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Electrode Protection in High-Efficiency Li-O₂ Batteries

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ABSTRACT: The aprotic $\text{Li}-O_2$ battery possessing the highest theoretical energy density, approaching that of gasoline, has been regarded as one of the most promising successors to Li-ion batteries. Before this kind of battery can become a viable technology, a series of critical issues need to be conquered, like low round-trip efficiency and short cycling lifetime, which are closely related to the continuous parasitic processes happening at the cathode and anode during cycling. With an aim to promote the practical application of $\text{Li}-O_2$ batteries, great effort has been devoted to identify the reasons for oxygen and lithium electrodes degradation and provide guidelines to overcome them. Thus, the stability of cathode and anode has been improved a lot in the past decade, which in turn significantly boosts the electrochemical performances of $\text{Li}-O_2$ batteries. Here, an overlook on the electrode protection in high-efficiency



 $Li-O_2$ batteries is presented by providing first the challenges of electrodes facing and then the effectiveness of the existing approaches that have been proposed to alleviate these. Moreover, new battery systems and perspectives of the viable near-future strategies for rational configuration and balance of the electrodes are also pointed out. This Outlook deepens our understanding of the electrodes in Li-O₂ batteries and offers opportunities for the realization of high performance and long-term durability of Li-O₂ batteries.

1. INTRODUCTION

The aprotic $Li-O_2$ battery with a theoretical energy density of \sim 3500 Wh/kg far transcends those of today's available battery systems, especially the widely used Li-ion batteries, and thus has been recognized as a most promising post Li-ion battery technology.^{1,2} A typical Li–O₂ battery consists of a porous O₂ diffusion cathode, a metal Li anode, and an organic Li conducting electrolyte (Figure 1) and follows the electrochemical reaction of $2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$ with the formation and decomposition of Li2O2.3,4 Although this reaction looks simple, the actual process is quite complicated. During discharge, the battery can follow either a surfaceadsorption route (eqs 1 and 2, the ads means the species adsorb on the cathode surface) or a solution-mediated route (eqs 3-5, the sol refers to the species dissolve in the solution).²⁻⁴ The main difference between these two routes is whether the reduced superoxide can dissolve into the electrolyte solution to facilitate the solution growth of Li₂O₂. Instead of the "sudden death" of the battery by

$$O_2(g) + Li^+(sol) + e^- \rightarrow LiO_2(ads)$$
(1)

$$\mathrm{LiO}_{2}(\mathrm{ads}) + \mathrm{Li}^{+}(\mathrm{sol}) + e^{-} \rightarrow \mathrm{Li}_{2}\mathrm{O}_{2}(\mathrm{ads}) \tag{2}$$

 $\text{LiO}_2(\text{sol}) \leftrightarrow \text{Li}^+(\text{sol}) + \text{O}_2^-(\text{sol})$ (4)

$$2\text{LiO}_2(\text{sol}) \to \text{Li}_2\text{O}_2(\text{sol}) + \text{O}_2(\text{g})$$
(5)

the full cover of Li_2O_2 on the cathode surface via the surfaceadsorption route, the solution-mediated route can enable the growth of large sized Li_2O_2 , leading to higher discharge capacities.⁴ Different from the discharge process, there is still less consensus on the charge process. In early studies, researchers found that the decomposition of Li_2O_2 was through a direct $2e^-$ electrochemical process (eq 6), since no LiO_2 intermediate could be detected.^{2,4} Later, it was confirmed that the charge process could proceed via a mixed solid-solution and liquid-phase mediated decomposition process (eqs 7–10),^{2,4} which depends on the solvating properties of

$$Li_2O_2(s) \to 2Li^+(sol) + 2e^- + O_2(g)$$
 (6)

$$\operatorname{Li}_{2}O_{2}(s) \to \operatorname{Li}_{2-x}O_{2}(s) + x\operatorname{Li}^{+}(\operatorname{sol}) + xe^{-}$$
(7)

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or

(

$$D_2 + \text{Li}^+(\text{sol}) + e^- \rightarrow \text{Li}O_2(\text{sol})$$



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(3)

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Outlook



Figure 1. Schematic illustration and main challenges of aprotic Li-O₂ batteries.

$$\text{Li}_{2-x}\text{O}_2(s) \to (2-x)\text{Li}^+(\text{sol}) + (2-x)\text{e}^- + \text{O}_2(g)$$
(8)

or

$$Li_{2-x}O_2(s) \rightarrow LiO_2(sol) + (1-x)Li^+(sol) + (1-x)e^-$$
(9)

$$2\text{LiO}_2(\text{sol}) \to \text{Li}_2\text{O}_2(s) + \text{O}_2(g)$$
(10)

the electrolyte. It is clear that both the discharge and charge processes are often accompanied by the presence of reactive oxygen species, like O_2^{-} , O_2^{2-} , and singlet oxygen (1O_2).^{5,6} These active intermediates together with the insulating Li₂O₂ discharge product induce the electrochemical reaction to proceed in a sluggish manner and the electrode and electrolyte to be continuously degraded during cycling,¹⁻⁷ which cause poor round-trip efficiency and unsatisfactory durability of Li-O₂ batteries. Moreover, the dendrite growth and infinite volume change of metal Li anode further deteriorate the lifetime of $Li-O_2$ batteries.^{8,9} All these issues make the achievable energy density and the cycle life of Li-O2 batteries have a big disparity to the theoretical values and are far away from practical applications. Therefore, in the past decade, significant efforts have been invested to unlock the full potential of the Li-O₂ battery as well as to promote it suitable for real-world implementation.^{7,10-12}

> The continuous degradation of the cathode and anode of the Li-O₂ battery during cycling makes its performance far away from practical application.

The performance of the Li–O₂ battery is mainly determined by the characteristics and properties of the three major components that are used to assemble the battery as well as the system integration and engineering involved. Presently, carbon-based materials, like graphene and carbon nanotubes (CNTs), are the most widely used O_2 cathodes for Li– O_2 batteries.^{13–17} However, the vulnerability of carbon materials toward the aggressively oxidative species can induce severe cathode passivation and a fast increase in charge voltage,^{7,18–21} consequently, lowering the round-trip efficiency and sustainable cycling of Li-O2 batteries. For the anode part, the ultrahigh capacity (3860 mAh/g) and the lowest redox potential (3.04 V vs SHE) of metal Li make it indispensable and the only choice for the $\text{Li}-\text{O}_2$ battery to achieve the theoretical specific capacity.^{8,22,23} Although with these advantages, metal Li has its own limitations, like highly reactive nature induced electrolyte decomposition, hostless Li plating/stripping rendered crack generation, and easy dendritic Li formation produced dead Li and a mossy structure,^{24,25} resulting in limited Coulombic efficiency and durability and sometimes even safety problems. The situation is more complicated when metal Li is used in the Li-O2 battery system, since the O₂, reactive oxygen intermediates, and H₂O from electrolyte decomposition will crossover to the Li anode,^{2,11,12} causing the accumulation of byproducts (LiOH, Li_2O , Li_2CO_3 , etc.) on its surface and accordingly affecting the morphology and composition of the solid electrolyte interphase (SEI) film at the electrolyte/Li interface. It is no doubt that the protection of the carbon-based cathode and Li anode from degradation will promote the high-efficiency and long-term running of Li-O₂ batteries.^{6,7} Despite promising, the accomplishment of effective electrode protection is challenging. It requires innovations in structure and architecture design of electrodes and their rational balance.

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Figure 2. Advantages, challenges, and potential solutions of carbon-based cathodes. (a) Electrical conductivity of some representative carbon-based materials.²⁷ (b) Density as a function of pressure for some representative carbon-based materials.²⁶ (c) Carbon materials with various porous structures.²⁹ (d) Schematic representation of N-doped graphene or CNTs.²⁸ (e) Free-standing nanoporous N-doped graphene film.³⁰ (f) Schematic representation for TiO₂ nanowire coated carbon textiles.³¹ (g) Schematic illustration of N-doped graphene encapsulated RuO₂.³² (h) The mechanism of a soluble redox mediator in the decomposition of Li₂O₂.³³ (i) Structures of some representative single oxygen quencher.⁵ (j) Schematic illustration of Cu nanoneedle with Au coating on a Cu foam.³⁴ Images reproduced or adapted with permission from refs 5 and 26–34. Copyright 2015 American Chemical Society, 2012 Elsevier, 2015 IOP Publishing Ltd., 2015 MDPI, 2020 Wiley-VCH, 2017 Wiley-VCH, 2015 Springer Nature, 2015 Wiley-VCH, 2017 Royal Society of Chemistry, and 2020 American Chemical Society, respectively.

The sections below review the strategies toward stable electrodes for $\text{Li}-O_2$ batteries, followed by providing a clear picture for the full exploration of their potential prospects.

2. ADVANTAGES, CHALLENGES, AND POTENTIAL SOLUTIONS OF CARBON-BASED CATHODES

The cathode is a fundamental part of the $Li-O_2$ battery with key functions of providing (1) a three-phase interface (solid cathode phase, gas O₂ phase, and liquid electrolyte phase) for the oxygen reduction reaction (ORR, Li2O2 formation) and oxygen evolution reaction (OER, Li2O2 decomposition) to occur; (2) porous channels for Li^+ and O_2 transport; (3) free space to accommodate insulating/insoluble Li₂O₂ discharge product; (4) surface for guiding the morphology of Li_2O_2 .^{2,5,} Because of the high electrical conductivity, low mass density, low cost, facile porous architecture processing, adjustable electronic structure, as well as abundant allotropes (Figure 2ad),^{26–29} carbon-based materials can fulfill all the above critical functionalities of the O2 electrode required and thus are the primary choice for the basis of the cathodes and ubiquitous in Li-O₂ batteries. Although with great potential, the carbonbased materials will experience degradation during both the discharge and charge processes.¹⁸⁻²⁰ During discharge, the formation of the Li₂O₂ will oxidize the carbon cathode through

the reaction of $2\text{Li}_2\text{O}_2 + \text{C} \rightarrow \text{Li}_2\text{O} + \text{Li}_2\text{CO}_3$ ($\Delta G^\circ = -533.6$ kJ/mol at 300 K) or $Li_2O_2 + C + 1/2 O_2 \rightarrow Li_2CO_3 (\Delta G^{\circ} =$ -542.4 kJ/mol at 300 K) with the generation of Li₂CO₃ at the carbon-Li2O2 interface.5,19 At the carbon-electrolyte interface, the dissolved oxidative intermediates, like O2-, LiO2, and ${}^{1}O_{2}$, will also corrode the carbon to form Li₂CO₃.⁵ The situation is different for the charge process, during which the carbon cathodes are subject to serious decomposition upon charging above 3.5 V.7 The generated undesirable byproducts, like Li₂CO₃, will enlarge the charge overpotential and deteriorate the durability of Li-O2 batteries. Therefore, besides the efforts devoted to boosting the functionality of the carbon-based cathodes, the stability of themselves should also be improved to promote the Li-O2 battery cycling with high efficiency and long-term stability. In this section, we focus on the instability of carbon-based cathodes and strategies for protecting them.

2.1. Binder-Free Design. Polymeric binders are usually adopted to integrate carbon-based materials to prepare porous cathodes. However, the commonly used binders, like PVDF, PAN, PVP, have been confirmed unstable to the nucleophilic O^{2-} radical and $Li_2O_{2^{j}}$ ^{5,21,35} producing unwanted products that tend to cover the cathode surface and block the available catalytic sites, subsequently inhibiting the Li– O_2 reactions to proceed smoothly, and causing drastic capacity fading and

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Only when the functionalization and protection of the carbonbased cathodes are carried out simultaneously can the strict cathode requirements of the Li– O_2 battery be satisfied.

early death of Li– O_2 batteries. The construction of carbon cathode without using binder can eliminate the challenges from binder degradation, helping to enhance the electrochemical performance of Li– O_2 batteries. With this in mind, various binder-free cathodes, such as free-standing porous Ndoped graphene film (Figure 2e), graphene foam, and CNT film, have been prepared and exhibited improved performances with large capacity and cycling stability.^{30,36,37} It is worth mentioning that the adoption of the binder-free cathodes still cannot guarantee their long-term stability.

2.2. Surface Protection. Except for the polymeric binder induced cathode passivation, challenges from the intrinsic chemical instability of carbon materials toward oxidative species still exist. The intermediates $(O^{2-} \text{ and } {}^{1}O_{2})$ and final discharge product (Li₂O₂) can oxidize carbon to produce parasitic Li₂CO₃ byproduct, a wide-gap insulator that is more difficult to be decomposed than Li₂O₂, easily leading to the generation of Li_2CO_3 covering the carbon surface.^{5,18-20} As cycling goes on, Li₂CO₃ will continuously accumulate on the carbon surface, limiting charge transfer and finally diminishing the catalytic sites. These adverse effects give rise to increased charge overpotential and eventually impede the ORR and OER to proceed any more, making Li-O₂ batteries with limited lifetime. Constructing a shield layer on the surface of carbon to physically prevent it from directly contacting the oxidative species can be an effective strategy to mitigate carbon degradation.^{38,39} As a demonstration, by growing TiO₂ nanowire arrays onto carbon textiles to form a core-shell free-standing cathode (Figure 2f), prolonged cycling life has been realized. In this regard, separating the carbon surface away from nucleophilic species by oxidation-resistant material can make sense for protecting the carbon cathodes.³¹ The existence of defects and surface oxygen on carbon is also vulnerable to be attacked by the oxygen radicals to form carbonates.¹⁸ Therefore, the construction of a stabilized carbon surface by minimizing defects and surface oxygen is of vital importance. This can be realized by high-temperature annealing carbon materials under an inert atmosphere.³⁷ For example, the thermally treated graphene cathode with reinforced surface chemistry displayed an obviously improved cycling stability but still degraded in the long run.⁴

2.3. Catalyst Incorporation. It is well-known that carbon is susceptible to decomposition at a charge voltage above 3.5 V with the generation of Li_2CO_3 .^{4,18–20} Since the oxidation of Li_2CO_3 is more difficult than that of Li_2O_2 , the amount of Li_2CO_3 formed above 3.5 V surpasses its decomposition, resulting in the continuous accumulation of Li_2CO_3 on the electrode surface over cycling,^{41,42} thus a further enlarged charge polarization. This high polarization, in turn, accelerates the corrosion of carbon, leading to rapid burying of active sites and a clog of the porosity of the cathode and eventually terminating the ORR and OER processes in $\text{Li}-\text{O}_2$ batteries. To tackle this, the incorporation of solid catalysts into carbon cathodes to facilitate the decomposition of Li_2O_2 with a lower

charge overpotential works well (Figure 2g).³² As such, a range of catalysts has been developed, including noble metals and their oxides, transition metal oxides/carbides/nitrides, and also the recently developed single atoms catalysts (Co or Ru single atoms),^{43,44} and demonstrated reduced damage to the carbon materials and improved OER kinetics and battery recharge-ability.^{2–5,7} Although effective, most catalysts only exhibit a low overpotential at the initial stage of charge, and the charge voltage experiences a gradual increase to 4.0 V or higher with a deeper stage of charge, making the long-term cycling of Li–O₂ batteries be wild wishes. What's worse, some catalysts also exhibit oxidation activity to the organic electrolyte,⁶ which further degenerates the cells' durability. More efforts should still be paid to explore advanced catalysts that can conquer above limitations.

2.4. Redox Mediators. Just as mentioned above, the poor charge transfer rate induced by insulating Li2O2 and the limited contact area between catalysts and Li₂O₂ make the charge voltage continuously increase with the increase of charge depth, which can still render carbon cathodes decomposition and shorten the lifetime of Li-O₂ batteries. Redox mediators (RMs) with functions of donating electrons to O₂ or accepting electrons from Li₂O₂ can act as soluble catalysts to facilitate the formation and decomposition of $Li_2O_{21}^{\prime 41,45-49}$ improving the ORR and OER kinetics and consequently providing a potential solution to address the above issues. For OER RM, during charging, it is first oxidized to RM⁺ at the cathode surface and then diffuses to the Li₂O₂ surface to chemically decompose it with the regeneration of RM (Figure 2h).^{33,46,48} Since RM is soluble in the electrolyte and the oxidation potential of RM itself determines the charge voltage of the Li-O₂ battery, the use of OER RM cannot only enlarge the reaction region for Li2O2 decomposition and circumvent the low charge transfer rate through Li₂O₂, but also offer a typically flat charge profile during the whole charge process. Thereby, it enhances the stability of the carbon cathode and the Coulombic efficiency, rate capability, as well as durability of Li-O₂ batteries.² For example, the use of tetrathiafulvalene (TTF) and LiI as OER RMs could reduce the charge potential down to 3.4 and 3.3 V, 46,50 respectively, as a result, much-improved battery performance was achieved. Despite their advantages, the mobile nature of RM can make it cross over to the Li anode, leading to rapid failure of RM, active Li loss of the Li anode, self-discharge or even short circuit of the cell. Moreover, most RMs are organic molecules. They may also be vulnerable to decomposition by the oxidative species.⁶ With regard to these challenges, a combination of searching chemical and electrochemical stable RMs and Li anode surface protection should be taken into account.

2.5. Functional Additives. Singlet oxygen $({}^{1}O_{2})$ has now been identified as a major cause for parasitic reactions associated with the carbon cathode and electrolyte during cycling of Li-O₂ batteries.⁵¹⁻⁵³ It forms at both stages of discharge and charge, and especially experiences a serious increase as the charge potential rises.⁵⁴ Therefore, the existence of ${}^{1}O_{2}$ poses severe limitations to the high-efficiency and long-term cycling of Li-O₂ batteries. To put forward the Li-O₂ battery to become a reality, the quenching of ${}^{1}O_{2}$ once it is formed or the decrease of ${}^{1}O_{2}$ formation is essential. Encouragingly, it has been demonstrated that the introduction of appropriate functional additives into the electrolyte, like 4-oxo-TEMP, DMAn, DABCO, etc. (Figure 2i), can behave as ${}^{1}O_{2}$ quencher to chemically or physically deactivate it, 53,55,56 as

a result, alleviates the degradation of carbon and electrolyte and improves the performance of $\text{Li}-\text{O}_2$ batteries. For minimizing the generation of ${}^{1}\text{O}_2$, it requires the cell to be operated at voltages well below 3.5 V. Although the incorporation of RMs can bring the charge potential down to 3.5 V, unfortunately, some RMs will decompose when encountering the ${}^{1}\text{O}_2$,⁵⁷ making them gradually lose functions as cycling continues. Therefore, the combination use of ${}^{1}\text{O}_2$ quencher and ${}^{1}\text{O}_2$ stable charge RMs with redox potential close to 2.96 V can be an effective approach for boosting the performance of Li-O₂ batteries. However, up until now, there is only a few ${}^{1}\text{O}_2$ quenchers available, and more efforts should be devoted to this area.

2.6. Carbon-Free Cathodes. As discussed, the above strategies provide chances to alleviate the degradation of carbon-based cathodes. However, none of them are successful yet to completely conquer the intrinsic chemical instability of carbon materials. In this regard, the construction of carbon-free cathodes that are resistant against the aggressively oxidative environment of $\text{Li}-\text{O}_2$ batteries can circumvent the fatal drawbacks arising from carbon corrosion. With this in mind, some all-metal cathodes (porous gold, Cu nanoneedle with a

Au coating on Cu foam (Figure 2j), and nanoporous Ni with a AuNi alloy surface on Ni foam) and transition metal oxide/ carbide cathodes (Co₃O₄ nanowire on Ni foam, TiC) have been developed and exhibit high chemical stability with much improved electrochemical performance.^{34,58–60} Despite promising, the high mass density of these carbon-free cathodes will sacrifice the specific capacity and energy density advantage of Li–O₂ batteries. Moreover, the mechanical instability of some carbon-free cathodes cannot withstand the Li₂O₂ formation

The stability of the Li metal anode determines the lifetime and safety of $Li-O_2$ batteries.

and decomposition induced volume change, which will cause cell performance deterioration. More work should be done to establish mechanical stable carbon-free cathodes with low density, high porosity, and ample free space to boost the performance of $\text{Li}-\text{O}_2$ batteries further.

It is no doubt that there is a close relationship between the designed cathode structure and the performance of $\text{Li}-\text{O}_2$



Figure 3. Protection strategies for Li metal anodes. (a) Illustration of dendrite suppression by Li–Na alloy.⁶¹ (b) Schematic of a porous N-doped graphene-Li composite anode.²² (c) Schematic of gold nanoparticles induced Li deposition in carbon nanocapsules.⁶⁴ (d) Ilustrating the function of alloy layer protected lithium anode.⁶⁵ (e) Schematic illustration of carbon spheres stabilized SEI layer.⁶⁶ (f) Schematic diagram of polymer nanofiber network guided homogeneous Li deposition.⁶⁷ (g) Schematic illustration of LiF and LiN_xO_y coexisting interface protected Li anode from corrosion and dendrite growth.⁶⁸ (h) Schematic of colloidal silica and Li salt anion triggered stable Li anode.⁹ (i) Schematic representation of hybrid solid electrolyte enabled dendrite-free lithium anode.⁶⁹ Images reproduced or adapted with permission from refs 9, 22, 61, and 64–69. Copyright 2019 Elsevier, 2018 Springer Nature, 2019 Springer Nature, 2015 American Chemical Society, 2016 Springer Nature, 2017 Springer Nature, 2014 Springer Nature, 2020 Royal Society of Chemistry, and 2020 China Science Publishing & Media Ltd., respectively.

batteries. The cathode should posse a suitable porous structure that permits fast mass transport and provides large free space for Li_2O_2 storage. Besides, an efficient catalyst should be incorporated into the cathode to facilitate the formation and decomposition of Li_2O_2 with less byproducts and to protect the cathode from degradation. Last, the construction of an abundant three-phase interface is also definitely important since it is the place where the ORR and OER occur. The cathode designed in this way will significantly boost the lifetime, achievable capacity, and rate capability of the $\text{Li}-\text{O}_2$ batteries.

3. PROTECTION STRATEGIES FOR LI METAL ANODES

The promising high energy density of Li–O₂ batteries can only be realized by the usage of Li metal anode. However, its cycling stability and efficiency are still far from satisfactory up until now. Different from the extensive research on the cathode part, the role of the Li metal anode does not get the attention it deserves, thus blocking the further development of Li-O2 batteries. In addition to the dendrite growth, infinite volume changes, and instability in the electrolyte faced by all Li metal anodes, the semiopen system and the O2 involved electrochemical reactions of Li-O2 batteries impose new challenges, such as oxygen related species/CO2/H2O crossover, reaction product accumulation, and RMs shuttle.^{11,12} These features complicate the matters of Li metal anode further. Given all the issues of the Li metal anode encountered in Li-O₂ batteries, it is imperative to develop effective strategies to protect it, so as to boost the performance of Li-O₂ batteries. In this section, we will illustrate the efforts that have been devoted to this field from the aspects of electrode design, interface modification, and electrolyte engineering with the aim of providing inspiration for future design of a stable Li metal anode for high-performance Li-O₂ batteries.

3.1. Electrode Design. 3.1.1. Alloy Anode. Considering the intrinsic dendrite growth issue of the Li metal anode,²⁴ the most direct protocol is to substitute it with large-capacity and Li containing alloy anodes (i.e., LiNa (Figure 3a), Li_xSi , and Li_xAl) that have higher stability.⁶¹⁻⁶³ For example, the use of a Li Si anode can avoid the formation of Li dendrites and thus provide a relatively stable environment for Li-O₂ battery operation.⁶³ Although these alternative alloy anodes can alleviate some of the Li metal associated challenges, they usually have a limited amount of Li source and also introduce a heavier element other than Li to the anode part which, to some extent, sacrifices the energy density of Li-O₂ batteries. Moreover, most of the alloy anodes are fabricated by the chemical or electrochemical lithiation process,^{62,63} complicating the electrode preparation procedures. Besides, the alloy anodes could also encounter side reactions with the electrolyte and species crossover from the cathode side, which quickly exhaust the limited Li source, and consequently inactivate the alloy anode and degrade the battery performance. Hence, both effective prelithiation process and surface protection are required to further boost the stability of the alloy anodes to cater to the strict anode requirements of Li-O₂ batteries.

3.1.2. Li Metal Host. Given the hostless nature, Li metal anode will experience massive volume deformation during cycling,²⁴ which can destroy its integrity and the electrode/ electrolyte interphase, accelerating the failure of the battery. Therefore, there is a great need to engineer the Li metal anode to withstand the volume shrinkage/expansion. It has been demonstrated that the construction of 3D architecture hosts to

accommodate the Li metal can address this issue.^{22,70} The 3D hosts cannot only provide large surface areas to dissipate the current density but also afford free spaces and voids to relieve volume alteration, leading to the composite Li metal anode with stable cycling and dendrite-free properties.²³ For example, Chen et al. reported a porous graphene/Li anode by infusing molten Li into a free-standing, bicontinuous porous N-doped graphene scaffold (Figure 3b).¹³ This composite anode can simultaneously resolve the dendrite growth and pulverization of Li metal anode, as a result, significantly boosting the cycling stability of Li $-O_2$ batteries. However, it should be noted that the introduction of the 3D host will undoubtedly decrease the energy density of the Li $-O_2$ batteries, whereas the high surface area increases the possibility of Li metal involved side reactions. Light host materials and surface modification are primarily required for this method.

3.1.3. Li Deposition Regulation. The random Li nucleation and growth during plating are the roots of dendrite growth. If the Li deposition behavior is rationally regulated, the dendrite issue can be ruled out. This can be realized by homogenizing the Li⁺ flux or nucleation sites, which consequently guide uniform Li deposition.²⁴ The introduction of functional groups with adsorption ability to Li⁺ on the current collector has been demonstrated efficiently in redistributing the Li⁺ and therefore achieve dendrite-free Li plating.^{67,71} Moreover, the engineering of the nucleation seeds provides an opportunity to homogenize the sites for Li nucleation and growth.⁶⁴ For example, the Au seeds or charged nanodiamonds can behave as uniform nucleation sites to eliminate dendritic Li formation (Figure 3c).⁶⁴ Unfortunately, both of these two methods leave the volume change and SEI stability issue of Li metal anodes behind. It would be better to combine these methods with a 3D host or surface modification together.

3.2. Interface Modification. 3.2.1. Artificial SEI. The most negative electrochemical potential of Li $^{+}/\text{Li}~(-3.04~\text{V})$ nearly makes all available aprotic electrolytes be reduced on the surface of a Li metal anode with the formation of SEI layers.¹¹ Therefore, the stability of the SEI layer plays a predominant role in the deposition/dissolution behavior and cycling life of the Li metal anode. Moreover, the integrity and robustness of the SEI layer are also of vital importance in Li-O₂ batteries where oxygen related species and RMs can shuttle freely to attack the Li metal anode.¹² All these make the SEI layer engineering a pivotal aspect in resolving the Li metal anode related challenges. One common approach is to build a robust artificial SEI layer to passivate the Li surface from directly contacting the electrolyte and shuttled species (Figure 3d).⁶⁵ With rationally designed artificial SEI layer, the troublesome issues such as side reactions from electrolyte decomposition, corrosion reactions owing to the crossover of the oxygen and RMs, and Li dendrite growth can be effectively alleviated, enabling long-term and high-efficiency cycling of the Li metal anode, thus comprehensively improving the performance of $Li-O_2$ batteries.^{6,72} For example, the construction of a stiff and uniform graphene-polydopamine composite layer on the Li anode can protect it from dendrite formation and the occurrence of undesired reactions with O₂, moisture, and RMs, rendering the $Li-O_2$ battery to maintain a high energy efficiency of above 80% over 150 cycles.⁷³ Although it has been demonstrated that the artificial SEI layers display unique superiorities on stablizing the Li metal anode than the original SEI, its long-term stability is still questionable. Moreover, the built artificial layers will undoubtedly increase the cell

resistance. More in-depth studies are required to elucidate the functional mechanism of the artificial layers so as to provide guidelines to further reinforce their functionalities.

3.2.2. Nanoscale Interfacial Engineering. In view of the fragile nature of the in situ derived SEI layer, the introduction of a mechanically and chemically stable interfacial scaffold to strengthen the SEI layer can be a powerful method to protect the Li metal anode from serious side reactions with the electrolyte and dendritic Li formation.^{24,74,75} This method can be defined as nanoscale interfacial engineering. Ideally, the scaffold should be homogeneous, ion conductive, but electron insulating, guiding the SEI generated on its surface and Li deposition underneath. Moreover, the interaction between the scaffold and the Li metal anode or the current collector should be weak enough that permits the SEI and the scaffold together to move up and down during the Li plating/stripping without fracturing. For example, Cui and co-workers coated a monolayer of interconnected amorphous and poorly conductive hollow carbon nanospheres on the Cu surface (Figure 3e),⁶⁶ which afforded a stable SEI layer and dendrite-free column-like Li deposition, consequently, achieving high efficiency (~99%) Li metal cycling for more than 150 cycles. It should be noted that when extending this method to $Li-O_2$ batteries, the stability of the scaffold toward the reactive oxygen species must be taken into consideration. Furthermore, even with the presence of the scaffold that can reinforce the SEI layer, dendritic Li growth still occurs in some cases. More fundamental studies should be performed to give a clear picture of the origins of this dendrite formation and aid the rational selection and design of the scaffold. The burgeoning of the large family of 2D materials, like boron nitride, can be good choices.

3.2.3. Homogenizing Li-lon Flux. The in situ electrolyte decomposition derived SEI layer is usually composed of different components with multiple Li⁺ conductivities, resulting in spatial inhomogeneity of the Li⁺ flux on the electrode surface and consequently diverse Li deposition/ dissolution behaviors at different sites.⁷⁶ This will make the SEI layer experience a nonuniform volume change and, ultimately, fracture, accompanied by Li dendrite formation. If we could develop some tactics that can prehomogenize the Li⁺ ion flux, the dendritic Li growth will be greatly delayed or even disappear. This can be realized by either a uniform electricfield distribution or by decreasing the Li⁺ concentration gradient through engineering of the anode surface.^{71,77-79} A practical and effective method is to introduce nonconductive polymer layers full of polar functional groups to bind Li⁺ on top of the Li metal anode or current collector, such as glass fibers (Figure 3f), polyacrylonitrile nanofibers, etc.^{67,71,79} Although these layers themselves are not involved in Li plating, they can regulate the Li⁺ distribution and confine uniform Li deposition. Nevertheless, these layers can disconnect the deposited Li and make it lose electrical connection to the anode easily. Also, the weight ratio of these layers should be exactly controlled without sacrificing the energy density of the batteries.

3.3. Electrolyte Engineering. 3.3.1. Liquid Electrolyte. Since most of the organic electrolytes are vulnerable to the Li metal, electrolyte regulation provides a direct strategy to stabilize the Li metal anode.^{68,80-82} Before doing this in Li–O₂ batteries, we should also consider the attack of the reduced oxygen species on the electrolyte solvent, which will cause serious electrolyte decomposition, limiting the cycling lifetime

of Li-O₂ batteries. Through modulating the electrolyte composition, optimizing the coordination structure of Li salt and solvent, or designing functionalized Li salt, the conductivity of Li⁺, the solubility of gases, Li⁺ and contaminants, as well as the composition of the SEI layer can be controlled as needed.^{68,80-82} Among them, increasing the salt concentration to prepare highly concentrated electrolyte has been proved to be an efficient approach to decrease the electrolyte related side reactions and engineer the SEI layer due to the much reduced free solvent molecules, enabling the stable operation of the Li metal anodes, and thus enhancing the performance of Li-O₂ batteries.^{80,83} However, the concentrated electrolytes are often accompanied by disadvantages like high viscosity, low Li⁺ conductivity, and high cost, limiting their practical applications. To conquer these, recently, Zhang's group developed a new electrolyte design guideline by regulating the Li⁺ solvation structure under a medium concentration of electrolyte to protect the Li metal anode from corrosion and dendrite growth in Li–O₂ batteries (Figure 3g).⁶⁸ The optimized electrolyte not only inherits the advantages but also overcomes the disadvantages of the concentrated electrolytes. More works should be done to defeat the shortcomings of the concentrated electrolytes, such as the design of locally high-concentration electrolytes and the production of Li salts with low costs.

3.3.2. Electrolyte Additive. Electrolyte additives, especially SEI forming additives, have been demonstrated effective in protecting the Li metal anode.^{9,45,84} These additives can adsorb, polymerize, or decompose on the Li anode surface, regulating the physicochemical properties of the SEI with the purpose of strengthening its robustness or adjusting the Li⁺ distribution. For example, the addition of 10 wt % hydrophobic silica nanoparticle in 1 M LiCF₃SO₃/tetraethylene glycol dimethyl ether (TEGDME) electrolyte could prevent the Li metal anode from irregular dendrite growth and serious corrosion in Li-O₂ batteries (Figure 3h).⁹ Further, boric acid (BA) was proved to be an efficient additive in facilitating the generation of a continuous and durable SEI layer, more than six-times prolonging of the lifetime of the Li–O₂ batteries.⁸⁴ However, besides the additive, the SEI formation is also accompanied by the Li salt and solvent decomposition, resulting in the SEI with multiple components and inhomogeneous distribution. This will cause some areas of the SEI to easily rupture and the continuous consumption of the additive, which will lose function in the long run.

3.3.3. Solid/Quasi-Solid Electrolyte. Given that the irregular protuberance feature of the Li dendrites, the substitution of the traditional liquid electrolytes with solid/quasi-solid-state electrolytes that possess a high Young's modulus is beneficial for inhibiting dendritic Li growth from the viewpoint of mechanical suppression.^{13,85,86} Moreover, the use of solid/ quasi-solid-state electrolytes can also help in eliminating leakage issues and preventing the detrimental crossover from the cathode or electrolyte. As a routine quasi-solid-state electrolyte, gel polymer electrolyte (GPE) with low cost and moderate Li⁺ conductivity has been demonstrated effective in reducing side reactions, suppressing dendrite growth, and inhibiting RMs induced shuttle attack in the Li metal anode, enabling its stable operation in Li-O2 batteries.¹³ Although these positive effects, the GPE with a limited amount of liquid electrolyte still suffers from the issues of low Young's modulus, volatilization, and less efficient O2 blockage. As a result, solidstate electrolyte (SSE) stands out owing to its unique

advantages of relative high Young's modulus, nonvolatility, as well as the only Li⁺ transportation ability that fully isolates the crossover of undesirable components.⁸⁷ Generally, the SSE can be broadly classified into polymer electrolyte and inorganic electrolyte.⁶⁹ Both of them could make the Li-O₂ batteries exhibit improved stability. Despite promising, at this moment, the realization of high-performance all-solid-state $Li-O_2$ (ASS $Li-O_2$) batteries is still challenging. The main obstacles come from the insufficient Li⁺ conductivity of polymer electrolyte at room temperature, large interface resistance from poor contact between the inorganic electrolyte and the Li metal anode, and limited triple-phase boundaries at the air cathode. Hybrid polymer/inorganic electrolyte that integrates the softness of the polymer electrolyte and high Li⁺ conductivity of the inorganic electrolyte (Figure 3i)⁶⁹ together with the air cathode design may be an ultimate solution for conquering all these issues.

Developing ASS $\text{Li}-O_2$ batteries is still at an infant stage. Exploring advanced SSEs with seamless interfacial compatibility, superior Li^+ conductivity, and high endurance to the rigorous oxidative environment of $\text{Li}-O_2$ batteries is highly required. Moreover, the processability of the inorganic electrolyte should also be taken into account due to its brittle nature rendered the hard large-area preparation.

4. NEW BATTERY SYSTEMS

While enormous efforts have been devoted to protecting the carbon cathode and Li metal anode, the performance of $Li-O_2$ batteries is still far from practical application. Therefore, researchers exploited some new battery systems to mitigate the challenges of Li-O2 batteries. For example, the photoassisted charging was found effective in reducing the overpotential of Li-O2 batteries.⁸⁸ The sealed cell based on reversible Li2O-Li₂O₂ redox conversion could simplify the cell environment and avoid O²⁻ and ¹O₂ related side reactions.⁸⁹ Moreover, a Ni-based cathode together with a molten nitrate electrolyte enabled Li-O2 batteries to follow a stepwise four-electron Li₂O formation and decomposition process,⁹⁰ circumventing the carbon cathode corrosion and organic electrolyte decomposition. Also, the organic-oxygen battery by substituting the metal anode with biphenyl complex liquid anode resolved the long-lasting issues of metal anode, realizing long-term and high-efficiency cycling.^{91,92} These novel battery systems provide new directions to tackle the challenges of high overpotential, cathode, electrolyte, and anode degradation, etc. of Li-O₂ batteries. Below, we will discuss the essential characteristics and connotations of these systems for deepening the mechanistic understanding of Li-O₂ batteries.

The versatile O_2 electrochemistry and new battery systems provide new opportunities to address the challenges associated with $Li-O_2$ batteries.

4.1. Integration with Solar Cell. In consideration of the sustainability, abundant supply of solar energy, and the decreased polarization enabled by photoassisted charging of $\text{Li}-\text{O}_2$ batteries, the integration of solar cell into the $\text{Li}-\text{O}_2$ battery holds great promise to utilize the solar energy to self-charge the $\text{Li}-\text{O}_2$ battery as well as improve its round-trip

efficiency.^{88,93} However, this requires the air cathode with both photocatalytic and electrocatalytic activities while possessing a large surface area. As a demonstration, Zhang's group constructed a bifunctional air cathode by in situ growing porous TiN/TiO₂ nanowires on the carbon cloth, which reduced the overpotential of Li–O₂ battery to 0.19 V under solar illumination.⁸⁸ Moreover, they also fabricated a flexible self-powered energy system by combining the solar cell and Li–O₂ battery together (Figure 4a). It is worth noting that both the energy band structure and the separation efficiency of the photogenerated electron–hole pairs should be considered when designing the bifunctional air cathode. Moreover, the photoassisted discharging is still unexplored and the system temperature increase under long-time illumination should also not be overlooked.

4.2. Li₂O as the Discharge Product. To overcome the challenges arising from the gas-open nature of $Li-O_2$ batteries, researchers proposed a sealed cell architecture by utilizing a discharged state cathode composed of Li2O2/Li2O and conductive carbon.^{89,94,95} A preliminary attempt was made by Okuoka et al. where a solid phase $Li_2O-Li_2O_2$ conversion was realized by controlling the charge potential.⁹⁶ Although this new battery system sacrifices a fraction of the energy density, it dramatically simplifies the cell environment by circumventing the O_2/O_2^- related electrochemical process as well as avoiding the cell components degradation induced by the nucleophilic O²⁻ and ¹O₂ attack. However, this kind of battery is still facing many technological challenges. One of the most difficult ones is the lack of efficient catalysts to drive the facile conversion of the insulating Li₂O with extended charge depth. Meanwhile, the overcharge induced O₂⁻ formation and O2 evolution should be restrained, which otherwise will lead to low Coulombic efficiency and irreversible capacity loss. Representatively, in 2019, by using a Li₂O-embedded Ir-rGO cathode (Figure 4b), Zhou's group extended the O_2/O_2^- -free charge capacity to 630 mAh/gLi20 with a round-trip overpotential of only 0.12 V and achieved over 2000 stable $\mathrm{Li}_2\mathrm{O}/$ Li₂O₂ interconversion cycles with a Coulombic efficiency up to 99.5%.⁸⁹ More recently, they introduced a new low-cost Nibased catalytic matrix for Li2O-based cathode, which further extends the charge depth to 750 mAh/ g_{Li20} .⁹⁴ With the optimization of the electrolyte and Li metal anode, they also made a high-performance rechargeable 500 Wh/kg Li metal pouch-type full cell (only ~20% energy density fading after 100 cycles). These results demonstrate that this emerging battery system offers enormous promise to practical application and to build a high energy-density battery that far exceeds those of commercial Li-ion batteries. However, the fundamental mechanism of how this system operates is still unclear. More efforts should be devoted to elucidate how the solid catalyst enables the Li₂O-Li₂O₂ conversion, how the Li⁺ transports within the Li2O/Li2O2 particle, and how the electron transfers between Li2O/Li2O2 and the electrode. Only by understanding these can this technology be further developed.

Instead of sacrificing the energy density by limiting the conversion of Li_2O to Li_2O_2 , Nazar et al. recently reported a $\text{Li}-\text{O}_2$ battery based on a four-electron redox of Li_2O by taking advantage of a Ni-based cathode and a molten nitrate electrolyte that operated at 150 °C (Figure 4c).⁹⁰ The use of a noncarbonaceous cathode and chemically stable inorganic electrolyte makes this cell eliminate the carbon corrosion and electrolyte decomposition issues that are often encountered in



Figure 4. New battery systems. (a) A self-powered energy system by integrating flexible $\text{Li}-O_2$ battery with solar cell.⁸⁸ (b) Schematic of the Li-ion battery via reversible $\text{Li}_2\text{O}-\text{Li}_2\text{O}_2$ conversion.⁸⁹ (c) Configuration of a $\text{Li}-\text{O}_2$ battery based on a reversible four-electron conversion to $\text{Li}_2\text{O}.^{90}$ (d) Schematic illustration of an organic-oxygen battery built with Li-based liquid anode and MOFs separator.⁹¹ (e) Configuration of an organic-oxygen battery.⁹² Images reproduced with permission from refs 88–92. Copyright 2019 Wiley-VCH, 2019 Springer Nature, 2018 AAAS, 2020 Wiley-VCH, and 2019 Springer Nature, respectively.

conventional aprotic Li-O2 batteries. As a result, a very low overpotential of 0.2 V and a high Coulombic efficiency close to 100% were achieved, and the cell could maintain 150 times of stable cycling without obvious performance decay. This work demonstrates that if properly chosen cell components that can overcome their associated problems, highly reversible and high Coulombic efficiency operation of the Li-O2 battery is possible. Despite being promising, the research in this direction is at a very early stage, and the selection of the cell components that can withstand the harder operation conditions, such as elevated temperatures, is not easy work. Further investigation needs to be conducted to give atomistic insights into the four-electron ORR and OER process in the system, to provide theoretical instruction for material design, and also to find out what such a direction can bring to the Li-O₂ battery technology?

4.3. Liquid Based Anode. The highly reversible plating/ stripping of Li metal anode is one of the prerequisites to enable stable and long-term operation of the $\text{Li}-O_2$ batteries. However, as mentioned above, none of the existing methods can effectively tackle all the challenges related to the Li metal anode. Instead of protecting it, Zhou's group introduced an organic liquid anode (biphenyl Li complex) to replace the Li metal anode.⁹¹ This newly metal-free liquid anode with low redox potential, high reversibility, fast kinetic and high safety completely avoids the notorious problems of the Li metal anode. When paired with a MOF separator and a dual redox mediator, the assembled organic-oxygen battery (Figure 4d) displayed significantly improved rate performance and cycling durability (100 cycles at 2000 mAh/g and 4000 mA/g). Similarly, Lu and co-workers reported a biphenyl-K liquid anode based organic-oxygen battery with reversible KO_2 conversion (Figure 4e).⁹² Such novel cell design achieved 3000 times stable cycling with an average Coulombic efficiency up to 99.8% at 0.25 mAh/cm² and 4 mA/cm². These inspiring results encourage us to further investigate this kind of battery to provide guidelines for designing stable Li– O_2 batteries. Moreover, this organic-oxygen battery requires a Li⁺ conducting solid-state membrane to separate the liquid anode and the cathode electrolyte, while the suitable solid-state electrolytes face large-scale fabrication difficulty. Thus, greater efforts should be made to develop functional materials for constructing a high-performance membrane to further boost the performance and promote the practical application of organic-oxygen batteries.

CONCLUSIONS AND FUTURE OUTLOOK

Aprotic Li–O₂ battery is one of the most promising nextgeneration energy storage systems that can potentially rival the energy density of internal combustion engines. In this Outlook, we discussed the critical challenges related to the stability of the carbon-based cathode and Li metal anode and reviewed the strategies toward protecting them for high-efficiency Li–O₂ batteries. Also, some new battery systems that could circumvent the issues of high overpotential, cathode, electrolyte and anode degradation are shown. Despite the considerable progress in each section that has been achieved, the Li–O₂ battery is still at an early stage. Many challenges remain.

For the carbon-based cathode, its instable nature toward the rigorously oxidative species and high charge voltage will make it experience continuous corrosion, deteriorating the performance of Li-O₂ batteries. To this end, multiple strategies like binder-free design, surface protection, catalyst incorporation, RMs/functional additives introduction have been proposed to protect the carbon cathode for improving the cycling stability of Li-O₂ batteries. However, all these strategies face some limitations, and a sole method is not as effective as we thought. For this consideration, a combination of two or three methods may have the opportunity to prevent the carbon cathode from degradation. The integrated use of ¹O₂ quencher and ¹O₂ stable charge RMs (redox potential below 3.5 V) together with protected Li metal anode can be an effective approach. Other complementary methods that can simultaneously reduce the exposed carbon cathode surface to the oxidative intermediates and minimize the overpotential as low as possible may also work well. In addition, the exploration of mechanical stable carbon-free cathodes with low density and high porosity is also a choice of great potential.

For the Li metal anode, the electrode design, interface modification, and electrolyte engineering have been adopted to address the issues of Li dendrite growth, infinite volume change, and interface instability. We comprehensively summarized the existing effective approaches for protecting the Li metal anode to enable the high-efficiency and stable cycling of Li-O₂ batteries. However, none of these strategies is adequate to solve all the challenges associated with the Li metal anode. We still not fully understand the degradation mechanism of Li metal anode, especially at the corrosive environment of Li-O2 batteries. The comparison and rational combination of various methods are necessary to get a comprehensive and in-depth cognition of Li nucleation, growth, and dissolution. The construction of a 3D architectured Li metal anode with a stable SEI film or the combination of solid-state electrolyte and interface modification may enable the stable and persistent operation of the Li metal anode. Li metal anode is now undergoing a renaissance, requiring greater efforts in fundamental research and materials development to bring it one step closer to being a viable technology.

Of note, researchers have started to exploit some new battery systems to mitigate the challenges of $\text{Li}-\text{O}_2$ batteries, such as a photoassisted $\text{Li}-\text{O}_2$ battery, sealed cell based on $\text{Li}_2\text{O}-\text{Li}_2\text{O}_2$ conversion, high-temperature molten salt $\text{Li}-\text{O}_2$ battery, and organic-oxygen cell. Although these systems can to some extent mitigate/avoid carbon cathode corrosion, organic electrolyte decomposition, or Li metal anode related issues, they have their own shortcomings. The good thing is that they point out the versatile electrochemistries for a $\text{Li}-\text{O}_2$ battery, which deepens our mechanistic understanding, and provide new directions for us to modulate the O₂ electrochemistry to construct high-energy-density batteries with a promising application prospect. Works on these battery systems are still in progress, and more innovative efforts and designs are highly required.

In summary, protecting the carbon-based cathode or Li metal anode can undoubtedly improve the performance of Li– O_2 batteries. However, as an integrated system, independent studies on a single cell component are far away from realizing long-term and high-efficiency cycling of Li– O_2 batteries, not to mention the promotion of their practical applications. An integral approach with the rational configuration and balance of a stable cathode, electrolyte, and anode may have the chance to resolve all the challenges of Li– O_2 batteries. For example, when using the solid-state electrolyte, besides the Li⁺ conductivity and stable voltage window, we should also

consider its interface compatibility with the Li metal anode and the solid-solid contact induced limited three-phase interface. The design of the cell components depends much on the fully fundamental understanding of the mechanism of the O_2 reduction and evolution reactions in Li– O_2 batteries. More efforts should be devoted to conducting in situ and ex situ characterizations to get the essential points of each reaction. It should be noted that even if all of the issues of Li-O₂ batteries are solved, it cannot guarantee the stable operation of Li-O₂ batteries under ambient conditions with the presence of H2O, CO2, and N2. The effect of these components on the performance of Li-O₂ batteries should be systematically investigated. The development of oxygen selective membrane or new battery systems to avoid the adverse effect from these components should be taken into consideration.

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Notes

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