested by He et al. [170]. LAGP would decompose into impurity phase Li_3PO_4 after being immersed in $LiOH$ alkaline aqueous solution. However, it has excellent stability in saturated $LiCl-CH_3COOH-H_2O$ and $LiCl-LiOH-H_2O$ solutions. These findings gave some candidate aqueous electrolytes for long-term operation of lithium-air batteries.

Since high-concentration and a strong acid (e.g., HCl) could improve the theoretical energy density, to solve the instability of NASICON-type glass ceramic, one useful method is to utilize the buffer additive in the electrolyte. For example, phosphoric acid is a moderately strong acid and could corrode the LAMP membrane. However, applying a phosphate buffer solution consisting of a mixture of 0.1 M phosphoric acid and 1 M LiH_2PO_4 with a net pH value of 3.14 at room temperature can avoid the corrosion of the LAMP membrane [171]. Li et al. presented an approach by adding an equivalent amount of imidazole to the acid solution to store protons in the imidazole-acid complex [172]. Experimental results showed that with the addition of 6.06 M of imidazole to 6 M HCl , the solution had a mild pH of ~ 5.0 , and thus alleviate the corrosion of the solid-state electrolyte and facilitate the battery with a high capacity of 136 $mA\ h\ g_{cathode}^{-1}$.

2.4. Summary of challenges in electrolytes

For non-aqueous electrolytes, the main challenge is the stability in the oxidation environment, which is the key for reasonable cycling life. To achieve this target, both solvents and lithium salts should be taken into account, and functional additives aimed at stabilizing the electrolyte should be developed. In addition to stability, high transport properties, such as the oxygen solubility and diffusivity, are important for the battery performance. Recently, it is reported that the choice of salt species and concentration have an outsized influence on oxygen solubility, while solvent choice has the major influence on oxygen diffusivity. The stability of superoxide reaction intermediates is also affected by variations in salt concentration and the choice of solvent [173]. Hence, these values are also crucial criteria for the selection of suitable electrolytes. For solid-state electrolytes, a high lithium ion conductivity is essential for reasonable capacity and power output. At the current stage, LAMP is the most widely used ceramic-based electrolyte, due to its relatively high conductivity and good protection

for the lithium electrode. However, its low stability towards the electrolyte and lithium metal needs to be addressed. Polymer-based composites demonstrate comparable lithium ion conductivities to those of non-aqueous electrolytes and show promising applications in flexible batteries, but the long-term stability should draw more concerns. For aqueous electrolytes, owing to their participation in electrochemical reactions, the energy density is an underestimated issue that should be paid great attention when building a battery with a high capacity. Moreover, the stability towards the solid-state electrolyte membranes is crucial for the performance and the safety, and thus a careful assessment is needed.

3. Air electrodes

Since both ORR and OER occur in the air electrode, it poses major technology challenges for lithium-air batteries. The ultimate goal is to achieve high capacity and power density, high round-trip efficiency, and a long cycling life. Reaching that goal depends on the material and the microstructure. To obtain a high capacity, the reaction pathways among oxygen, lithium ions, and electrons in the air electrode should be kept as long as possible. Consequently, the structure of air cathodes in different types of lithium-air batteries need be designed and optimized accordingly. In addition to improving the transport kinetics, catalysts should be introduced into air electrodes to facilitate electrochemical reactions during discharge and charge. Since air electrodes may be corroded to form unresolvable by-products which can lead to a decrease of cycle life, the stability needs to be further improved. Moreover, to enable the operation in ambient air, solving the contaminations of carbon dioxide and water and suppressing the evaporation of liquid electrolytes are challenging.

3.1. Structure design

Generally, a large reaction area associated with good electric conductivity is preferred for an air electrode, and a porous structure is required for oxygen transport. In non-aqueous and solid-state lithium-air batteries, the discharge product, Li_2O_2 , is in the solid phase. Consequently, the solid Li_2O_2 that is stored in the porous cathode can affect the transport of oxygen, lithium ions, and electrons, and thus decide the battery capacity. Even in aqueous and hybrid lithium-air batteries where the discharge product can be dissolved in aqueous electrolytes, the transport of oxygen and lithium ions can also be affected by the porous cathode. Therefore, the structure is a big issue for porous cathodes.

3.1.1. Enlargement of reaction boundaries in solid-state lithium-air batteries

In non-aqueous, aqueous, and hybrid lithium-air batteries, cathodes are partly or fully saturated by the liquid electrolytes. Oxygen and lithium ions are transported in the electrolytes and react with electrons transported in the air electrode at the interface of liquid electrolyte/solid electrode. In solid-state lithium-air batteries, due to the absence of liquid electrolytes, lithium ions are transported only through the solid electrolyte. Hence, reactions can occur only at the boundaries among the solid electrolyte (for Li^+ transport), the electrode (for electron transport) and gaseous oxygen [43].

To address the small amount of reaction boundaries, integrating the air electrode and the solid-state electrolyte together to form lithium ion conducting networks is a useful approach, as proposed in Fig. 5a [174]. In this structure, not only the pathways of lithium ions in the cathode could be increased, but also the interfacial impedance could be greatly reduced. Following this line, Kitaura

and Zhou integrated an air electrode and a solid-state electrolyte membrane through adding the solid-state electrolyte particles into the carbon nanotubes to produce three continuous path structures for electrons, lithium ions, and oxygen, respectively, leading to an improved discharge capacity of $1700 \text{ mA h g}_{\text{carbon}}^{-1}$ [153]. Zhu et al. proposed and fabricated a novel solid-state battery with an integrated electrolyte and cathode structure, as shown in Fig. 5b [175]. This design allows a thin electrolyte layer of about $36 \mu\text{m}$ and a highly porous cathode with a porosity of 78%, both of which were prepared using the same LTP material, eliminating the interfacial resistance. In addition, carbon nanoparticles are uniformly coated onto the cathode surface and serve as both an electron conductor and a catalyst for the electrochemical reaction. As a result, the battery outputs a discharge capacity as high as $14,200 \text{ mA h g}_{\text{carbon}}^{-1}$ at 0.15 mA cm^{-2} , and can sustain 100 cycles at a fixed capacity of $1000 \text{ mA h g}_{\text{carbon}}^{-1}$. For the polymer solid-state electrolyte, Bonnet-Mercier et al. presented a new design for a three-dimensional (3-D) solid polymer electrolyte (SPE) structure by incorporating the carbon nanotube (CNT) cathode, as schemed in Fig. 5c [176]. The void spaces in the porous CNT/SPE film allowed an increased depth of diffusion of O_2 gas, providing an enlarged active reaction sites where lithium ions, oxygen, and electrons can interact. Consequently, the 3-D CNT/SPE cathode enhanced the capacity of the SPE-based lithium-air battery to $300\text{--}500 \text{ mA h g}_{\text{CNT}}^{-1}$, higher than that of a conventional cathode with the capacity of $125 \text{ mA h g}_{\text{CNT}}^{-1}$.

3.1.2. Design of proper structures in non-aqueous lithium-air batteries

To obtain more reaction sites in the air electrode, materials with the high specific surface area are desirable. Among them, carbon materials with various microstructures (e.g., carbon powder, ordered mesoporous carbons, carbon nanotubes/fibers, graphene) have attracted great attention and been widely applied in lithium-air batteries [177]. Due to the formation of solid Li_2O_2 , the reaction places will be covered by the product, and the void volumes will be occupied. The solid product continuously grows on the pore-solid surfaces with an increase in the discharge capacity [178], and ultimately clogs the pores and blocks the oxygen transport pathway. Meanwhile, due to the low lithium ion conductivity [77] and electric conductivity [18] of solid Li_2O_2 , the lithium ion and electron transport can also become resistant to the growth of the discharge product. To obtain a capacity close to the theoretical value during the discharge process, the transport pathways of oxygen, lithium ions, and electrons should be kept as long as possible. Therefore, a profound understanding of the relationship between the capacity and the cathode structure in non-aqueous lithium-air batteries is important.

In the early stage of non-aqueous lithium-air batteries, the relationship between the capacity and the cathode geometrical properties had already been investigated [179–181]. However, all the results were obtained from the battery with carbonate-based electrolytes, which resulted in the formation of Li_2CO_3 or other by-products rather than Li_2O_2 . Based on the relatively stable solvents (e.g., DME, TEGDME), the correlations between the discharge capacity and the cathode structure have been further studied. Meini et al. found a strong correlation between the specific discharge capacity and the cathode specific surface [182]. On the contrary, Chervin et al. showed that the macroporous nanofoams (50–200 nm) yield the specific capacity approximately twice that of the mesoporous nanofoams (5–50 nm), even though the macroporous foams have lower specific surface areas [183]. Ding et al. found that the discharge capacity was hardly affected by the surface area or pore volume, but directly correlated with the pore size [177]. Tan et al. proposed and fabricated a composite cathode made of carbon powder and nanotubes [184], and found that the composite cathode could achieve a larger capacity than that of the cathode made

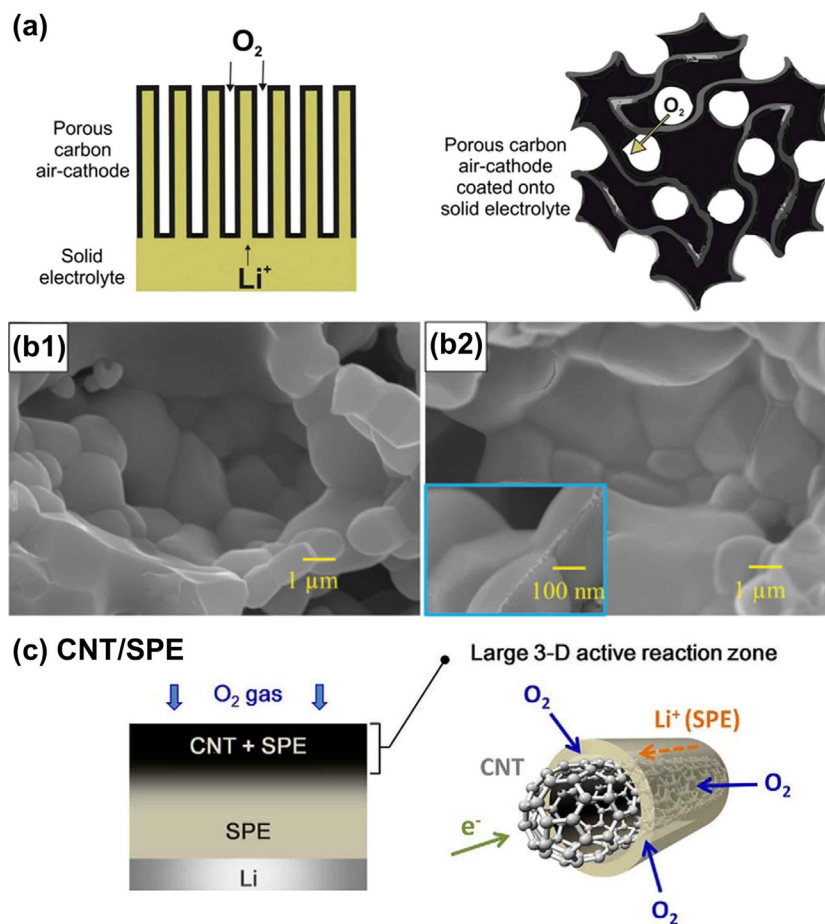


Fig. 5. Approaches to increase reaction boundaries in solid-state lithium-air batteries: (a) Schematic of the continuous lithium ion conduction path and porous carbon coated on the surface [174]; (b) scanning electron microscope (SEM) images of one pore in the porous LATP electrode before (b1) and after (b2) carbon loading [175]; (c) enlarged active reaction zone in 3-D CNT/SPE architecture [176].

of pure carbon powder, even though the specific surface area decreased, which may be mainly attributed to the improved oxygen transport as the result of enlarged pore spaces.

In addition to the pore size and volume of the cathode, the pore size distribution along the thickness of the cathode also has a significant role in the battery performance. In the initial discharge period, the oxidation reaction is predominately controlled by the transport of oxygen. Due to the slow transport rate of oxygen [185], the oxygen concentration in the porous cathode decreases from the air side to the separator side during discharge. Higher oxygen concentration will result in a higher reaction rate. Hence, the fraction of the solid product will be larger at the air side, decreasing toward the separator side, as illustrated by both experimental observations [183,186] and modeling results [187–192]. In a porous cathode with uniform pore size distribution, the solid product will be in the scenario as illustrated in Fig. 6a. Such a distribution of the solid product means that although the remaining pores toward the separator side are still open, the pores at the air side will be blocked first with an increase in the discharge capacity, terminating the discharge process and resulting in a low discharge capacity. Consequently, a thick cathode usually leads to a low specific capacity, due to the low utilization of the reaction sites and void volume [192]. The above-mentioned issue can be addressed by forming a porous cathode with a gradient distribution in pore size, as illustrated in Fig. 6b. The implementation of such a gradient will enable a more uniform oxygen transport pathway along the electrode thickness, and thus increase the discharge capacity [193].

It is worth noting that the morphology of solid Li_2O_2 can significantly affect the discharge capacity [177]. Apart from the film-like Li_2O_2 [177], the product morphology could also be toroid-like [183,193], disc-like [194], particle-like [64], and other irregular shapes [78,195]. For a same structured pore, the particle-like morphology will indeed lead to a higher capacity than that of the film-like one due to the improved void volume utilization. Bruce et al. showed that the solvent property, donor number (DN), influences

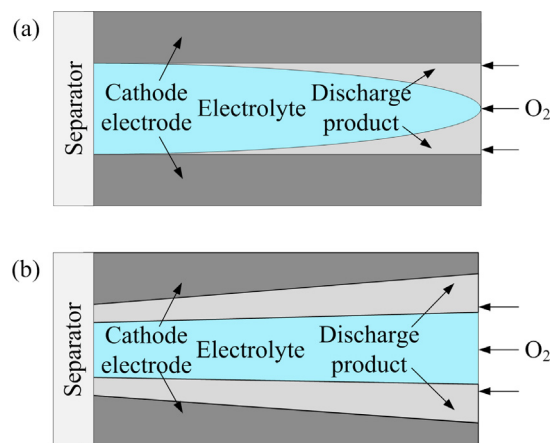


Fig. 6. Schematic of the discharge process in the pore of a (a) uniform and (b) gradient porous cathode.

O₂ reduction through its effect on the solubility of LiO₂ [196]. Large Li₂O₂ particles are observed in high-DN solvents at high potentials, while the Li₂O₂ film is observed at low potentials and in low-DN solvents at all potentials. Hence, the optimization of the porous cathode structure for low- and high-DN solvents will be different. Besides solvents, Sharon et al. showed that the level of dissociation of the salt also plays an important role in Li₂O₂ morphology [197]. In addition to electrolytes, the product morphology is also affected by the operation conditions [198–202]. Therefore, to maximize the discharge capacity, detailed investigations on the correlations between the cathode microstructures and the synergy transport are required.

3.1.3. Enhancement of species transport in liquid electrolytes

In conventional non-aqueous lithium-air batteries, the air electrode is fully saturated by the electrolyte, as schemed in Fig. 7a. Oxygen dissolves into the electrolyte at the oxygen/electrolyte interface and is then transported to the reaction sites. Due to the limited transport rate of oxygen in the electrolyte [203], the oxygen concentration decreases substantially from the air side to the separator side. The insufficient supply of oxygen near the separator side limits the chemical reaction, leading to a lower power density output. Hence, a critical issue is to optimize the distribution of electrolyte inside cathode pores that can facilitate the transport of species [204]. A possible remedy is to replace the fully-saturated cathode into a partially wetted one, as illustrated in Fig. 7b. Oxygen can reach the inner region, and the electrolyte

can be pushed away from the separator with an increase in the solid discharge product. With the optimum quantity of electrolyte, such a structure can help adapt the electrolyte distribution while Li₂O₂ is produced. However, this method does not offer a complete solution because the dry areas are unused during discharge due to the lack of lithium ions. Hence, a more desirable distribution of electrolyte inside cathode pores should be aimed at creating a uniform concentration distribution of both oxygen and lithium ions on the entire cathode surface, as schemed in Fig. 7c. Gaseous oxygen can rapidly penetrate the entire pore and can be quickly transported to the reaction sites through the thick-reduced electrolyte, and lithium ions are present on the surface. Consequently, the enhanced transport of species leads to the improved battery performance.

Following this strategy, Xia et al. fabricated a partially wetted carbon cathode by evaporating of diethyl ether from the organic electrolyte, and obtained a discharge capacity 60% higher than that of a conventional fully-saturated cathode [206]. Kim and Park modified the surface of carbon by a polydopamine coating to enhance its wettability and achieved an increased capacity [207]. Zhang and Zhou designed a cathode made of the cross-linked single-walled carbon nanotubes and a gel electrolyte [99,208], which allows the passage of oxygen through the indispensable oxygen diffusion channels arising from the numerous small chinks and pores. As a result, the conventional electrochemical interface could be expanded into 3-D networks. Balaish et al. designed two interpenetrating network channels in the cathode: one network consists of channels filled with O₂-transporting perfluorinated carbon liquids (PFCs) for fast oxygen transport and the other is filled with a Li⁺-conducting electrolyte for Li⁺ transport, increasing the discharge capacity [209].

In aqueous and hybrid lithium-air batteries, aqueous electrolytes also play as reactants in the electrochemical reactions. Hence, a large amount of aqueous electrolytes may be required for a high discharge capacity. Chen et al. designed a lithium-air flow battery system, which contained an electrochemical reaction unit and a combined electrolyte storage/oxygen exchange unit [210]. Different from other lithium-air flow battery systems which just renew the electrolyte [27,32], the fresh electrolyte which saturated with oxygen is pumped into the reaction unit, while the used electrolyte is sent to the oxygen exchange unit to be refreshed. As a result, the cathode does not open directly to the atmosphere to receive the oxygen but circulates the electrolyte continuously between the reaction unit and electrolyte storage unit, and thus the oxygen concentration and transport rate could be greatly improved. Using this system, a power density as high as 7.64 mW cm⁻² at a constant discharge current density of 4.0 mA cm⁻² was achieved. The merit of this flow system is not only limited to aqueous and hybrid lithium-air batteries, but also may be applied in the non-aqueous lithium-air batteries to further increase the oxygen transport [211].

3.2. Reaction kinetics

Accelerating the reaction kinetics and lowering the overpotential are essential for the need of round-trip efficiency in lithium-air batteries. In aqueous and hybrid lithium-air batteries, due to their high similarities in reaction mechanisms (Reaction 6) of alkaline fuel cells and metal-air batteries (e.g., Zn-air battery), various catalyst materials for ORR and OER in aqueous solutions have been tried [212–214]. To develop rechargeable batteries, bifunctional catalysts, which have the abilities to catalyze both ORR and OER in aqueous media, have also been developed [215], and the “decoupled” bifunctional air electrode which separates the ORR and OER catalysts into two independent electrodes has also been proposed [212,216]. In this section, we mainly focus on the catalysts applied

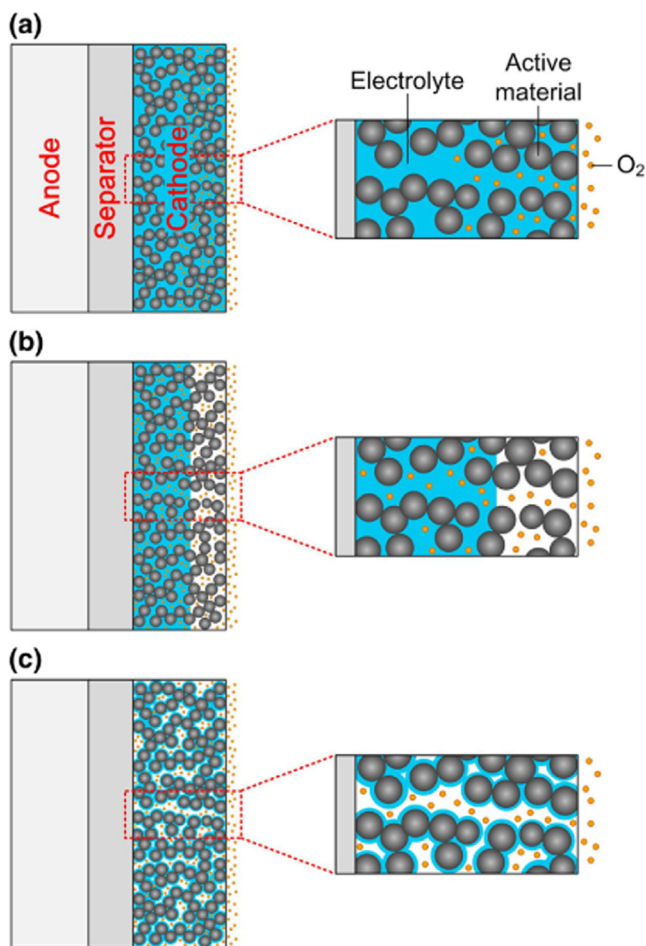


Fig. 7. Schematic of a non-aqueous lithium-air battery with the air electrode: (a) fully-saturated; (b) partially-wetted; and (c) fully-wetted and partially-saturated [205].

in non-aqueous lithium-air batteries based on relatively stable electrolytes (e.g., TEGDME, DME, DMSO) [217]. Different types of catalysts are first briefly reviewed, and then the catalytic mechanisms in the discharge and charge processes are discussed. Although element-doped [218–222] and surface-modified [223] carbon materials have also been used as catalysts, here the “catalyst” only refers to the material associated with carbon supporters. The stability issues of carbon materials and carbon-free cathodes will be introduced in the following section.

3.2.1. Types of catalysts

Various metal materials, such as Pt [224], Au [225], Pd [226], and Co [227], have been applied as catalysts with some new designs. Huang et al. encapsulated a series of noble metal nanoparticles (Pd, Pt, Ru, and Au) inside end-opened carbon nanotubes [228]. These cathode materials exhibited a dramatic reduction of charge overpotentials compared to their counterparts with nanoparticles supported on CNT surface. This is attributed to the strengthened electron density on CNT surfaces due to the encapsulation of noble metal. In addition to single-kind metal catalysts, the performance of bimetallic metal catalysts has also been evaluated. Li et al. reported the performance of Au-Pt core-shell nanoparticle chains, which showed excellent catalytic activity with a voltage of 2.82 V in discharge and 3.77 V in charge at the current density of 50 mA g_{loading}^{-1} with a fixed capacity of 1000 mA g_{loading}^{-1} [229]. Choi et al. designed PdCu bimetallic nanoparticles as efficient catalysts, which exhibited a low OER potential of 3.4 V and demonstrated a reversible cycle life up to 50 cycles and outstanding rate capability even at a high current density of 5000 mA g_{carbon}^{-1} [230].

Besides metallic catalysts, a variety of metal oxides have also been investigated. For instance, Oloniyo et al. studied the catalytic activities of different crystallographic phases of MnO_2 , including α -, β -, γ - MnO_2 nanowires, α - MnO_2 nanospheres, and α - MnO_2 nanowires on carbon, and found that β - MnO_2 sustained the least capacity loss and α - MnO_2 supported on carbon provided the highest capacity [231]. Su et al. synthesized single crystalline Co_3O_4 nanocrystals with different crystal planes, and found that the essential factor to promote the OER is the surface crystal planes, and the correlation between different Co_3O_4 crystal planes and their effect on reducing charge-discharge overpotential was $\{1\ 0\ 0\} < \{1\ 1\ 0\} < \{1\ 1\ 2\} < \{1\ 1\ 1\}$ [232]. Oh et al. reported a novel metallic mesoporous pyrochlore catalyst, which showed promising catalytic activity and resulted in a cathode with a high reversible capacity of ~ 1000 mA h g_{cathode}^{-1} [233].

In addition to using metal or metal oxide alone, metals associated with metal oxides have also been applied. Oh et al. engineered bio $Co_3O_4/Co(OH)_x$ nanowires with thermal treatments and incorporation of Ni nanoparticles, leading the round trip efficiency and the cycle life to improve from 68.5% to 75.1% and from 27 to 48 cycles, respectively [234]. In another research, they introduced Au nanoparticles onto the surface of pyrochlore, and found that the ORR performance was significantly improved [79]. Liu et al. prepared α - MnO_2 nanotubes decorated with Pt nanoparticles [235]. Due to the high surface area, highly dispersed and uniform Pt deposition, a battery with 5 wt% composite catalyst showed the highest catalytic activity and lowest charge overpotential of 1.07 V. Qu et al. synthesized a wheat-like Ag- Mn_3O_4 nanocomposite, which led to a large discharge capacity of 4835 mA h g_{cathode}^{-1} and significantly reduced the average charge voltage to ~ 3.5 V [236].

Recently, other types of catalysts have also been utilized. For example, Shui et al. reported a dispersed Fe/N/C composite catalyst that has high selectivity in promoting the decomposition of Li_2O_2 [237]. Park et al. synthesized bimodal mesoporous TiN/C microfibers which formed a catalyst-membrane architecture for the accommodation of a large amount of Li_2O_2 ($19,100 \pm 500$ mA h g_{carbon}^{-1})

and for the efficient mass transfer of the electrolyte and oxygen [238]. Li et al. synthesized novel composites of Fe/Fe₃C carbon nanofibers (Fe/Fe₃C-CNFs), which exhibited a capacity of 6250 mA h g_{loading}^{-1} and better reversibility than those of pure carbon [239]. Luo et al. reported a free-standing macroporous graphene@C₃N₄ composite cathode, which exhibited a 0.48 V lower charge plateau and a 0.13 V higher discharge plateau than those of pure graphene cathode with a capacity of nearly 17,300 mA h $g_{\text{composite}}^{-1}$ [240]. Luo et al. fabricated B₄C nanowires which enabled a terminal discharge voltage higher than 2.2 V after 120 cycles at a current density of 0.4 mA cm^{-2} and a high round-trip efficiency of 76% [241]. Ma et al. synthesized nickel sulfides with two different morphologies (flower-like and rod-like). Both of them demonstrated excellent catalytic activities towards the formation and decomposition of Li_2O_2 , and the flower-like one can give the highest capacity and the lowest charge voltage [242].

3.2.2. Mechanisms of catalysts in discharge and charge

The above section summarized different kinds of catalysts applied in non-aqueous lithium-air batteries. Although some promising electrochemical performance has been reported, different electrode configurations (e.g., catalyst loading, electrode thickness), electrolyte employments (e.g., DMSO, TEGDME), and operating conditions (e.g., current density) result in a systematical comparison inapplicable [243,244]. At the present research stage, understanding the roles of catalysts in discharge and charge is crucial to design the suitable and effective catalyst for performance improvements.

During the discharge process, the first electron reduction most likely proceeds by the formation of superoxide species such as O_2^- and LiO_2 , as expressed in Reaction 1. Then, LiO_2 may chemically disproportionate or electrochemically undergo a second electron reduction to form Li_2O_2 . Unlike traditional ORR process with H atoms involved, the ORR process in non-aqueous Li-O₂ batteries shows different behaviors due to the unavoidable influence of Li atoms and the accumulating of discharge products [222,245,246]. Lu et al. studied catalytic activity trends of Li^+ -ORR, and found a volcano-like tendency with activity decreased in the order of Pd > Pt > Ru \approx Au > GC on bulk surfaces [247], which were further obtained by density functional theory (DFT) calculations [248], as shown in Fig. 8 [249]. The results indicated that oxygen adsorption energy can be a descriptor for Li^+ -ORR activities, and an active Li^+ -ORR catalyst needs to have a close O atom adsorption energy with that of Pt or Pd. Too strong O atom adsorption on the catalyst (e.g., Ru) diminishes the bonding with lithium atom in subsequent reactions, while too weak adsorption (e.g., GC, Au, Ag) hinders O_2

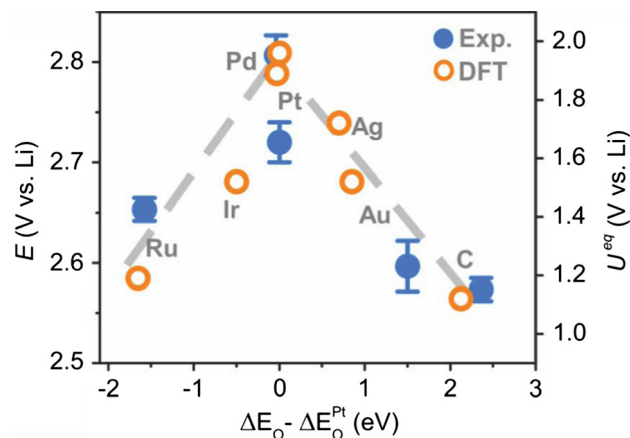


Fig. 8. Comparison of non-aqueous Li^+ -ORR potentials as a function of calculated oxygen adsorption energy from experiments and DFT calculations [249].

activation. In addition, the step edges of metals are more active than the close-packed ones. Using similar models, other Li^+ -ORR catalysts were further investigated and the descriptors for Li^+ -ORR were proposed. For example, Kim et al. calculated the catalytic effect of Pt (111), Pt_3Co (111), PtCo (111) and Co (0001) as the bi-functional catalysts, and found a corresponding discharge overpotential of 1.02, 1.02, 0.19 and 1.77 eV, respectively [250]. They also suggested that the low ORR overpotential is closely related to strong Li adsorption. After the formation of LiO_2 , it is suggested that an equilibrium exists between LiO_2 adsorbed on the electrode and LiO_2 dissolved in the electrolyte solution. Hence, the detailed mechanism is governed by the competition between the LiO_2 solubility and the adsorption free energy of LiO_2 on the oxygen electrode surface [196]. For a given electrolyte, different electrode surfaces have different adsorption energies and therefore play a key role in determining the Li_2O_2 morphology and the discharge performance [251–254], while the detailed mechanisms are still under investigation.

During the charge process, the solid discharge product Li_2O_2 needs to decompose to lithium and oxygen. Since both the catalyst and the reactant (Li_2O_2) are in the solid state, and Li_2O_2 will block at least partly the catalyst surface, the transport of solid reactant and the interaction between catalyst and Li_2O_2 would become additional limiting factors of the OER kinetics. The efficiency of electrocatalysts was questioned by McCloskey et al. [73]. Their results indicated that in lithium-air batteries employing DME as a solvent where Li_2O_2 was the dominant discharge product, metal (Pt and Au supported on Vulcan Carbon) and metal oxide (α - MnO_2 nanowires mixed into VC) catalysts did not lower the OER potential compared to pure carbon. Moreover, the onset potential at which oxygen evolution occurs was nearly identical for all cathodes and was just above the open circuit voltage of the discharged battery (~ 2.8 V). However, the batteries under test were only discharged to a very low capacity (~ 130 mA h $\text{g}_{\text{carbon}}^{-1}$), which is significantly below the observed capacity of most lithium-air batteries. Consequently, such conclusions may only be representative of the very initial charging behavior. To examine the different activities of catalysts towards OER, Shao-Horn et al. used cathodes consisting of non-catalyzed and catalyzed VC and chemically synthesized Li_2O_2 , and found that VC and Au nanoparticles supported on VC (Au/C) were fairly inactive for catalyzing the Li_2O_2 oxidation, while Pt and Ru nanoparticles supported on VC (Pt/C and Ru/C) could significantly increase the kinetics of the Li_2O_2 oxidation, and showed quick initiation of the Li_2O_2 oxidation [255]. In the following study, they revealed three major reaction stages upon the charge process [256]: During the oxidation of the first sub-nanometer layer of Li_2O_2 , the reaction exhibits a sloping voltage profile, requires relatively low overpotentials (< 400 mV), and is insensitive to catalysts and charge rates, which can explain the observation in McCloskey's work. The subsequent flat voltage plateau is found to be highly sensitive to charge rates, catalysts, the thickness of Li_2O_2 (discharge capacity), and the rate at which the Li_2O_2 is formed (discharge rate). This process could be attributed to oxidation of the bulk of the Li_2O_2 with large barriers associated with nucleation and growth of supercritical nuclei. Finally, the potential rises sharply toward the end of the charge reaction, which most likely results from oxidation of parasitic carbonates and electrolytes. This study revealed a number of factors that can influence the OER overpotential and offered a possible explanation to bridge the different thoughts regarding the OER kinetics and the role of catalysts on the OER kinetics. Nazar et al. applied nanocrystalline Co_3O_4 grown on reduced graphene oxide ($\text{Co}_3\text{O}_4/\text{RGO}$), and suggested that $\text{Co}_3\text{O}_4/\text{RGO}$ does not act as conventional electrocatalyst to lower the activation energy through electron transfer, but acts as a promoter to enhance surface transport of Li_xO_2 species by reducing their binding energy in both the forward and reverse electrochemical processes [257]. They further

used *operando* X-ray diffraction (XRD) to observe the oxidation of Li_2O_2 , and found that the oxidation of electrochemically generated Li_2O_2 occurs in two stages: The oxidation proceeds first through a non-crystalline lithium peroxide component; followed at higher potential by the crystalline peroxide via a Li deficient solid solution ($\text{Li}_{2-x}\text{O}_2$) phase [258].

To unravel the OER mechanism in the solid-solid interface, a variety of works has been carried out by both experiments and theoretical calculations. Shao-Horn et al. investigated the oxidation kinetics of commercialized Li_2O_2 on metal nanoparticles of Mo, Cr, Ru, Co and Mn as well as their corresponding metal oxides of MoO_3 , Cr_2O_3 , RuO_2 , Co_3O_4 , and α - MnO_2 [259]. Results showed that the specific activities decreased in the sequence of $\text{Mo} > \text{Cr} \approx \text{Ru} > \text{MoO}_3 \approx \text{RuO}_2 \approx \text{Cr}_2\text{O}_3 > \text{Co} \approx \text{Co}_3\text{O}_4 \approx \alpha$ - $\text{MnO}_2 > \text{Mn}$, and transition metal nanoparticles had higher activities than their oxides counterparts, particularly for highly active ones (e.g., Mo, Cr, Ru). Moreover, a solid-solid catalytic mechanism was proposed through conversion reactions of:



where M_aO_b is the surface composition of the promoter. The Li_2O_2 firstly chemical reacted with the promoter to obtain lithium metal oxide $\text{Li}_x\text{M}_y\text{O}_z$, then electrochemical delithiated, which showed better kinetics than direct oxidation. Thus, the reduced activities from transitional metals to metal oxides result from the relative stability of metal oxides in the presence of Li_2O_2 . Using DFT calculations, Zhu et al. built the interfacial model of solid Li_2O_2 supported on Co_3O_4 surfaces to explain the solid-solid interface catalytic effects. They found that O-rich Co_3O_4 (1 1 1) surface has the highest catalytic effect in reducing charge overpotential and O_2 desorption barrier, while Co_3O_4 (1 1 0) surface leads to a high charge voltage due to its promotion to Li_2O_2 decomposition into Li_2O [260–262]. They also found that the $\text{Li}^+ \rightarrow \text{Li} \rightarrow \text{O}_2$ is the thermodynamically favorable pathway in OER process, and the Lewis acid sites on surfaces have a high catalytic activity due to enhanced electrons transfer. Similar calculations were further carried out on the surfaces of TiO, MnO, NiO, ZnO, MoS_2 , TiCl_3 and TiN. Surface acidity was then concluded to be a descriptor for OER, which showed linear and volcano relationships with charging voltage and Li^+ desorption energies, as shown in Fig. 9 [262].

An important feature of the OER process in lithium-air batteries is that due to the formation of solid Li_2O_2 , the OER kinetics is not only determined by the catalyst itself, but also affected by how Li_2O_2 is produced, which is closely related to the ORR process. Therefore, the OER and ORR processes in lithium-air batteries are entangled, and the study of the OER process should take the ORR process into account. First, the discharge product composition can be affected by catalysts. Yang et al. observed two charge

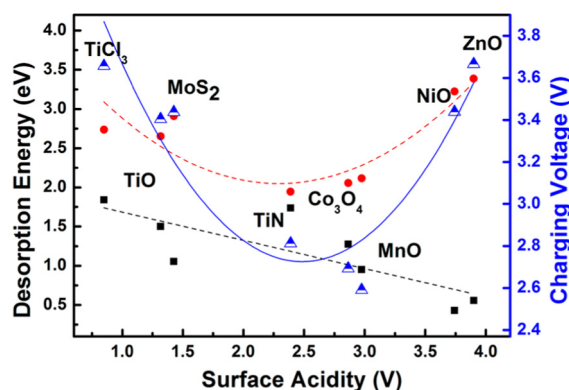


Fig. 9. Desorption energies of Li^+ , O_2 , and charging voltage versus surface acidity [262].

voltage plateaus at 3.2–3.5 V and 4.2–4.3 V, and the lower plateau corresponds to a form of Li_2O_2 with superoxide-like (LiO_2) properties [263]. This finding indicated that the discharge product may be a combination of LiO_2 and Li_2O_2 , rather than pure Li_2O_2 . Later on, the formation of LiO_2 species during the discharge process was reported by Xia et al. [264] and Zhai et al. [265,266]. Liu et al. reported that a cathode composed of ZnO nanoparticles anchored on vertically aligned carbon nanotubes could significantly suppress LiO_2 disproportionation, forming the composites of LiO_2 , Li_3O_4 and Li_2O_2 in nanometer size as the final discharge products [267]. Xiao et al. found that owing to the stronger binding energy between LiO_2 and the Pd surface, amorphous Li_2O_2 with higher ionic conductivities of Li^+ and O_2^{2-} was generated, resulting in the improved charge performance with the voltage as low as 3.08 V [252]. Through using a reduced graphene oxide (rGO) cathode with Ir nanoparticles, Lu et al. developed a lithium-oxygen battery based on LiO_2 as the discharge product, which is stable enough to be repeatedly charged and discharged with a very low charge voltage of ~ 3.2 V [251]. In addition to the product composition, the product morphology also has a great influence on the charge overpotential [77,268]. As Li_2O_2 has poor electrical conductivity, the smaller sized product allows better contact between Li_2O_2 and electrolyte/catalyst/conducting agent, which lowers charge voltage. The changes of product morphology by using catalysts were widely reported, which was changed from large aggregated particles into layer structures or thin films [228,269,270]. The contact situation was greatly improved, reducing the charge voltage.

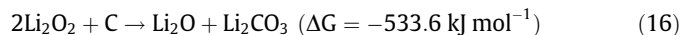
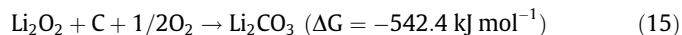
The detailed mechanisms of catalysts in the discharge and charge processes still need further investigations [271]. It is worth noting that in addition to using charge voltage profiles, more characterization techniques should be applied to test the real effects of catalysts. Peng et al. used differential electrochemical mass spectrometry (DEMS) to monitor the charge process. They found that the noble metals (e.g., Pd, Ru) did not work according to the desired electrochemistry [272]. Instead, as shown in Fig. 10, the presence of noble metal catalysts decreased O_2 recovery efficiency but increased CO_2 evolution during charge, impairing the reversibility. Nazar et al. found that for nanostructured metallic carbide (Mo_2C), although the low charge voltages in different electrolytes have been observed [273], an extremely high ratio of e^-/O_2 during charge was revealed (11.6 for TEGDME and >15 for DMSO) by DEMS, demonstrating the misleading of the charge profiles [274]. Hence, the estimation of catalysts should be built on a comprehensive scope to get truly improved performance [46].

3.3. Long-term stability

3.3.1. Instability of carbon materials

In non-aqueous lithium-air batteries, carbon materials have been widely applied as catalysts or supporters due to the large sur-

face area, proper pore size and volume, reaction activities, and economic merits. However, both the highly oxidizing environment and the discharge product (Li_2O_2) can lead to the decomposition of carbon materials [275]. For example, Li_2O_2 can chemically react with carbon through the highly exothermic reactions as:



where ΔG is the free energy change at 300 K. McCloskey et al. used both quantitative isotropically labeled differential DEMS and X-ray photoelectron spectroscopy (XPS) to show that Li_2O_2 reacts with a carbon cathode chemically during discharge to form a thin Li_2CO_3 film at the carbon interface [275]. Such monolayer carbonate layer at the carbon- Li_2O_2 interface causes a ~ 10 – 100 -fold decrease in the exchange current density, leading to the high overpotential during charge. A latter study performed by Bruce et al. demonstrated that carbon is relatively stable below 3.5 V on discharge or charge, especially so for hydrophobic carbon; but is unstable on charging above 3.5 V in the presence of Li_2O_2 . As the major contribution to carbon decomposition occurs on charging above 3.5 V, direct chemical reaction with Li_2O_2 is not primarily responsible, but involves reaction with an intermediate, such as LiO_2 [276]. Since oxidation of Li_2CO_3 on charging to ~ 4 V is incomplete; the net effect is that Li_2CO_3 accumulates in the electrode, leading to rapid polarization on charge as well as electrode passivation and capacity fading on cycling. Moreover, carbon electrodes also have the activity to decompose electrolytes, especially hydrophilic carbon, leading to a short cycling life. Thus, how to increase the cycling life of carbon materials is a big issue.

Since the carbon surface, especially with defects, can cause the decomposition of electrolytes, a natural thought to deal with this issue is to protect the carbon surface. Lu et al. passivated the defects on a porous carbon surface by a protective Al_2O_3 coating applied by atomic layer deposition. Meanwhile, small Pd nanoparticles attached to the surface acted as effective electrocatalysts and promoted the formation of a nanocrystalline form of Li_2O_2 with good electronic transport. Using this architecture, the charge potential was significantly reduced to about 3.2 V, with an overpotential of only about 0.2 V [277]. A similar method was used by Xie et al. through growing a thin layer of FeO_x on three-dimensionally ordered mesoporous carbon. When decorated with Pd nanoparticle catalysts, the new cathode exhibited a capacity greater than $6000 \text{ mA h g}_{\text{carbon}}^{-1}$ and cyclability of more than 68 cycles [278]. Zhou et al. uniformly coated a RuO_2 shell on the surface of core CNTs to prevent the direct contact between CNT and the discharge product Li_2O_2 , and thus avoid or reduce the formation of Li_2CO_3 [279]. The battery with this cathode showed a round-trip efficiency as high as 79% at a current of $100 \text{ mA g}_{\text{carbon}}^{-1}$, with a discharge and charge overpotential of 0.21 and 0.51 V, respectively. Kim et al.

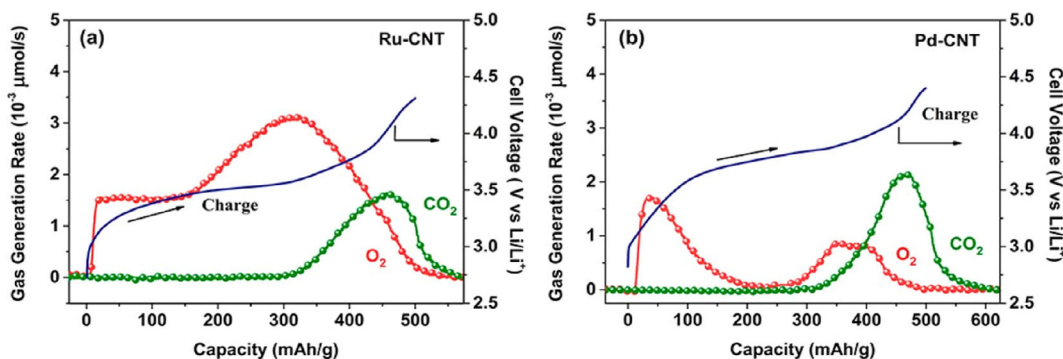


Fig. 10. DEMS results of O_2 and CO_2 evolution during the charge process based on (a) Ru-CNT and (b) Pd-CNT cathodes [272].

used a polydopamine coating on the surface of carbon to not only improve the electrolyte wetting conditions, but also passivate surface defects [207]. Electrochemical tests indicated that the introduction of the polydopamine layer could increase the capacity to $\sim 6000 \text{ mA h g}_{\text{cathode}}^{-1}$, lower the charge potential than the pristine electrode, and increased the cycle number to 49 at the current density of $400 \text{ mA g}_{\text{cathode}}^{-1}$. Cao et al. developed a carbon-embedded $\alpha\text{-MnO}_2$ @graphene nanosheet composite cathode with the graphene fully covered by MnO_2 particles to prevent the side reactions on the surface [280]. XPS analysis showed that the Li_2CO_3 by-product was significantly reduced due to the isolation of carbon with the electrolyte and Li_2O_2 . Thus, the composite cathode could deliver a reversible capacity of $2413 \text{ mA h g}_{\text{composite}}^{-1}$ with an extremely high discharge voltage of 2.92 V and a low charge voltage of 3.72 V.

The above-mentioned approaches focused on the isolation of carbon with the electrolyte and Li_2O_2 . To fully cover the carbon surfaces, a large amount of catalyst/film was usually used (e.g., >50%), lowering the practical specific capacity [279]. Hence, a new strategy targeting the decomposition of side products, especially Li_2CO_3 is of great interest. Wang et al. found that NiO can act as the catalyst to electrochemically decompose Li_2CO_3 after charging up to about 4.1 V [281]. When incorporated nanoporous NiO catalysts on the CNT electrode, the oxidation efficiency of carbonate and carboxylate species could be remarkably enhanced [282]. As shown in Fig. 11, transmission electron microscope (TEM) images at 0, 50%, and 100% depth of the 5th charge show that the products homogeneously passivated on the NiO/CNT appear to form agglomerates next to the NiO in the interim, then disappeared at the completion. More importantly, the nanoporous NiO is stable and has a negligible contribution to the electrolyte oxidation. As a result, NiO greatly improves the cycling life to more than 70 cycles. In addition to NiO, Zhang et al. found that ultrafine iridium-decorated boron carbide ($\text{Ir/B}_4\text{C}$) nanocomposite can decompose Li_2CO_3 with an efficiency close to 100% at a voltage below 4.37 V [283]. They also investigated a redox mediator, binu-

clear cobalt phthalocyanine (bi-CoPc), as a mobile catalyst to facilitate the decomposition of Li_2CO_3 . They demonstrated that bi-CoPc could significantly accelerate Li_2CO_3 oxidation by 2.88 times, improving the cyclability by 8 times to 171 cycles under CO_2/O_2 (2:1, v/v) and 6 times to 211 cycles under N_2/O_2 (78:22, v/v) with cut-off capacity of 500 mA h g^{-1} [284].

3.3.2. Application of non-carbon electrodes

The instability of carbons has driven to develop non-carbon cathode for non-aqueous lithium-air batteries. Cui et al. developed a free-standing cathode composed of Co_3O_4 catalyst and Ni foam by chemical deposition reaction, as shown in Fig. 12a [64]. Consequently, carbon and binder were no longer needed so that the stability was expected to be improved. However, the use of unstable carbonate electrolytes in their work limited the advantages of this nickel-based cathode. Later on, the cathodes based on nickel substrate were developed with direct grown of various materials, such as Co_3O_4 with different morphologies [82,285], sponge-like $\epsilon\text{-MnO}_2$ [286], wave-like NiCo_2O_4 [287], CoO nanowire array [288], flower-like Co-Ti layered double oxide [289]. Kim et al. developed a cathode with Au nanoparticle-coated on Ni nanowire substrate [290]. This optimized cathode not only showed a high capacity of $921 \text{ mA h g}_{\text{Au}}^{-1}$ at the current density of $300 \text{ mA g}_{\text{Au}}^{-1}$, but also exhibited excellent cycle stability with the capacity retention of 98.1% after the 100th cycle at $500 \text{ mA g}_{\text{Au}}^{-1}$.

A TiC cathode was developed based on a stainless steel mesh [195]. The results showed that this cathode could greatly reduce side reactions compared with carbon and exhibit better reversible formation/decomposition of Li_2O_2 even than nanoporous gold. Nazar et al. further demonstrated that even as thin as 3 nm insulating TiO_2 surface layers on TiC can completely inhibit the charge reaction [291]. They further applied metallic Magnéli phase Ti_4O_7 with a crystallite size between 10 and 20 nm as the cathode material [292], and demonstrated that this material can oxidize Li_2O_2 on charge just above 3 V, comparable to gold and TiC, and the majority ($\sim 65\%$) of oxygen release occurs in the 3–3.5 V. Based on a stainless

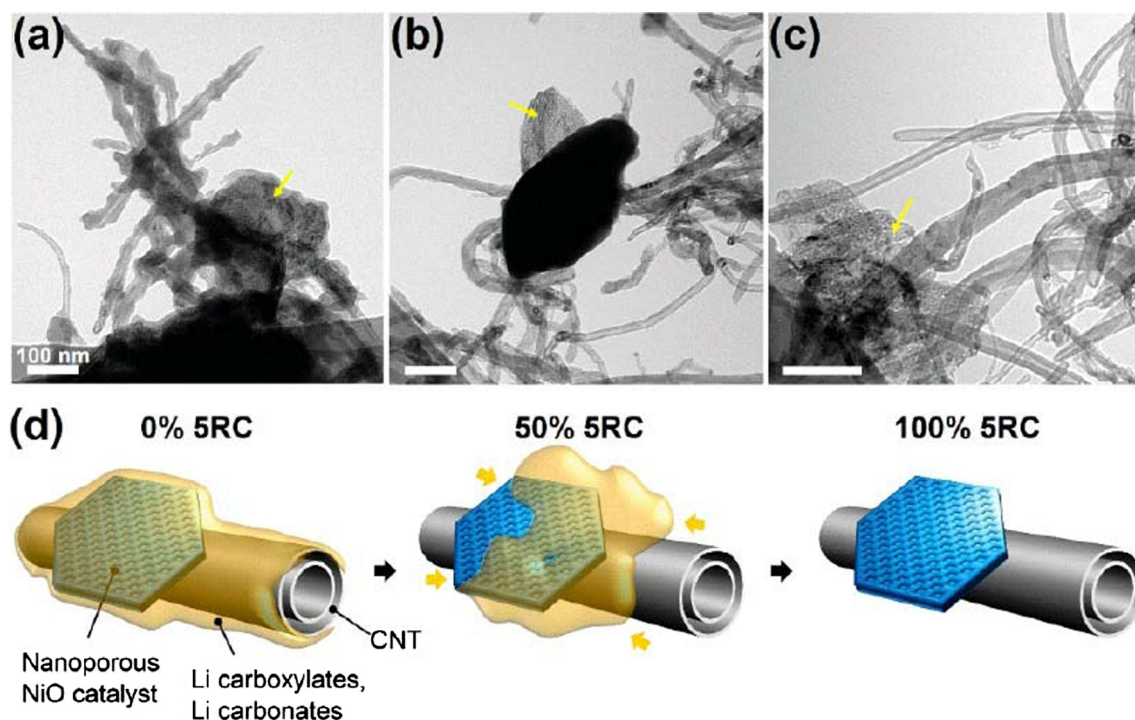


Fig. 11. Decomposition process of the passivation layer of carbonate/carboxylate species on NiO/CNT: (a–c) TEM images at (a) 0, (b) 50%, and (c) 100% accomplished 5th charge. The scale bars are 100 nm. (d) Schematic illustration of carbonate/carboxylate decomposition [282].

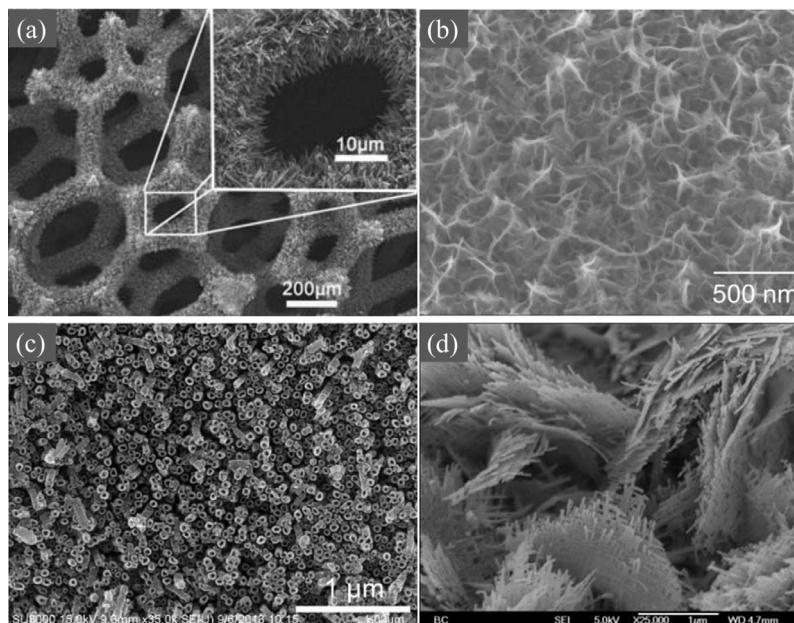


Fig. 12. SEM images of various non-carbon air electrodes: (a) a free-standing Co_3O_4 catalyst at a Ni foam [64]; (b) MnO_2 nanosheets on a stainless steel felt [295]; (c) Pt modified TiO_2 nanotube arrays [297]; and (d) Ru-decorated TiSi_2 nanonets on Ti mesh [301].

steel substrate, other catalysts have been reported, such as manganese oxides (MnO_x) [293–295] (Fig. 12b) and porous AgPd-Pd composite nanotubes [296].

TiO_2 nanotube arrays as the catalyst support were used by Sun et al. to construct a carbon- and binder-free cathode, as shown in Fig. 12c [297]. After being coated with Pt nanoparticles by a cool sputtering approach, a battery with this cathode realized enhanced cyclability of more than 140 cycles with a fixed capacity of $1000 \text{ mA h g}_{\text{Pt}}^{-1}$ at $1.0 \text{ A g}_{\text{Pt}}^{-1}$. Later on, they replaced Pt with RuO_2 catalyst on the TiO_2 nanotube arrays, and the battery exhibited 130 cycles with a fixed capacity of $1000 \text{ mAh g}_{\text{loading}}^{-1}$ at $1770 \text{ mA g}_{\text{loading}}^{-1}$ [298].

A stable conductive indium tin oxide (ITO) embedded with Ru nanoparticles was fabricated on a Ti mesh and introduced as a carbon-free cathode [299]. A good stability with 50 cycles was obtained, due to the superior catalytic activity of Ru nanoparticles toward ORR and OER and the absence of carbon to avoid the formation of Li_2CO_3 . However, due to the heavy mass of ITO, the specific capacities were still low. To overcome such issue, they applied Sb-doped tin oxide (STO) supported Ru nanoparticles (Ru/STO) on an Al mesh [300]. A battery with this cathode obtained a large specific capacity of $750 \text{ mA h g}_{\text{loading}}^{-1}$ at 0.1 mA cm^{-2} . Based on Ti mesh, Ru-decorated TiSi_2 nanonets (Fig. 12d) [301], and TiSi_2 with Co_3O_4 and Pd have also been reported [302]. The resulting heteronano structure enabled a lithium-air battery that could be discharged and charged for more than 100 cycles with average round-trip efficiencies larger than 70% [301]. Zhao et al. developed a Ti nanowire arrays with Au nanoparticles on Ti foam. A battery with this cathode can be cycled at a current density of 5 A g^{-1} with a capacity limitation of 1000 mA h g^{-1} for 640 cycles [303].

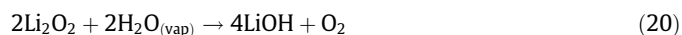
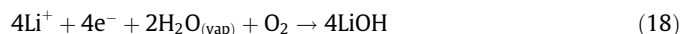
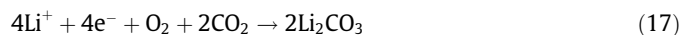
With the applications of non-carbon electrodes in non-aqueous lithium-air batteries, the formation of Li_2CO_3 is effectively suppressed, leading to an improved cycling life. However, it should be noting that even applying non-carbon electrodes, decomposition may still occur. For example, Veith and Dudney demonstrated that nickel foam promotes the electrochemical degradation of carbonate-based electrolytes at potentials greater than 3.5 V [304]. In relatively stable electrolyte DMSO, the decomposition caused by Ni form has been demonstrated [305]. Moreover, the lar-

ger densities of non-carbon materials (e.g., Ni, Au) will result in a low specific capacity. Therefore, both the capacity penalty and the long-term stability should be taken into account when developing non-carbon electrodes.

3.4. Operation in the air

3.4.1. Oxygen selective membranes

To achieve the most striking feature of high capacity and energy density, obtaining oxygen from atmospheric air is essential. However, most lithium-air batteries investigated in literature were tested in a pure oxygen environment with an oxygen pressure equal to or greater than 1.0 atm , while the common ambient atmosphere is composed of oxygen with a partial pressure of only 0.21 atm and other gases, such as nitrogen, carbon dioxide, and water moisture. Even though a lithium-protected anode could be applied in the battery to avoid the contamination of lithium metal, carbon dioxide and water moisture could lead to side reactions in the cathode during discharge as follows:



For non-aqueous and solid-state lithium-air batteries in which Li_2O_2 is the dominant discharge product, although carbon dioxide and water moisture could lead to an increase of capacity [137,306,307], the poor rechargeability of LiOH and Li_2CO_3 has been theoretically [308] and experimentally demonstrated [138,264]. Hence, one solution to enable the operation of lithium-air batteries in ambient air is introducing an oxygen selective membrane to prevent the contaminations of other gasses.

Zhang et al. evaluated several polymer membranes as oxygen diffusion membrane and moisture barrier [309]. It showed that high-density polyethylene can provide sufficient oxygen flow at a

current density of $0.05\text{--}0.1\text{ mA cm}^{-2}$. They further improved the battery stability with a surface-modified polypropylene separator and obtained a specific energy of $344\text{ Wh kg}_{\text{battery}}^{-1}$ in ambient air with a relative humidity (RH) of $\sim 20\%$ [310]. Liu et al. applied silicon oil as an O_2 -selective liquid, and found that the silicon oil of high viscosity showed the better performance [311]. The new membrane materials and structures were effective in blocking the moisture while allowing oxygen permeate through, and could even prevent the evaporation of electrolyte. Based on silicon rubbers, Crowther et al. developed an oxygen selective membrane in a primary non-aqueous lithium-air battery, which exhibited high permeability for oxygen and impeded water transport from the atmosphere and solvent loss [312]. They also applied Teflon coated fiberglass cloth as the O_2 selective membrane for primary non-aqueous lithium-air batteries [313]. These membranes could transport O_2 to support a rate of approximately 0.2 mA cm^{-2} , and suppress the electrolyte evaporation with approximately 2% loss over 40 days. Zhou et al. developed a hydrophobic diffusion layer based on carbon and PTFE to suppress water moisture from the air in a quasisolid-state lithium-air battery [99]. With this hydrophobic diffusion layer, a battery exhibited a discharge capacity of $10,730\text{ mA h g}_{\text{carbon}}^{-1}$ at 2.0 V and then a completely reversible charge process at about 4.0 V with a mid-potential deviation of 1.17 V . Cao et al. developed a novel mixed matrix membrane by incorporating polydopamine-coated metal organic framework crystals into a polymethylmethacrylate matrix, which possesses the advantages of high oxygen permeability, high capability of carbon dioxide capture, and excellent hydrophobic behavior [314]. When operated at the ambient atmosphere with 30% RH, a battery with this membrane exhibited a discharge capacity of $1480\text{ mA h g}_{\text{carbon}}^{-1}$ and 66 cycles at the fixed capacity of $450\text{ mA h g}_{\text{carbon}}^{-1}$.

For oxygen selective membranes, the substantial thickness and limited surface area can cause an increase in the oxygen transport distance and a limited oxygen permeation area, resulting in a sacrifice in the battery performance. To address these issues, Zhu et al. reported a solid-state lithium-air battery with a thin silicone oil film coated on the cathode pores [315]. Different from the traditional design (Fig. 13a), this integrated design as schemed in Fig. 13b can not only block water vapor and carbon dioxide from reaching reaction sites but allow a high rate of oxygen transport. As a result, a battery with this integrated oxygen selective membrane can operate in ambient air at $5000\text{ mA h g}_{\text{carbon}}^{-1}$ for 50 cycles and reaches a charge/discharge rate as high as 2.0 mA cm^{-2} .

Although the integrated oxygen selective membrane shows the promising for practical application, such design is hard to be applied in other types of lithium-air batteries due to the liquid electrolytes. Hence, developing a membrane with high oxygen permeability and selectivity is still challenging.

3.4.2. Decomposition of side products

In addition to developing the oxygen selective membrane, a new strategy to enable the operation of a lithium-air battery in ambient air is to find a suitable catalyst that can efficiently promote the decomposition of side products. The main side products in non-aqueous and solid-state lithium-air batteries are lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH) come from carbon dioxide and water in ambient air. The combination of proper catalysts may realize the operation of lithium-air batteries in ambient air.

Wang et al. used gold/ δ -manganese-dioxide ($\text{Au}/\delta\text{-MnO}_2$) catalyst to evaluate the practical operation in ambient air. $\text{Au}/\delta\text{-MnO}_2$ could catalyze the decomposition of LiOH in some extent, and the battery was able to be operated in open air (RH = 35%) for 16 cycles [316]. Wu et al. integrated a hydrophobic ionic liquid-based electrolyte and a cathode composed of electrolytic MnO_2 and RuO_2 supported on Super P for a lithium-air battery. The battery can

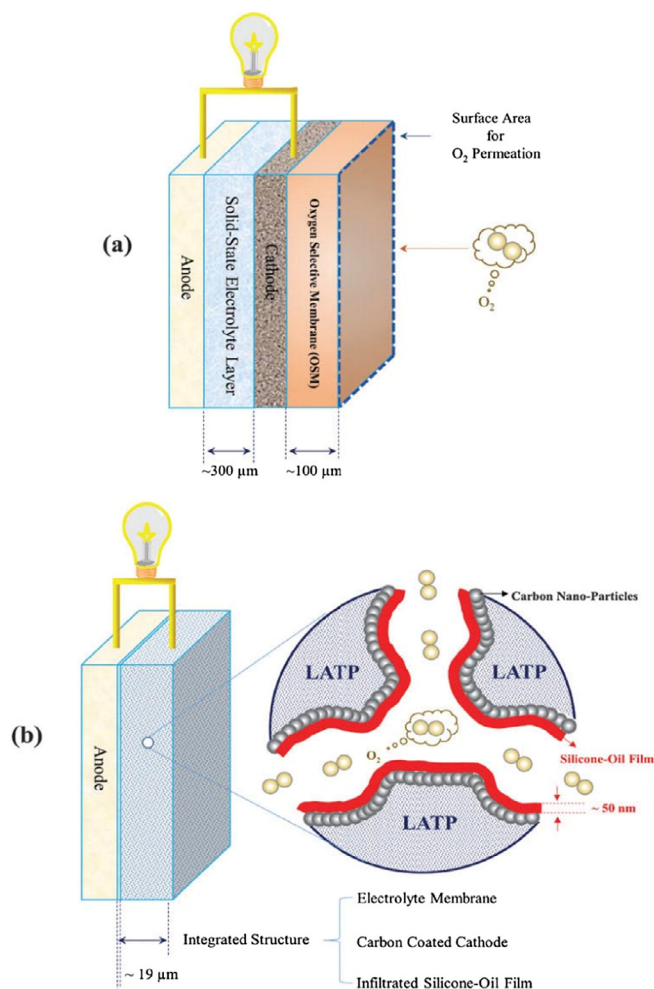


Fig. 13. Schematic representations of architectures for (a) conventional solid-state lithium-air batteries with a thick solid-state electrolyte layer and a planar oxygen selective membrane, and (b) an integrated structure of a carbon-coated LAMP cathode with a silicone-oil film inside [315].

be sustained in a humid atmosphere (RH = 51%) with a high discharge voltage of 2.94 V and the low charge voltage of 3.34 V for 218 cycles due to the synergistic effect of the unique hydrophobic electrolyte and the electrochemical activity towards LiOH [317]. Tan et al. fabricated a cathode composed of RuO_2 nanoparticle-decorated NiO nanosheets, in which RuO_2 can catalyze ORR and OER, as well as promote the decomposition of LiOH , while NiO nanosheets can promote the decomposition of Li_2CO_3 and meanwhile provide a large surface area for the utilization of RuO_2 nanoparticles [305]. This electrode enables the battery to be operated in ambient air with a RH of $60 \pm 5\%$ at 500 mA h g^{-1} for 200 cycles (800 h), with stable Coulombic efficiency (100%) and high round-trip efficiency ($\sim 75\%$) as presented in Fig. 14. Recently, Wang et al. developed a battery supported by a polymer electrolyte containing 0.05 M LiI . The polymer electrolyte alleviated the lithium passivation induced by attacking air, and the I^-/I_2 conversion in polymer electrolyte acted as a redox mediator to facilitate the electrochemical decomposition of discharge products during the charge process. As a result, the battery could be stably cycled 400 times in ambient air with a RH of 15% [318].

Even with progress, the operation in the air still has a long way to go. Developing functional membranes on the air electrode to selective oxygen and suppress the liquid electrolyte evaporation, and meanwhile applying catalysts with high activities toward side products, are great challenges.

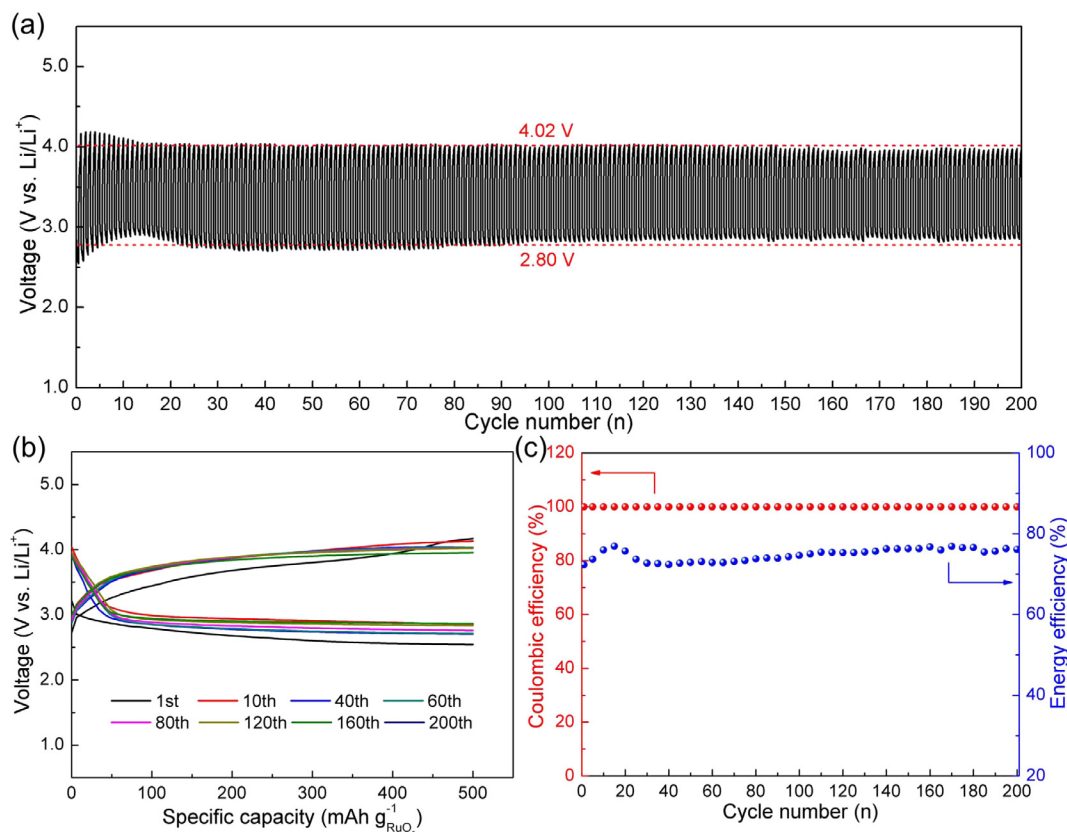


Fig. 14. Cycling stability of a battery fitted with the RuO₂/NiO cathode in ambient air: (a) Discharge-charge profiles with cycling; (b) discharge-charge profiles of selected cycles; and (c) coulombic efficiency and round-trip efficiency [305].

3.5. Summary of challenges in air electrodes

For non-aqueous lithium-air batteries, during discharge the surface area and pore structure of the air electrode are changed due to the formation of solid discharge product Li₂O₂, affecting the transporting kinetics. It has been shown that the product morphologies are associated with electrolyte properties and distribution, electrode surfaces and structures, and operating conditions, which eventually determine the discharge capacity. Hence, to obtain a high capacity, new insights into the complex correlations are required and will give important guidance for the structure design and optimization. During charge, the potential for the electrochemical decomposition of Li₂O₂ is high, resulting in low round-trip efficiency. To this end, various kinds of catalysts have been applied in the air electrode. Although certain striking achievements have been made, the decomposition mechanism and the role of catalysts are still under investigation, making it difficult in catalyst selections. Carbons, owing to the high specific surface area, proper porosity, and low cost, are usually used as the air electrode materials with a high discharge capacity. However, carbon materials may be corroded or promote the decomposition of electrolytes in the oxidizing environment to form carbonate species covering the electrode surface, leading to a short cycling life. As a result, applying a protective layer or catalysts with activities towards the decomposition of carbonate species onto carbon surfaces may be effective in increasing the cycling life. In addition, non-carbon electrodes exhibit a prolonged cycling life and therefore attract research interests. However, because of their lower specific surface areas than those of carbons, the actual discharge capacities of non-carbon electrodes are usually low and should be further improved for practical application.

For aqueous and hybrid lithium-air batteries, the basic reactions are similar to that in alkaline solutions, with the formation of the soluble product LiOH. To facilitate the electrochemical reactions in the discharge and charge processes and increase the round-trip efficiency, developing cost-effective catalyst materials is important, especially with bifunctional catalytic activities for both ORR and OER. As the oxygen solubility and diffusivity in liquid electrolytes are not high enough, facilitating the transport of species through designing novel electrode structures (e.g., using a flow system) is crucial for improving the power output.

For solid-state lithium-air batteries, although the discharge product is reported to be the solid Li₂O₂ as that in non-aqueous lithium-air batteries, its formation and decomposition mechanisms are still unknown, and the effects of catalysts have few been investigated yet, resulting in the lack of guidance for further improving the round-trip efficiency. In addition, as lithium ion and electron can only transport through the solid electrolyte and the air electrode, respectively, the reaction boundaries are limited, resulting in a low discharge capacity. Hence, novel structures with the integrated electrolyte-electrode should be developed.

The reported lithium-air batteries are usually operated in pure oxygen instead of ambient air, which is attributed to the fact that other gasses can participate in the reaction to form side products that passivate the air electrode and lead to the failure of the battery. Whereas the high theoretical energy density of lithium-air batteries can be delivered only when they can be operated in ambient air. To achieve this target, it is essential to apply catalysts with activities toward the decomposition of side products and/or develop an oxygen-selective membrane with high oxygen selectivity and permeability. Such a membrane should meanwhile suppress the evaporation of liquid electrolytes to enable the long-term operation.

4. Lithium electrodes

In most reported lithium-air batteries, lithium metal is directly chosen as the anode, which is expected to achieve the highest capacity and energy. However, using lithium metal as the electrode has long-standing issues including the uncontrollable dendritic lithium growth and the limited Coulombic efficiency during repeated charge and discharge cycles [319]. In non-aqueous lithium-air batteries, the reactions on the interface between lithium and electrolytes are far more complicated due to the participation of oxygen. Even using a solid-state lithium ion conducting membrane to block oxygen crossover as the situations in aqueous, hybrid, and solid-state lithium-air batteries [37,38], the dendrite formation is still a serious issue. Therefore, in this section, we first discuss the effect of oxygen crossover on the degradation of the lithium electrode in non-aqueous lithium-air batteries and possible solutions. Then, the dendrite formation and suppression approaches will be introduced. Furthermore, alternatives of lithium metal in the application of lithium-air batteries will also be summarized.

4.1. Contaminations from O_2/H_2O crossover

In non-aqueous lithium-air batteries, glass fiber paper or polypropylene membranes are widely used as separators. Such separators are of porous structure and saturated with electrolytes, which cannot prevent the dissolved oxygen from reacting with the lithium. Meanwhile, by-products (e.g., H_2O , CO_2) from decompositions of electrolytes and cathodes can also diffuse through the separator and react with the lithium anode.

The SEI formation in the presence of O_2 in the carbonate electrolyte was studied by Younesi et al. [320]. The results indicated that the presence of O_2 not only influenced the composition of the SEI, but also increased the resistance of the battery and affected the lithium stripping and plating. Based on a more stable solvent, TEGDME, Assary et al. investigated its stability in an oxygen environment at the lithium anode [321]. The results demonstrated the formation of LiOH and carbonates at the anode, which block the migration of lithium ions, leading to the failure of the anode. Shui et al. investigated the reversibility of the anodic lithium inside of a lithium-air battery using spatially and temporally resolved synchrotron X-ray diffraction and 3-D micro-tomography technique [322]. The results revealed a constant conversion of metallic Li to LiOH during both discharge and charge stages, as shown in Fig. 15, possibly resulting from the reaction of Li with H_2O formed through the electrolyte decomposition.

Since the contaminations from O_2/H_2O crossover can be a significant problem that leads to the failure of lithium-air batteries [13], protecting the lithium anode will be important for achieving a long cycle life. Although using a glass-ceramic membrane (e.g., NASICON-type oxides) can prevent O_2/H_2O crossover [37], the heavy densities cause a decrease in the practical capacity. Hence, other approaches that do not sacrifice the capacity should be applied. Kim et al. introduced poreless polyurethane separator as a simple and effective solution to solve the crossover issue, which prevents O_2 and H_2O while lithium ion diffusion is facilitated by high electrolyte uptake through the interchain space. As a result, a persistent capacity of 600 mA h g^{-1} is preserved for more than 200 cycles. Zhang et al. proposed a facile while effective strategy to protect the Li anode through artificially fabricating a protection film on the metal lithium [323]. They added fluoroethylene carbonate (FEC) into the traditional 1.0 M LiF_3SO_3 /TEGDME electrolyte, and then fabricated an artificially generated protection film consists of Li_2CO_3 , LiF, polyene, and C–F bond-containing compound through an electrochemical strategy. The obtained FEC-treated Li

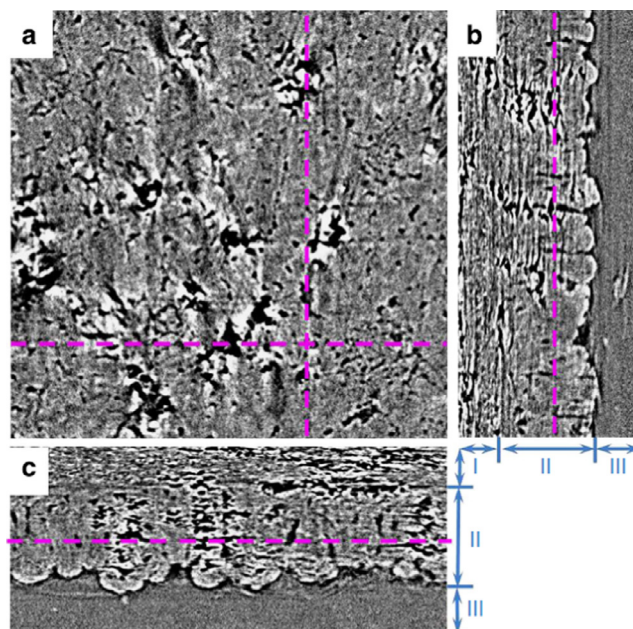
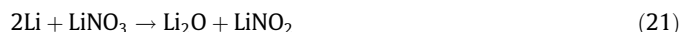


Fig. 15. X-ray tomography images of the used anode: (a) Planar cross-section of LiOH layer on the anode. (b, c) Vertical cross-sections through the anode and a small portion of the separator. I: separator, II: LiOH layer and III: Li metal. The dimension of (a) is $823 \mu\text{m} \times 806 \mu\text{m}$ [322].

metal anode could enable more than 100 stable cycles with a fixed capacity of 1000 mA h g^{-1} at a current density of 300 mA g^{-1} , which is more than three times that of the batteries with the pristine Li metal.

In addition to fabricating a protective membrane/film, another useful method to protect the lithium anode is to form a stable SEI on the lithium surface. Walker et al. demonstrated the successful cycling of a lithium anode in the presence of the DMA solvent by employing $LiNO_3$ as the lithium salt to stabilize the SEI through the following mechanism [324]:



where insoluble Li_2O contributes toward a stable SEI on the lithium anode surface. A lithium-air battery could cycle for more than 2000 h (>80 cycles) at a current density of 0.1 mA cm^{-2} with a consistent charge profile, good capacity retention, and oxygen as the primary gaseous product formed during charge. In addition, no evidence of dimethylamine was observed in the presence of 1 M $LiNO_3$, suggesting that the SEI formed in this electrolyte inhibited the reaction between DMA and lithium metal. In a subsequent study, a symmetric Li/Li battery using the same electrolyte could cycle for more than four months under O_2 without any observed failure, showing its effectiveness in maintaining SEI stability [325]. To understand such phenomenon, Uddin et al. demonstrated that the process of persistent stabilization of the SEI with the appearance of O_2 can be summarized by a sum of reactions following Reaction 21 as [326]:



which enables the formation of a stable SEI even with O_2 crossover.

4.2. Dendrite issues

The dendrite growth can significantly increase the surface area of the lithium, which tends to consume a larger amount of elec-

trolyte and generate a fresh passivation layer. Due to the consumption or the degradation of electrolytes, battery performance will deteriorate after a number of cycles. Moreover, the growing dendrites may damage the separator and reach to the cathode, resulting in an internal short-circuit and leading to a severe safety issue. Lithium dendrite growth in various non-aqueous [327–330] and polymer electrolytes [331–336] has been widely observed and studied, which raises critical challenges for the development of lithium-air batteries.

Several methods to suppress the lithium dendrite have been reported in lithium-air batteries. Lee et al. reported a composite protective layer (CPL) comprised of Al_2O_3 and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) for the lithium metal [337]. Al_2O_3 was introduced to provide a sufficient mechanical strength to suppress dendrite initiation and growth, and PVDF-HFP was to impart fast lithium ion transport through the CPL by forming a gel polymer electrolyte with liquid electrolyte. A lithium-air battery with the CPL-coated lithium metal anode exhibited a discharge capacity of $1000 \text{ mA h g}_{\text{carbon}}^{-1}$ at the 80th cycle, which was more than 3 times compared to that of a battery without such layer ($320 \text{ mA h g}_{\text{carbon}}^{-1}$). The SEM images for the cycled pristine lithium metal are presented in Fig. 16. The lithium metal without CPL presented the formation of mossy lithium, which is typical of dendritic growth and subsequent electrolyte deposition. While the surface of the lithium metal anode protected by the CPL was quite smooth, indicating the effective protection of the lithium anode. Kang et al. employed anodized aluminum oxide (AAO) membranes as model nanoporous separators with high density, uniform, nanometer-sized pores instead of common polymeric separators with irregular, tortuous pores in a non-aqueous lithium-air battery [338]. By employing the AAO membrane, uniform pathways of lithium ion are expected, which likely lead to laterally homogeneous plating/stripping of lithium. As a result, the surface roughening of lithium metal anode during cycles was suppressed and the cycle efficiency was strikingly improved. Recently, a new method using redox mediator to hinder the growth of lithium dendrite was reported by Lee and Park, who used CsI to dissolve in the electrolyte and ionize into Cs^+ and I^- , which perform their roles in the lithium anode and cathode, respectively. The I^- ions in the electrolyte facilitate the dissolution of Li_2O_2 in the cathode as a redox mediator, while the Cs^+ ions act as an electrostatic shield at the sharp points of the lithium anode, hindering the growth of lithium dendrite. The combined effects of reduced parasitic reactions and hindered Li-dendrite growth successfully improve the cycling life [339].

Although the lithium metal is the least widely studied component in lithium-air batteries, it is closely related to the cycling life

and safety of the battery. Therefore, further studies are required to develop a stable and robust lithium anode.

4.3. Alternatives of lithium metal

Given the stability issues associated with the safety concerns, alternative materials of lithium metal may be required for the anode. To avoid the reaction between the electrolyte and the anode and provide a stable lithium ion source, LiFePO_4 , which is widely used in Li-ion batteries, has been applied as the anode material in lithium-air batteries [129,294,340]. However, such material will lead to a capacity of 170 mA h g^{-1} only, which is a great sacrifice compared to that of lithium metal (3862 mA h g^{-1}). In addition, the combination of LiFePO_4 and O_2 leads to a potential that cannot be practically used. Therefore, alternatives of lithium metal should be stable and safe, and meanwhile have a high theoretical energy density.

To give a step forward to a safe lithium-air battery, Hassoun et al. demonstrated that a lithiated silicon-carbon composite electrode could be used to successfully replace the typically used lithium anode [341]. The anode was prepared through lithiation of a Si-C composite to form $\text{Li}_{2.6}\text{Si}$ with an expected specific capacity of 2300 mA h g^{-1} . This anode enabled a battery with a stable capacity of $1000 \text{ mA h g}_{\text{carbon}}^{-1}$ over 15 cycles. Meanwhile, the theoretical energy density of this $\text{Li}_x\text{Si-O}_2$ battery by considering both the anode and cathode was estimated to 980 W h kg^{-1} , higher than a conventional lithium-ion battery with graphite anode and lithium cobalt oxide cathode (384 W h kg^{-1}). Guo et al. prepared a lithiated Al-carbon composite electrode with a uniform SEI film as the anode in a non-aqueous lithium-air battery [342]. The discharge-charge voltage profiles of the lithium-air battery with a $\text{Li}_x\text{Al-C}$ anode could be cycled over 20 cycles in an oxygen atmosphere at a fixed capacity of $1000 \text{ mA h g}_{\text{cathode}}^{-1}$ with a total polarization of 1.3 V, much lower than that of a battery with a lithium anode (1.6 V). A silicon anode for hybrid lithium-air batteries was proposed by Teranishi et al. [343]. The silicon anode was composed of mechanically milled silicon powder with carbon fiber and a polyimide binder, which was capable to charge to $4000 \text{ mA g}_{\text{carbon}}^{-1}$ at 0.272 mA cm^{-1} . However, the cyclic performance was poor, due to the volume change of the silicon anode. Thus, to improve the cyclic performance, external pressure may be applied to the silicon anode.

In searching for the alternative anode materials, two-dimensional (2-D) materials, such as MXene [344], phosphorene [345], and borophene [346], have attracted much attention due to the high surface-volume ratio, small volume changes, and unique electronic properties. In addition, they were predicted to

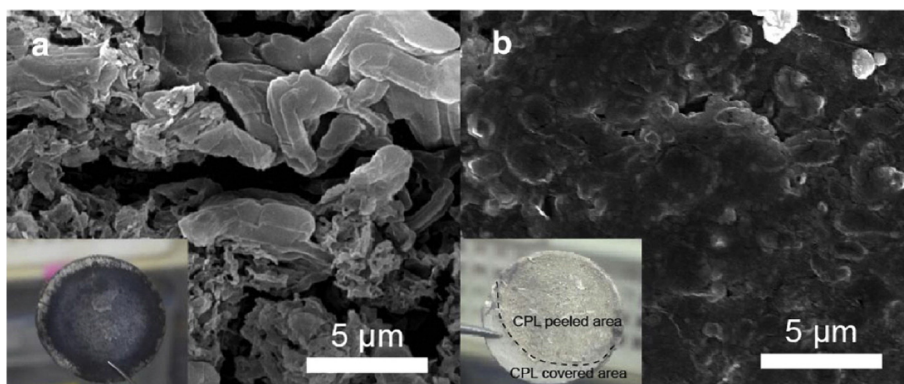


Fig. 16. SEM images of the Li electrode (a) without CPL and (b) with CPL after 80 cycles, the insets show a photograph of cycled Li electrodes [337].

be the potential anode candidates because of their high specific capacity and low lithium diffusion barrier. Their future application in lithium-air batteries is worthwhile expecting.

4.4. Summary of challenges in lithium electrodes

In this section, the challenges for lithium electrode and the corresponding strategies have been reviewed. Although the reactions between metallic lithium and organic electrolytes in lithium-based batteries have been intensively studied, the appearance of oxygen and other side products makes the reactions on the interface between the lithium anode and the electrolyte far more complicated. These undesired reactions consume lithium and result in a thick passivation layer on the lithium surface, increasing the lithium ion transport resistance and eventually leading to the performance decay and even the failure of the battery. Consequently, fabricating a protective membrane or forming a stable SEI on the lithium surface are crucial for lithium protection. In addition, the lithium dendrite formation and growth are crucial for the stable performance and safety. The related research in lithium-air batteries, however, is still rare in the current stage. The detailed dendrite formation mechanism, associated with the corresponding suppression approaches, calls for in-depth research. Since the metallic lithium brings the above-mentioned complex issues, alternative materials, such as Li-based alloys and 2-D materials, have attracted great interests. To practically develop alternative materials, a trade-off among the energy density, safety, and stability should be carefully considered.

5. Concluding remarks and perspectives

Although lithium-air batteries offer attractive prospect as a future electric power source, various scientific and technical limitations need to be overcome before they can become practical. In particular, the low practical capacity, low round-trip efficiency, and poor cycling life need to be addressed. This review considers four types of lithium-air batteries. The main challenges and future directions for the electrolyte, air electrode, and lithium electrode corresponding to each battery type are summarized as follows:

Electrolytes are considered as the most critical components to achieving a long cycling life:

- (i) For non-aqueous electrolytes, one of the main challenges at the current stage is the search for stable solvents and lithium salts. In addition, functional additives in electrolytes, aiming at stabilizing the electrolyte and/or promoting electrochemical reactions, need to be deeply investigated.
- (ii) For solid-state electrolytes, search for the one with a high lithium ion conductivity, a very low diffusion coefficient for the other species, and a high stability towards both electrolyte and lithium metal is in great need. In addition, polymer electrolytes with the promising applications in flexible lithium-air batteries should draw more research interests.
- (iii) For aqueous electrolytes, choosing the suitable one with a high energy density and a high stability towards the solid-state electrolyte membrane is significant.

In addition to electrolytes, air electrodes, which provide the place for electrochemical reactions, represent major challenges:

- (i) To obtain a high practical capacity, the reaction pathways among oxygen, lithium ions, and electrons should be maintained as long as possible. Consequently, the structure in different types of lithium-air batteries should be well designed. Specifically, for solid-state lithium-air batteries, the reaction

boundaries should be enlarged; for non-aqueous lithium-air batteries, detailed investigations on the correlations between the cathode microstructures and the synergy transport in the electrolyte are required; for liquid-based (including non-aqueous, aqueous, and hybrid) lithium-air batteries, facilitating the transport of species in the liquid electrolytes (e.g., optimizing the electrolyte distribution inside the cathode, or developing a flow system) is important.

- (ii) To facilitate the electrochemical reactions in the discharge and charge processes, catalysts are introduced. In aqueous electrolytes, finding inexpensive alternatives to noble metals, especially with bifunctional catalytic activities for both ORR and OER, should be the ultimate target. For non-aqueous and solid-state lithium-air batteries, understanding the roles of catalysts in the formation and decomposition of the solid product is essential to develop effective catalysts. In addition, advanced characterization approaches for monitoring the discharge and charge processes should be applied.
- (iii) To ensure a long cycling life, the instabilities of carbon materials should be well addressed. Effective approaches include applying a protective layer onto the carbon surfaces and applying catalysts with activities towards the decomposition of carbonate species. Besides, stable non-carbon cathodes have attracted great research interests, but achieving a large practical discharge capacity is challenging.
- (iv) To operate the battery in ambient air instead of pure oxygen, developing an oxygen-selective membrane with high oxygen selectivity and permeability, or applying catalysts with activities for the decomposition of side products (e.g., Li_2CO_3 and LiOH) are required. Meanwhile, a membrane that can suppress the evaporation of liquid electrolytes is needed for long-term operation of non-aqueous, aqueous, and hybrid lithium-air batteries.

Metallic lithium is typically chosen as the anode material in most studies of lithium-air batteries, which is expected to achieve the highest capacity and energy. The challenges for using lithium include:

- (i) In non-aqueous lithium-air batteries, the reactions on the interface between the lithium anode and electrolytes are far more complicated due to the oxygen/water/side products crossover. Consequently, protecting the lithium electrode through suitable membranes or passivation films is important.
- (ii) Although lithium dendrite formation in lithium-air batteries has been few reported in the current stage, the suppression approaches are important in further research.
- (iii) Given the stability issues associated with safety concerns, alternative materials of metallic lithium with a high stability, safety, as well as a high theoretical energy density are necessary.

Significant future works focusing on these challenges are essential to realize a safe, fully rechargeable lithium-air battery with high capacity, high energy density, and long cycling life for future EV industries.

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