Energy storage challenges have triggered growing interest in various battery technologies and electrocatalysis. As a particularly promising variety, the Li–O 2 battery with an extremely high energy density is of great significance, offering tremendous opportunities to improve cell performance via understanding catalytic mechanisms and the exploration of new materials. Furthermore, focus on nonaqueous electrolyte-based Li–O 2 batteries has markedly intensified since there could be a higher probability of commercialization, compared to that of solid-state or aqueous electrolytes. The recent advancements of the nonaqueous Li–O 2 battery in terms of fundamental understanding and material challenges, including electrolyte stability, water effect, and noncarbon cathode materials are summarized in this review. Further, the current status of water impact on discharge products, possible mechanisms, and parasitic reactions in nonaqueous electrolytes are reviewed for the first time. The key challenges of noncarbon oxygen electrode materials, such as noble metals and metal oxides-based cathodes, transition metals, transition metal compounds (carbides, oxides) based cathodes as well as noncarbon supported catalysts are discussed. This review concludes with a perspective on future research directions for nonaqueous Li–O 2 batteries.

1. Introduction

The electrical energy storage systems are attracting significantly more interest nowadays for energy sustainability. Among them, Li-ion battery is now dominating the power source market for portable electronic gadgets since its commercialization in the 1990s. However, the theoretical energy density (387 Wh kg −1, compared to that of gasoline 12 200 Wh kg −1) dramatically limited its broader applications. Recently, with the increasing demand for high-energy-density devices such as portable electronics, electric vehicles, and grid energy storage, a strong motivation behind the exploration of contenders that can exceed the stored energy of Li-ion exists.

As one of the most promising options, the Li–O 2 battery yields an extremely high theoretical specific energy of ≈11 700 Wh kg −1. The Li–O 2 battery is based on the reversible formation of lithium oxides by the reaction between Li metal and oxygen. Generally, four types of Li–O 2 batteries have been designated by the type of the electrolyte employed in batteries: aprotic, aqueous, all-solid-state, and hybrid aqueous/aprotic. Due to the insufficient ionic conductivity of the solid-state electrolyte and the parasitic corrosion of Li anode as well as the low decomposition voltage in the aqueous electrolyte, the majority of research efforts have been devoted to the aprotic Li–O 2 battery. For most of the aprotic Li–O 2 batteries, during discharge, oxygen is reduced to solid Li 2 O 2, via the reaction 2Li + O 2 ⇌ Li 2 O 2 (2.96 V vs Li/Li +), which will deliver a gravimetric energy of up to 3500 Wh kg −1.
It should be emphasized that the high energy gains offered by Li–O₂ chemistry can only be fully realized using lithium metal, rather than the conventional Li-ion negative electrode materials such as carbon. In addition, the cost of Li–O₂ batteries is potentially much lower than Li-ion batteries since O₂, one of the active materials, is readily available from the air, assuming that a selective membrane can be developed to prevent the permeation of other gases from the air.\textsuperscript{52–54}

Although the Li–O₂ battery is of great promise and notable progress has been made in its development, several critical challenges must be addressed to achieve a practical Li–air battery. A typical aprotic Li–O₂ cell is composed of a lithium anode, an aprotic electrolyte with dissolved lithium salt, and the air electrode.\textsuperscript{55} The instability of these three main cell components is a big issue from the materialistic point of view.\textsuperscript{52} For instance, carbonate-based electrolytes in Li–O₂ batteries are susceptible to nucleophilic attack, thus limiting anodic oxidation stability. More of the stable electrolytes, such as ether-based electrolytes and dimethyl sulfoxide (DMSO) have been widely used in Li–O₂ cells at this point in time.\textsuperscript{52,56,57} However, up to now, no stable electrolytes for Li–O₂ batteries have been reported.\textsuperscript{55}

This review focuses on some key material challenges and opportunities including the electrolyte, the oxygen electrode, as well as highlights the recent advancements of aprotic Li–O₂ battery research. It should be noted that water impurity in the electrolytes might strongly affect the Li–O₂ electrochemistry and chemistry. Furthermore, the research interest of water effect in Li–O₂ battery is stimulated but still under dispute. Here we provide a status report of this interest for better understanding.

2. Materials Challenges and Opportunities in Rechargeable Aprotic Li–O₂ Battery

2.1. Stability of Electrolyte

The exploration of stable electrolytes in rechargeable aprotic Li–O₂ batteries remains a great challenge.\textsuperscript{58} The solid-state electrolytes show higher stability, such as higher thermal, chemical and electrochemical properties as well as more stable ion transport property than those of liquid electrolytes.\textsuperscript{59} They are usually classified into three major categories: polymer electrolytes (PEs), inorganic ceramic electrolytes (ICEs), and single-crystal silicon membranes. Specifically, PEs can be categorized into three groups: i) gel polymer, in which polymer network is mixed with liquid electrolyte; ii) solid polymer, where the polymer host together with a solid solvent of lithium salt; and iii) composite polymer, which integrates ceramic fillers into the organic polymer host.\textsuperscript{60} Compared to ICEs, the more cost-effective PEs exhibit better flexibility, thus presenting a low oxygen electrode/electrolyte interfacial resistance. Various PEs, such as poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-hexafluoropropylene), poly(methyl methacrylate), and poly(acrylonitrile) have been applied in all-solid-state polymer or gel electrolytes of Li–air batteries.\textsuperscript{61} However, some polymer electrolytes are decomposed since polymer matrices (e.g., PVDF) are susceptible to a nucleophilic attack of superoxide radicals, thus exhibiting poor cycling performance.\textsuperscript{62} While in solid polymer, the common lithium salt of LiPF₆ suffers from decomposition when exposed to moisture.\textsuperscript{61,63} The low mechanical strength of PEs at working temperature limits the ability to prevent Li dendrite from penetrating.\textsuperscript{64–66} The suppression of Li dendrite can be achieved by ICEs due to their excellent mechanical properties. Among them, NASICON-type glass ceramics, including lithium aluminum titanium phosphate (LiₓAlₓTi₂–x(PO₄)₃, LATP) and lithium aluminum Germanium phosphate (Li₁ₓAlₓGe₂–x(PO₄)₂, LAGP) have been widely...
investigated in Li–air batteries.\(^{[62]}\) However, LATP is unstable in direct contact with lithium metal and hence a buffer layer is required.\(^{[67]}\) Although LAGP has favorable chemical stability against lithium metal, the large interfacial resistance between the lithium metal and the LAGP plate is still challenging.\(^{[68]}\)

The silicon membrane can also effectively protect the lithium anode from the crossover of oxygen molecules, but it still needs modifications to improve the conductivity for the practical applications.\(^{[62]}\)

Nonaqueous carbonate-based electrolytes have been widely used in Li-ion batteries in the past few decades.\(^{[69–71]}\) However, experimental results strongly suggest that they could not be shifted directly to aprotic Li–O\(_2\) batteries as their anodic oxidation stability goes against superoxide radical intermediates.\(^{[72,73]}\)

The theoretical evidence further suggests the activation barriers of decomposition pathways for ethylene carbonate and dimethyl carbonates are only 12.4–15.5 kcal mol\(^{−1}\).\(^{[74–77]}\) Ethers, including tetraglyme, dimethoxyethane (DME) and polyethylene oxide was certainly more stable to reduced O\(_2\) species. Further investigations implicate that their decomposition to form Li\(_2\)CO\(_3\), HCO\(_2\)Li, and CH\(_3\)CO\(_2\)Li leads to the increasing instability upon cycling, DMSO was investigated as the possible electrolyte since the increased stability. DMSO-based Li–O\(_2\) batteries exhibit promising cycling performance as well as the enhanced electrolyte stability with porous carbon and gold electrodes. Unfortunately, DMSO is unstable when in contact with Li metal. Ionic liquids that are completely composed of ions have the advantages of wide electrochemical window, negligible vapor pressure, high ionic conductivity, and hydrophobicity. Furthermore, systematical investigation demonstrates ionic liquids exhibit promising stability toward the superoxide radical. The benefit from these features is that ionic liquids have been explored as the electrolyte. The use of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amid as the electrolyte has also been evaluated for operation over 56 days with the capacity of 5360 mAh g\(^{−1}\) on discharge. However, the limited O\(_2\) solubility and diffusivity may cause poor discharge capacity and rate capability of Li–O\(_2\) batteries. Other solvents, such as acetonitrile (AcN), dimethylformamide (DMF), triethyl phosphate, N-methyl-pyrrolidone, and methoxybenzene have also been attempted as the electrolytes in Li–O\(_2\) batteries. They encountered the difficulties of high vapor pressure or quick capacity decay with cycling.

Apart from the above solvents with single composition, mixed solvents that are composed of two or more solvents are also employed as the electrolyte. Mixed solvents may improve the stability via combining the merits of each component. Insight was gained from the Li-ion battery when solvents of tetraethylene glycol dimethyl ether (G4) and ionic liquid N-methyl-(n-butyl) pyrrolidinium bis(trifluoromethane sulfonyl) imide (PYR14TFSI) were mixed in a Li–O\(_2\) battery. The stable potential reached 4.8 V versus Li/Li\(^{+}\), and the charge potential was 500 mV, lower than that of pure G4.

Beyond the stability of solvents, another main cause of the electrolyte instability arises from the parasitic chemistry and electrochemistry at the electrolyte/Li\(_2\)O\(_2\) interface. For example, side chemical reactions with carbon oxygen electrode defect sites or on Li\(_2\)O\(_2\) surfaces could form LiOH or Li\(_2\)CO\(_3\) on the oxygen electrode. The theoretical modeling\(^{[78]}\) showed that a “barrier-less” reaction between propylene carbonate and Li\(_2\)O\(_2\) surface could occur, thus decomposing the electrolyte, as shown in Figure 1d. Interestingly, the simulation results also revealed that the side reaction is likely kinetically unfavorable with a reaction barrier as high as 40 kcal mol\(^{−1}\). Another potential source for the electrolyte decomposition is the oxygen crossover in which the diffusion of oxygen from the carbon cathode to the lithium anode occurs. Lu and co-workers investigated the stability of the tetraglyme electrolyte with the presence of O\(_2\) in Li–O\(_2\) batteries and indicated that the crossover of O\(_2\) from the cathode to the anode could result in the formation of LiOH and different decomposition reactions at the Li–anode.\(^{[79]}\) In the above O\(_2\)-rich environment at the cathode, the unpaired spin states related with superoxide anion radical, solvated O\(_2\) and Li\(_2\)O\(_2\) species, O\(_2^*\), O\(_2^{2−}\), and LiO\(_2^*\) electrode surface-bound species (in which * represents an adsorbed species), Li\(_2\)O\(_2\) and oxygen-rich Li\(_2\)O\(_2\) surfaces may be involved.\(^{[80]}\) A DFT study shows the high-spin states of Li\(_2\)O\(_2\) nanoparticles usually lead to the formation of Li–O–Li bridging site, which

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**Figure 1.** a) Field emission scanning electron microscopic (FESEM) images of the discharged SP cathode when the discharge capacity is limited to 3000 mAh g\(^{−1}\). White scale bars: 1 μm. Green scale bars: 400 nm. b) The FESEM images of the discharged HSC deposited onto CP cathode. White scale bars: 1 μm. Green scale bars: 400 nm. c) The images of the discharged P-HSC deposited onto CP cathode. White scale bars: 1 μm. Green scale bars: 400 nm. The insets in (a)–(c) are the corresponding enlarged FESEM images. d) Corresponding PXRD patterns of the three kinds of discharged cathode. It is found that the PXRD peaks can be assigned to Li\(_2\)O\(_2\), although the morphology of the discharge product is different. Reproduced with permission.\(^{[11]}\) Copyright 2013, Nature Publishing Group.
could be the most favorable reaction site in the ether solvent decomposition reaction on the surfaces of stoichiometric Li2O2 nanoparticles.[80,81] Furthermore, the interaction between the carbon cathode and the discharge product (Li2O2) as well as its associated highly oxidizing environment during charge could also be responsible to the instability of the Li–O2 system. Indeed, Li2O2 is metastable on the carbon surface with the presence of O2 since the following reactions occur with highly exothermic behavior

\[
\text{Li}_2\text{O}_2 + \text{C} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{CO}_2 \quad (\Delta G = -542.4 \text{ kJ mol}^{-1})
\]

(1)

\[
2\text{Li}_2\text{O}_2 + \text{C} = 2\text{Li}_2\text{O} + \text{Li}_2\text{CO}_3 \quad (\Delta G = -533.6 \text{ kJ mol}^{-1})
\]

(2)

However, it should be noted that no more than a few monolayers of Li2CO3 could form at the C–Li2O2 interface, considering that the already formed Li2CO3 would block the further access of Li2O2 to carbon cathode that is required for these reactions to proceed. The experimental evidence was obtained by using both a quantitatively isotopically labeled DEMS and an XPS analysis. A thin Li2CO3 layer was formed at the carbon interface during discharge because of the chemical reaction between the formed Li2O2 and a carbon cathode. McCloskey et al. found that a roughly equivalent amount of Li2CO3 was formed by the reaction of Li2O2 with the ether electrolyte and carbon cathode, respectively. This carbonate will ultimately form a monolayer at the Li2O2–electrolyte interface during the charging, which could have a significant impact on the charging behavior of the Li–O2 battery. It is expected that a 10 to 100-fold can be decreased in the exchange current density when an monolayer carbonate layer is formed at the Li2O2–C interface. Furthermore, it also causes the rising potential during galvanostatic charging and consequent electrolyte stability issues. The carbon surface may promote the electrolyte decomposition upon its hydrophobicity/hydrophilicity, which could also involve potential-dependent carbon decomposition.

Regarding the intrinsic chemical instability and compatibility issue with Li anode, we are currently unaware of any electrolyte satisfied the sufficient stability for practical rechargeable Li–O2 batteries.[82] While most of the effects on the electrolyte stability focused on the solvents and parasitic chemical reactions of the electrolyte components and carbon electrode, with Li2O2 during discharge, and electrochemical reactions during charge, less importance was given to lithium salts as well as impurities (e.g., CO2, H2O) in the electrolytes. The more commonly used Li salts seemed to be stable against the nucleophilic attack of Li2O2.[83] However, it was suggested that the possibility of salt anions being attacked by Li2O2 or O2 in previous investigations was overlooked.[84] The impurities can affect either the solubility of Li2O2 or serve as electron redox shuttles,[85] thus prohibiting the reversible cycling, leading to the dramatical decrease.[86]

2.2. Water Effect

Li–O2 electrochemistry and chemistry are crucially dependent on electrolytes and gas impurities, e.g., H2O.[72] However, the water effect for the fundamental understanding of Li–O2 batteries is still under dispute.

2.2.1. Discharge Products

A limited amount of water in the electrolyte has been demonstrated to affect the morphologies of discharge products (e.g., Li2O2) and the cell performance. Specifically, the formation of Li2O2 toroids and sheets in ethereal electrolytes at a fixed discharge current density was initially observed.[78] As shown in Figure 1.[79] Further investigations with different H2O contents offered the insights into the relationship between water contamination and Li2O2 morphologies (Figure 2a–f).[81] They revealed that even trace amounts of water could promote the formation of Li2O2 toroids, and thus significantly improve the battery capacity (Figure 2g,h).[81] Moreover, higher water concentrations for enhancing discharge capacity at greater discharge rates was also demonstrated.[82] However, water in electrolytes also resulted in the rapid increase of charge potential and hence limited cycling ability[83] as well as the deterioration of lithium metal in Li–O2 batteries.[84]

It should be noted that the cycling degradation in the presence of water was originally claimed to associate with the formation of LiOH, which cannot be charged back.[83] Detailed evidence, however, clarified the core role in the promotion of discharge capacity, which was mainly related with Li2O2 toroids. This is due mainly to the fact that they could circumvent the Li2O2 charge transport limitations (1–10 nm). Further, the LiOH phase was undetectable even with the electrolyte containing 4000 ppm water.[81] Interestingly, the cycling stability was enhanced to 200 cycles at 500 mA g−1 via a transformation of the discharge product from Li2O2 to LiOH and its following decomposition on charging in the presence of both water and the Ru/MnO2/ Super P catalyst.[85] Building upon this, LiOH has been successfully cycled in a Li–O2 battery using water contaminated electrolyte with Li as a redox mediator and reduced graphene oxide (rGO) electrode. That LiOH cell exhibits impressive cyclability of 2000 cycles at 1000 mA g−1, and a high capacity closer to the theoretic value with a voltage gap as small as ≈0.2 V.[86]

2.2.2. Possible Mechanisms

A fundamental understanding of the electrochemical path involves the water effect for Li2O2 growth which is extremely critical to achieving high discharge capacities. To address this issue, two possible discharge reaction mechanisms of Li2O2 formation associated with O2 reduction in nonaqueous electrolytes are briefly introduced as background knowledge.[81,87,88]

i) Surface electrochemical growth. The mechanism can be given by the following equations. Li2O2 conformal film on the electrode may be generated by either Equation (4) or Equation (5). However, the film thickness can only be around 10 nm underlying the limitation of charge transfer, which causes sudden death of the battery.

\[
\text{O}_2(\text{g}) + \text{Li}^+ + \text{e}^- \rightarrow \text{LiO}_2^* \quad (3)
\]
ii) Solution growth. The generation of soluble oxygen species in the presence of water is assumed via Equation (6). The oxygen intermediates subsequently serve as redox mediators on existing Li$_2$O$_2$ sites to promote the formation of Li$_2$O$_2$ toroids through Equation (7).

\[
\text{LiO}_2^* \leftrightarrow \text{Li}^+ + e^- \quad (4)
\]

\[
2\text{LiO}_2^* \leftrightarrow 2\text{Li}_2\text{O}_2(s) + \text{O}_2(g) \quad (5)
\]

\[
\text{LiO}_2^* \leftrightarrow \text{Li}^+\text{(aq)} + \text{O}_2\text{(aq)} \quad (6)
\]

\[
2\text{Li}^+\text{(aq)} + 2\text{O}_2\text{(aq)} \leftrightarrow 2\text{Li}_2\text{O}_2(s) + \text{O}_2(g) \quad (7)
\]

Indicators characterized by the Guttman donor number (DN) and acceptor number (AN) for measuring the ability of an electrolyte to solvate Li$^+$ and O$_2^-$ in governing the mechanism were proposed. The ability of LiO$_2$ solubility in an electrolyte is qualitatively given by

\[\Delta G_{\text{soln}} \approx a\text{DN} + b\text{AN}\]

where $a \approx 0.1$, $b \approx 0.01$. The solution growth mechanism is favored with the electrolyte having a higher LiO$_2$ solubility, leading to Li$_2$O$_2$ toroidal and a higher discharge capacity. Conversely, the surface electrochemical growth is mainly driven by lower LiO$_2$ solubility, results in Li$_2$O$_2$ thin films, and lower capacity. For instance, anhydrous DME has an AN of around 10 and hence cannot induce enough LiO$_2$ solubility for solution growth mechanism. A scheme of the surface and solution growth mechanisms of Li$_2$O$_2$ in different electrolyte solutions is shown in Figure 3.[89]

The electrochemical paths remain elusive in different water containing electrolytes due to the strong irreversibility and a series of complex electrochemical reactions during multistep electron-transfer processes. Gasteiger et al. found that the additive water in the cathodes.

---

*Figure 2.* a–f) Li$_2$O$_2$ discharge product morphology control. SEM images of a Vulcan XC72 carbon cathode without any discharge (a) and of similar cathodes discharged to a capacity of 1 mAh at a rate of 50 µA using nominally anhydrous (<30 ppm) 1 M LiTFSI in DME as the electrolyte (b) and with water contents of 500 ppm (c), 1000 ppm (d), 2000 ppm (e), and 4000 ppm (f) in the electrolyte. The size of the Li$_2$O$_2$ toroids increases with the amount of water in the electrolyte. The thin platelets observed in (d) and (f) probably increase in size and number of layers to form toroids. All scale bars, 1 µm. g,h) Discharge capacity increase with increasing water content in the electrolyte. g) Experimental gravimetric discharge capacities for batteries with XC72 carbon cathodes and 1 M LiTFSI in DME with varying water content in the battery electrolyte. The experimental discharge capacities were obtained from galvanostatic discharges to a reductive potential of 2.3 V (vs Li/Li$^+$) at a discharge rate of 250 µA. Error bars represent uncertainty in the gravimetric capacity calculation and are computed from the standard deviation of carbon loading in the cathodes. h) Theoretically predicted discharge capacities from the developed electrochemical model. A cathode surface area of $\approx$200 cm$^2$ was assumed for the capacity calculation. The model predicts an approximately fivefold enhancement due to the addition of water through the triggering of the solution mechanism. Dotted lines are guides to the eye. Reproduced with permission.[12] Copyright 2015, Nature Publishing Group.
(≤1000 ppm) significantly increased the discharge capacity and that the capacity was close to the value calculated by the following reaction:\(^{(90)}\)

\[
4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{LiOH}\tag{8}
\]

They further made attempts on the water influence during charge in the Li–O\(_2\) battery by using premixed Li\(_2\)O\(_2\)/C on separator as a cathode.\(^{(91)}\) The charge profile of the battery with dry diglyme (≈20 ppm water) as an electrolyte had a peak of initial activation for the degradation of the electrolyte at 4.6 V. The author proposed that a hypothesis of water was produced during the initial activation for the enabling of the solution-transfer of Li\(_2\)O\(_2\) through soluble H\(_2\)O\(_2\).

\[
\text{Li}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{Li}^+\tag{9}
\]

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^-\tag{10}
\]

Compared to the situation with intentionally adding water to the electrolyte, the initial activation voltage significantly decreased, indicating that trace amounts of water may have a great effect on the activation voltage. Building upon this, Yang et al. found that water addition increased the proton availability and thus biased the discharge product toward LiOH.\(^{(92)}\) They believed that the formation of the H\(_2\)O\(_2\) was not a result of reaction (9) and attributed it to the disproportion of O\(_2^-\). To avoid the side products caused by the reaction of superoxide radicals with carbon powders or binders, carbon paper was applied to investigate the water influence in Li–O\(_2\).

2.2.3. Parasitic Reactions

Water also caused the enhancement of parasitic reactions, such as the formation of H\(_2\)O\(_2\) and the decomposition of LiTFSI. The titration results showed that H\(_2\)O\(_2\) continuously formed during the discharge. As the author identified, the OER was only related to Li\(_2\)O\(_2\) rather than other species, e.g., LiOH, Li\(_2\)CO\(_3\) or Li\(_2\)O in their previous study.\(^{(72,93)}\) They proposed that the formation of the H\(_2\)O\(_2\) was not a result of reaction (9) and attributed it to the disproportion of O\(_2^-\). To avoid the side products caused by the reaction of superoxide radicals with carbon powders or binders, carbon paper was applied to investigate the water influence in Li–O\(_2\).
Discharge Reactions

1. electrochemical: \( 4Li^+ + O_2 + 4e^- \rightarrow 4LiO_2 \)
2. chemical: \( 4LiO_2 + 2H_2O \) (via the action of Li) \( \rightarrow 4LiOH + 3O_2 \)

Charge Reactions

1. electrochemical: \( 6I^- \rightarrow 2I_2 + 4e^- \)
2. chemical: \( 4LiOH + 2I_2 \rightarrow 4Li^+ + 6I^- + 2H_2O + O_2 \)

Figure 5. Schematic mechanisms for the formation and removal of LiOH in iodide redox-mediated Li–O_2 cells in the presence of water. The electron/LiOH molar ratios during discharge and charge are both equal to 1. Reproduced with permission. \[17\] Copyright 2015, Science.

batteries. Similar experimental results, e.g., the morphology change of Li_2O_2 and the capacity change with different water content were obtained. Additionally, Guo et al. tested the Li–O_2 battery in pure O_2 with a relative humidity (RH) of 15% and 50%, respectively. \[94\] With increasing amounts of water, the side reactions became more severe. Furthermore, the manner in which the water functions with other additives (e.g., LiI) still needs more investigation.

2.3. Noncarbon Oxygen Electrode

Solving the problem of electrolyte stability alone is not sufficient to improve cell performance. The design of oxygen electrodes can induce pronounced enhancement for the performance. However, the oxygen electrodes in the Li–O_2 batteries also encounter serious problems. Unlike the conventional oxygen electrodes, in which reduction half-reaction occurs, the cathode in a Li–O_2 battery forms a bifunctional electrode: on discharge, O_2 gets reduced and the solid Li_2O_2 forms on the cathode. During charge, the process is reversed, i.e., the discharge product Li_2O_2 decomposes and releases O_2. In this section, to be specific, we use the term “oxygen electrode” instead of “cathode.” Due to the bifunctional character, the oxygen electrode is the principal determinant of the performance of the Li–O_2 battery, i.e., the specific capacity, the power capability, and the cyclability. A desired oxygen electrode material should have the attributes including sufficient electronic and ionic conductivity, fast oxygen diffusion, porous structure to store the discharge product Li_2O_2, high activity for the interfacial electrochemical processes (oxygen evolution reaction (OER) and oxygen reduction reaction (ORR)), nontoxic, low-cost, and especially the chemical/electrochemical stability during the operation of the batteries.

Carbonaceous materials, which are highly conductive, light weight, nontoxic, easy to fabricate at a low cost attract tremendous research interest. Various carbon materials, such as commercial carbon black, carbon fiber, carbon nanotubes, and graphene-based materials have been widely studied. \[95-97\] The cathode design is critically linked to the cell performance and the mechanism. For instance, Lu et al. demonstrated a suitable cathode composed of rGO and Ir nanoparticles, which could be employed to stabilize crystalline LiO_2 for Li–O_2 batteries with high performance. The LiO_2 discharge product and subsequent electrochemical reactions are listed in Figure 6a. They found that the formation of the LiO_2 discharge product is strongly associated with the lattice match between LiO_2 and Ir_3Li. The kinetic stability of crystalline and amorphous LiO_2 was investigated in detail in Figure 6. The disproportionation rate is mainly ascribed to the following factors: i) the rate at which the O_2 leaves the surface; the desorption of an O_2 molecule from a crystalline LiO_2 surface into a vacuum has a barrier of \( \approx 0.9 \) eV (Figure 6b), that is higher than that of an amorphous LiO_2 (\( \approx 0.3 \) eV, Figure 6d); ii) the electrolyte effect, the solvent on the LiO_2 surface could further suppress disproportionation of the crystalline phase, thus crystalline LiO_2 surfaces can be thermally stable in vacuum at room temperature (Figure 6c). \[98\]

This work provides insight for future directions of matching lattices between discharge products and intermetallic substrate to decrease the parasitic reactions.

Although carbon materials were ubiquitously used as oxygen electrode, the parasitic reactions are a big issue. Furthermore, the carbon cathode materials have a modest impact on the understanding of Li–O_2 batteries. \[99\] In addition, the common binders used for preparing carbon electrode will get swollen, gelled, or dissolved by the electrolyte, especially at a higher temperature. The nonconductive nature of the binders also hinders the electron transfer process of the oxygen electrode, which limits the capacity and the cycle efficiency of the battery. Recently, increasing efforts have been focused on solving the problem of the carbon oxygen electrode in Li–O_2 batteries. Two strategies have been adopted for this issue. One is to passivate the carbon defects with different coating techniques, such as atomic layer deposition and physical vapor deposition. \[87,100-102\]

Alternatively, noncarbon materials have been used to fabricate the oxygen electrode even without binders. \[103\] In this review, we only focus on the noncarbon oxygen electrodes in Li–O_2 batteries since the carbon-based oxygen electrodes, such as commercial porous carbon, carbon nanotubes, graphene, mesoporous carbon, carbon nanofibers, and the carbon materials with catalysts have already been well summarized by several reviews.

2.3.1. Noble Metal and Noble Oxide Based Noncarbon Oxygen Electrodes

As previously mentioned, good electronic conductivity and stability are required for the oxygen electrode. Except for the high-cost noble metals, which are relatively inert with high conductivity, some of them are effective catalysts for ORR or OER.

The carbon-free and binder-free nano porous gold (NPG) electrode and DMSO-based electrolyte were employed to obtain reversible and high-rate Li–O_2 cells with a 95% retention of capacity after 100 cycles by Bruce Group. \[72\] The purity of Li_2O_2 formed on the electrode could still exceed 99% even after 100 cycles, as shown in Figure 7. The excellent cyclability was attributed to the stability of Au and the DMSO-based electrolyte during battery cycling. Though the NPG electrode-based Li–O_2 battery exhibits lower charging voltage and faster kinetics than that with carbon electrode, previous studies indicate no existing catalytic activity of Au in Li–O_2 batteries. \[104\] In order to reduce the weight and the cost of the Au electrode, Kim et al. deposited...
Au nanoparticles on Ni nanowire current collector as oxygen electrode via simple electrodeposition method and the Li–O_2 cell with tetrabutylammonium dodecyl sulfate (TBADDS) as the electrolyte showed an excellent reversibility up to 110 cycles.[105] In addition, Xu et al. showed that the 3D gold microlattice prepared by a 3D polymer scaffold could provide a useful surface to study electrochemistry in Li–O_2 batteries.[106] By using this well-structured micropore, the evolution of the discharge product was observed. They found that the toroid Li_2O_2 formed only under a relatively low current density (70 nA cm^{-1}) and the morphology gradually changed to plate-like with the accumulation of side products of lithium carbonate and lithium alkyl carbonate during cycling.

Apart from Au, Ru has also been studied as a noncarbon oxygen electrode due to its excellent OER/ORR catalytic activity in Li–O_2 batteries.[107–109] Here we only discuss the studies using Ru as both support and catalyst. For the research in which Ru serves as a catalyst on another conductive support will be introduced later. Su et al. made pure Ru oxygen electrode by mixing hierarchical Ru nanospheres with the PTFE binder, the discharge and charge overpotentials were dramatically reduced to $\approx 0.3$ V and a high discharge capacity of 3445 mAh g^{-1} was obtained.[110] To increase the specific capacity per unit mass, nanoporous Ru has also been directly grown on Ni foam by a replacement reaction as oxygen electrode.[111] The cells with Ru@Ni electrode showed good cyclability with the terminal charge and discharge potentials stable over 100 cycles at about 3.7 and 2.8 V (vs Li/Li^+), respectively.

Besides Ru, its oxide RuO_2 has also been demonstrated to produce good electrocatalytic activity in Li–O_2 batteries.[22,112,113] Interestingly, RuO_2 is a d-band metallic conductor with the highest electronic conductivity ($10^4$ S cm^{-1} for single crystal) among metal oxides.

**Figure 6.** Density functional calculations. a) Schematic showing lattice match between LiO_2 and Ir_3Li (see also Figure S13, Supporting Information) that may be responsible for the LiO_2 discharge product found on the Ir–rGO cathode. The two structures on the left are the side- and top-views representing epitaxial growth of crystalline LiO_2 in (111) orientation on a (121) facet of Ir_3Li (Li is yellow, O is red and Ir is green). The rod-like structures shown in the central figure are schematic representations of the crystalline LiO_2 morphology observed in the experiment. Two subsequent electrochemical reactions that the LiO_2 can undergo are shown on the right: that is, either further lithiation in the presence of Ar or further oxygen reduction in the presence of oxygen. b) DFT calculations of the barrier for desorption ($\Delta E_{\text{act}}$) of an O_2 molecule from the (101)LiO_2 surface in vacuum from nudged elastic band (NEB) calculation as a function of number of reaction steps, N. c) AIMD simulations of (111)LiO_2 and (101)LiO_2 surfaces in vacuum at room temperature. d) DFT calculations of the barrier for desorption of an O_2 molecule from an amorphous LiO_2 surface in a vacuum. e) DFT electronic band structure (left) and density of states (DOS) plot (right) of ferromagnetic bulk crystalline LiO_2 close to the Fermi level ($E_f$) based on a spin-polarized calculation with electronic spin-up and spin-down states shown. Reproduced with permission.[25] Copyright 2016, Nature Publishing Group.
Detailed study showed that the stability of the TiC originated from the surface oxidation layer (TiO₂ and TiOC). [117] Further, a detailed study showed that the stability of the TiC originated from the surface oxidation layer (TiO₂ and TiOC). [117] Further study showed that the stability of the TiC originated from the surface oxidation layer (TiO₂ and TiOC).

Not only the single noble metal, but also the bimetallic system has been applied to noncarbon electrode in Li–O₂ battery, e.g., the Ag–Pd porous nanotubes. [116] Though good performance of batteries has been achieved with noble metal noncarbon electrode, unfortunately, the high mass and cost of the noble metals render them impractical and uneconomical for applications.

2.3.2. Transition Metals, Transition Metal Compounds (Carbides, Oxides) Based Noncarbon Oxygen Electrodes

Pioneer work of seeking the effective noncarbon materials with low cost by the Bruce group has made oxygen electrode of the Li–O₂ battery by TiC, which is conductive and chemically inert. The Li–O₂ cell attained 98% retention after 100 cycles (Figure 8), which was even better than that with NPG electrode. Detailed study showed the stability of the TiC originated from the surface oxidation layer (TiO₂ and TiOC). [117] Furthermore, TiC has relatively high catalytic activity in Li–O₂ batteries due to its suitable surface acidity. [118] The first-principles calculation and experimental evidence suggested that the stability of TiC toward Li₂O₂ could be improved by oxidizing its surface. [119] The computational study also implied that the TiC(100) TiO surface might be the nucleation site for Li₂O₂. Similarly, the metallic Mo₂C oxygen electrode with high electrocatalytic activity has been applied to the Li–O₂ battery, with the stability of Mo₂C also resulting from the oxidized surface. [120]

Although the electronic conductivity of transition metal oxides is usually not as good as the carbides, their high catalytic activity in Li–O₂ batteries at low cost attracted lots of research efforts. For example, the promising bifunctional OER/ ORR catalysts cobalt oxides (CoO and Co₃O₄) [121–125] and MnO₂ [126] were directly grown on Ni foam as oxygen electrodes in Li–O₂ batteries by several groups. The overpotentials were significant reduced and the cyclability was greatly improved compared with those with carbon-based electrode. The Cu₂O as the bifunctional catalyst has also been used to fabricate noncarbon oxygen electrode within a Li–O₂ battery. The discharge and charge voltages of the Li–O₂ batteries remained at 2.5 and 3.6 V, respectively, even after 100 cycles.

The ternary oxides with spinel phase are also of great interests as a potential candidate of bifunctional OER/ ORR catalysts in Li–O₂ batteries. Kalubarme et al. reported that the spinel MnCo₂O₄ was hydrothermally grown on Ni foam as a carbon-free and binder-free oxygen electrode. [127] A reversible capacity as high as 10520 mAh g⁻¹, which means a specific area capacity of 6.8 mAh cm⁻², was obtained. Additionally, due to the superior catalytic activity of MnCo₂O₄, both the charge and discharge overpotentials were dramatically reduced. The discharge potential was 180 mV higher than the cells with carbon electrode, and the charge potential was 720 mV lower. The cyclability was also verified with 119 cycles under a capacity-limit mode of 1000 mAh g⁻¹. Other spinel oxides have also been investigated such as NiCo₂O₄ [128].

2.3.3. Catalysts on Noncarbon Support

The materials that are lightweight, stable, conductive, and have good electrocatalytic activity serve well as oxygen electrodes for Li–O₂ batteries, e.g., transition metal carbides. However, the materials satisfying these requirements are relatively rare. Benefiting from the combination of the catalysts and the suitable noncarbon support, the realm of the high-performance oxygen electrodes has been significantly expanded.

As previously discussed, the conductive Ru and RuO₂ elements have high electrocatalytic activities and stabilities in the Li–O₂ battery. However, the high mass and cost challenge its application. In order to reduce the amount of Ru in catalyst, Ru on various noncarbon supports have been verified as effective oxygen electrodes in Li–O₂ batteries, e.g., Ru/TiO₂ [129], Ru/MnO₂ [130], Ru/ITO [87], Ru/Sb-doped SnO₂ [81], Ru/Al-doped ZnO [88], Ru/TiSₓ [131], RuO₂/TiN [132], and Ru/Al-doped ZnO [113]. The catalyst Pt also has been attached to TiO₂ support, which exhibited an enhance cyclability of over 140 cycles at very high current densities, i.e., 1 A g⁻¹ and 5 A g⁻¹. [134] Au, even without electrocatalytic activity, can be performed as nucleation centers to direct a conformal growth of the small and thin Li₂O₂ anchored on the bifunctional catalytic MnO₂ [135] which can effectively improve the activity of electrode.
The noncarbon and nonbinder oxygen electrodes effectively solve the problem of the carbon-based electrodes. However, for practical applications, the structure of the electrode needs to be optimized to reduce the electrode mass, which is crucial to obtain a high specific capacity. Otherwise, the advantages of the Li–O2 batteries will be diminished. New material and new structures of the oxygen electrode are in demand, including the understanding of the electrochemistry and chemistry in Li–O2 cells, the development novel electrode and electrolyte materials, and the innovation of cell design.

3. Summary and Outlook

In this review, we have summarized the recent fundamental understanding and materials challenges in nonaqueous Li–O2 batteries, including electrolyte stability, water effect and the noncarbon cathode, as well as the brief introduction of the Li–O2 batteries and the discharge/charge mechanism. For the electrolyte, the stability issue has been a long-standing problem remaining to be solved. The water addition in the electrolyte can increase the discharge capacity, and here we firstly introduced the current status of water impact in Li–O2 batteries. Beyond the electrolyte, air cathode also has a great influence for the cell performance. For the noncarbon cathode, noncarbon oxygen electrodes with different kinds of metals, such as noble metal and oxide, transition metals, transition metal compounds (carbides, oxides), and noncarbon supported catalysts have been summarized.

The Li–O2 battery holds promise to be the advanced battery technology of the next generation. A personal outlook for the future research in nonaqueous Li–O2 batteries would include:

i) Li anode: the current use of Li metal electrode in Li–O2 battery is expected to achieve highest energy density. However, the transport rates of Li+ ions, electrons and O2 would be decreased or blocked if LiOH dense film were formed on the Li surface with a continuous supply of Li+ from the metallic Li.

ii) Solid-state electrolyte: The promising cubic garnet-type ceramic electrolytes with the advantages of high ionic conductivity (10−3 to 10−4 S cm−1) and good stability against Li metal generally encounter poor contact with Li anode, leading to high resistance and uneven current distribution at the interface. More importantly, solid-state electrolytes also face the challenge of storing active materials, making electrolyte design a significantly challenging task.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
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