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Why Do Li-O$_2$ Batteries Fail: The Parasitic Chemistries and Their Synergistic Effect

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As an electrochemical energy storage technology with the highest theoretical capacity, Li-O$_2$ batteries face critical challenges in terms of poor stabilities and low charge/discharge round-trip efficiencies. It is generally recognized that these issues are connected to the parasitic chemistries at the anode, the electrolyte and the cathode. While the detailed mechanisms of these reactions have been studied separately, the possible synergistic effects between these reactions remain poorly understood. To fill in the knowledge gap, this Minireview examines literature reports on the parasitic chemistries and finds the reactive oxygen species a key chemical mediator that participates in or facilitates nearly all parasitic chemistries. Given the ubiquitous presence of oxygen in all test cells, this finding is important. It offers new insights into how to stabilize various components of Li-O$_2$ batteries for high-performance operations and how to eventually materialize the full potentials of this promising technology.

1. Introduction

Based on the reversible formation and decomposition of Li$_2$O$_2$, aprotic Li-O$_2$ batteries hold great promise to meet the societal needs for high-capacity energy storage in areas such as electric vehicles.[1] The theoretical specific energy can reach 3,505 Wh/kg, much higher than other energy storage systems such as lithium ion (Li-Ion, 387 Wh/kg) and lithium sulfur (Li-S, 2,567 Wh/kg).[2] Even by the more conservative estimates, the specific energy of Li-O$_2$ batteries on a system level (300 Wh/kg) is still higher than state-of-the-art Li ion batteries (LIB, 120 Wh/kg) by a large margin.[3] Originally reported in 1996,[4] this technology gained significant attention since 2006.[5] Continued research, nevertheless, has revealed a number of important issues that limit further development of Li-O$_2$ batteries into a practical technology.[6,7] These issues include poor stabilities of all components of the test cells – the anode, the electrolyte and the cathode.[8-10] Additionally, much higher recharge potentials than discharge ones are often necessary, limiting the achievable energy efficiencies.[11] These issues and their chemical origins have been the topic of numerous recent review articles.[12-14] Briefly, it is generally recognized that carbon is an unstable cathode material that can be readily corroded during cell operations (for both discharge and recharge, but more so for the recharge process).[15-17] No stable electrolytes have been identified, although DME (dimethoxyethane), TEGDME (tetraethylene glyco dimethyl ether) and DMSO

(dimethtylsulfoxide) have been popularly used.[18-20] Without a stable solid-electrolyte-interface (SEI) layer, Li as an anode material faces critical problems.[21] But replacing it with other Li-containing materials will greatly reduce the achievable capacities, undermining the potentials held by Li-O$_2$ batteries.[22] The high overpotentials are responsible for the low round-trip efficiencies. While many catalytic materials have been studied and have shown promises for reducing the overptoentials, their role in the processes remains the subject of debates.[7,23-25] These challenges notwithstanding, intense research has significantly advanced our understanding on the chemical nature of Li-O$_2$ battery operations. While the parasitic chemistries at the anode, the cathode and within the electrolyte have received reasonable attention, the possible synergistic effects between them are rarely discussed and remain poorly understood. The main purpose of this Minireview is to fill in the knowledge gap. By focusing on the various parasitic chemistries, we find a clear sign of synergistic effect between them. The lack of attention to the possible synergistic effect may help explain why the progress on Li-O$_2$ battery research has been frustratingly sluggish. It points to the importance of system approaches in studying Li-O$_2$ batteries for future breakthroughs.

Key to the synergistic effect discussed in this Minireview is the ubiquitous presence of O$_2$ and its reactive derivatives. For an ideal Li-O$_2$ battery, the electrolyte (liquid), the cathode support as well as the Li$_2$O$_2$ product (solid) and O$_2$ (gas) form a three-phase interface.[1] At this interface, oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) take place. O$_2$ and its reactive derivatives are confined to this three-phase interface.[26] In reality, however, the cathode is typically flooded by the electrolyte, through which O$_2$ has to diffuse to reach the reactive sites during ORR and diffuse away during OER. Consequently, various reactive intermediates including superoxides and possible byproducts such as H$^+$ abound in the electrolyte.[14,27] The mixture of the electrolyte, O$_2$ and various reactive oxygen species provides ample opportunities for chemical feedbacks by chemistries that should be separated, creating synergistic effects that are poorly understood to date. For a systematic understanding of the complex processes, we first summarize literature reports on electrolyte decomposition based on their reaction pathways and then examine the possible synergistic effects between electrolyte decomposition and parasitic chemistries involving the anode and the cathode, respectively. Such a treatment of existing knowledge offers us new insights into the parasitic chemistries that limit the development of Li-O$_2$ batteries, which will be presented at the end of this Minireview.

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2. Decomposition pathways of the electrolytes

Due to the ORR and OER on the cathode and possible reactions between Li and dissolved O$_2$ (see section 3), reactive oxygen species (e.g., O$_2$$^{\cdot-}$, Li$_2O_2$ and Li$_{2-x}$O$_2$) are expected to co-

exist with molecular O_2 in the electrolyte.[12,28] Their reactivity toward the electrolyte is a critical reason for the electrolyte decomposition.[9] In accordance with the literature conventions, here we focus on the reactivity of the solvents. The possible roles of salts in the electrolyte decomposition are not considered in this Minireview.[29] For clarity, we categorize known electrolyte decomposition pathways into five groups, (1) nucleophilic attacks, (2) auto-oxidation, (3) acid-base reactions, (4) proton-mediated reactions, and (5) reduction by Li. The categorization is summarized in Scheme 1 and will be discussed in details next.
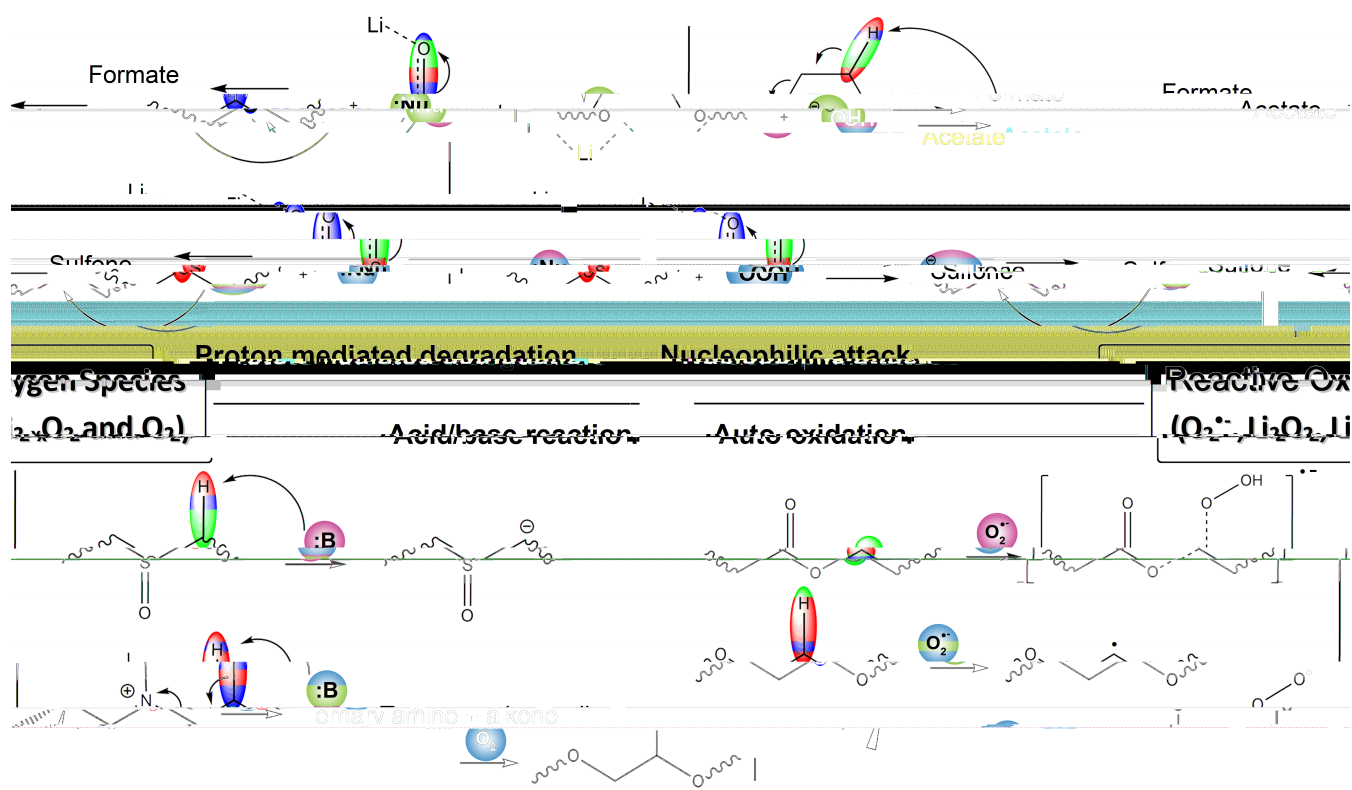
Scheme 1. Pathway of electrolyte decomposition by reactive oxygen species.

### 2.1 The role of oxygen species in nucleophilic attack

The desired product of O_2 reduction in an aprotic Li-O_2 battery is Li_2O_2.[4] As a nucleophile, its reactivity toward functional groups such as sulfoixdes (S=O) and carbonyls (C=O) is known.[30,31] A more problematic species toward electrolyte decomposition is $O_2^{·-}$, which is an important intermediate during both ORR and OER.[32,33] As an intermediate, $O_2^{·-}$ has been found not only at the cathode support where ORR and OER take place,[27] but also in the electrolyte as solvated species.[33,34] These reactive species serve as a promoter to the electrolyte decomposition. Indeed, carbonates used in early Li-O_2 battery studies were found to decompose severely due to the nucleophilic attacks by $O_2^{·-}$ to the C=O groups, producing Li alkyl carbonates and Li_2CO_3.[35] Computational studies have shown that other esters face similar issues.[36] DMSO has been explored by the Bruce group as an electrolyte for better stability against nucleophilic attacks than carbonates.[19] Its high donor numbers were also found to enable low discharge overpotentials and high discharge capacities.[34] However, research by Shao-Horn and Aubach et al. and others revealed that sulfoxide is susceptible to nucleophilic attacks by reduced oxygen species, as well.[30,32] Compared to ester and sulfoxide, amide is a weaker electron withdrawing group and has been studied for their potential as a stable electrolyte toward nucleophilic attacks.[36-38] The expectation is supported by computational calculations showing higher free energy barrier than DMSO and esters.[36,37] Experimental results on the stability of amides against nucleophilic attacks, however, are not conclusive.[39,40]

2.2 The role of oxygen species in auto-oxidation

One class of electrolyte, the ethereal-based ones such as DME and TEGDME, is notable for their stability against

nucleophiles owing to the lack of electron-withdrawing functional groups in their molecular structures. As a result, they have become the most widely used electrolytes in recent Li-O$_2$ literatures.[41] Their reactivity toward auto-oxidation,[20] nevertheless, presents significant problems (Fig. 1). For example, the α-H in ethers has been shown reactive toward superoxide radicals.[42] In fact, Shao-Horn et al. have shown that simple mixture of ethers with molecular O$_2$ leads to auto-oxidation through α-H abstraction.[43] These reactions further promote the release of protons, esterification and polymerization, leading to severe decomposition of the electrolyte. The detection of byproducts such as formate and acetate supports the auto-oxidation mechanism.[44] As far as auto-oxidation is concerned, superoxide radicals are not the only reactive species. Molecular oxygen has been shown to promote similar reactions as well. For instance, polyether-based electrolytes suffer auto-oxidation initiated by dissolved molecular oxygen.[43] The auto-oxidation of the α or β positions also contributes to the decomposition of carbonates.[35] It has been predicted by computational studies that auto-oxidation may be a general decomposition pathway,[37] presenting a significant challenge in the development of stable electrolyte systems for Li-O$_2$ batteries. The issue is especially severe for ether-based electrolytes.
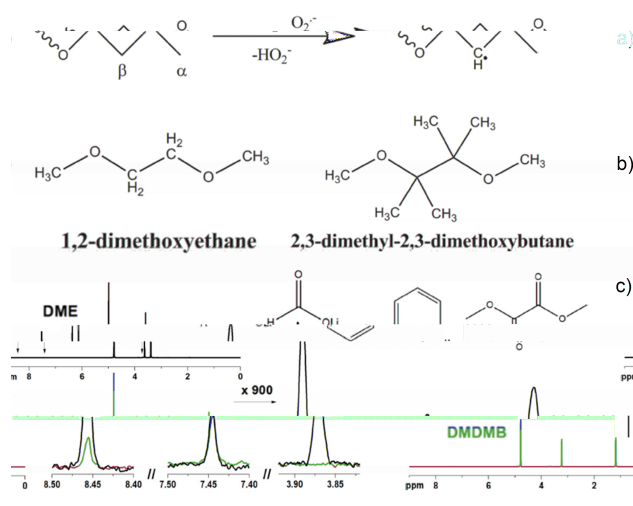
Figure 1. Electrolyte decomposition by auto-oxidation. a) Reaction mechanism of auto-oxidation of ethers. b) Methylation of the susceptible position. c) NMR result of DME decomposition and protection effect by methylation. Reproduced with permission from Ref. [20]. Copyright Wiley-VCH.

2.3 The role of oxygen species in acid/base reactions

The reduced oxygen species are strong Lewis bases in aprotic environments. They tend to attack the α- or β-H following an acid-base chemistry mechanism. The reactivity is enhanced by the presence of polarizing functional groups such as sulfoxide or charged atoms.[45] Consider DMSO as an example. Its α position can be readily deprotonated by superoxides and peroxides, including those in their solid forms (Li$_2$O$_2$, Li$_{2-x}$O$_2$; see Fig. 2).[30,46] The resulting anions lead to further degradation of the electrolyte, consuming the

intermediates or the final products or both and lowering the Coulombic efficiencies. Such an acid-base pathway is a main mechanism for the decomposition of ionic liquids, which were originally adopted for their low vapour pressure, low flammability, low H$_2$O content and possible stability against oxidation. However, as early as in 2012, McCloskey et al. evaluated the performance of several ionic liquids and raised questions about the stabilities of the cations.[11] In those experiments, H$_2$ was detected as a major gas phase byproduct during discharge, pointing to a β-H elimination mechanism by acid-base chemistry. Two recent studies by the Gasteiger group provided strong evidence to support the decomposition pathways of PYR$_{14}$TFSI (1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide) following the Hofmann elimination mechanism.[47,48] As a soft acid, PYRTFSI interacts favourably with superoxide, which is a soft base, according to the half-soft-acid-base (HSAB) theory.[49] This interaction helps stabilize superoxide in the electrolyte, promoting OER reactions following a one-electron process. Consequently, low recharge overpotentials are measured.[33] The relatively high concentration of superoxide in PYRTFSI, nonetheless, also promotes β-H elimination of PYR cation by the superoxide, leading to the decomposition of the electrolyte.[33,48]

2.4 The role of oxygen species in proton mediated degradation

Despite the best efforts to remove H$_2$O from the electrolyte, H$_2$O has been an inevitable impurity in all electrolytes reported in the literature. It is an important source of protons, which interact strongly with oxygen species such as superoxides and peroxides. These interactions produce protonated superoxides, peroxides and hydroxides that are nucleophiles and strong bases. They participate in the various decomposition reactions of the electrolyte as discussed above. Moreover, the strong interactions between protons and reduced oxygen species help dissolve the latter, further enhancing electrolyte decomposition by reactive oxygen.[50] Indeed, it has been shown that the existence of proton accelerates the degradation of the electrolytes, leading to the formation of formate and acetate byproducts.[51] Worse, the decomposition reactions liberate more protons to exacerbate the degradation of the electrolyte in a self-accelerating fashion.

Figure 2. XRD results showing that reduced oxygen species (Li_2O_2 and LiO_2) attack DMSO resulting in LiOH formation. Reproduced with permission from Ref. [30]. Copyright American Chemical Society.

2.5 The reduction susceptibility ~~with~~ by Li

As will be discussed more in Section 3, Li is a necessary component in order to actualize the potentials of Li-O_2 batteries as a high-capacity energy storage technology. Its reactivity with the electrolyte and dissolve oxygen species is

electrolyte, the reactivity of reduced oxygen species on Li surfaces and the reactions between oxygen species and the SEI layer.

3.1 ~~Direct reactions between~~ Corrosion of Li by ~~and~~ the electrolytes

As has been discussed in section 2.5, when the reactions between Li and electrolytes (e.g., DME, TEGDME and organic carbonates) are self-limiting, the insoluble products may serve as a pseudo-SEI layer to protect the Li anode.[53] These reactions will enable the utilization of Li as an anode material.[19] Nevertheless, it is important to note that these SEI layers are only quasi-stable. Dendritic Li growth during recharge still poses significant challenges.[62] Indeed, corrosion of Li has been observed previously in TEGDME as a result of cycling (Fig. 3), although it is unclear to what extent the anode corrosion contributes to the overall cell degradation.[60] When the reactions between Li and the electrolyte are not self-limiting, as is the case when DMA and DMSO are used as the electrolyte, the corrosion of Li is much more severe.[9] Unless stable artificial SEI layers can be achieved (see Section 5), these electrolytes are incompatible with Li.[19,54] Although the problem may be addressed by replacing Li with other Li-containing compounds,[57,58] such an approach would lead to significant reduction of cell voltages as well as increase of mass loading and therefore is not practical for Li-O$_2$ batteries.

Figure 3. Degradation of Li anode in TEGDME electrolyte. (a) The side of the Li anode facing the cathode. (b) The opposite side. (c) Significant decomposition after multi-cycle tests. Reproduced with permission from Ref. [60]. Copyright NPG.

3.2 Reactivity of reduced oxygen species on the Li surfaces

As discussed in the Section 1, for most Li-O$_2$ test cells, the electrolytes are saturated with O$_2$. The direct contact between Li and O$_2$ leads to redox reactions that produce reduced oxygen species such as superoxides (e.g., O_2^-, $O_2^{\cdot-}$, Fig. 4).[52,63] Under ideal conditions, the final product of these reactions would be Li$_2$O. It can serve as an SEI layer to prevent further reactions between Li and O$_2$, and the amount of reduced oxygen species due to these reactions is negligible. But due to the poor quality of the SEI layer and also due to the dendritic growth of Li, the reactions between Li and O$_2$ have been found to be continuous during repeated cycling of Li-O$_2$ test cells ~~(Fig. 4)~~.[52,60,63,64] It is therefore important to examine how the parasitic chemistries at the Li anode influence the overall stability of Li-O$_2$ batteries.

The reactivity of superoxide species toward the electrolytes has been discussed in the previous section. They are oxidative to attack the Li anode and the carbon cathode, basic to extract H from the organic electrolyte molecules and nucleophilic to attack carbonyl groups.[28] It is noted that as the necessary intermediates of ORR at the cathode (see Section 4.1), superoxide species already abound in the system. The additional ones produced at the Li anode are comparably low in quantities. Nevertheless, ~~the influence~~their influence of promoting the parasitic chemistries at the Li anode is profound ~~as they have been previously overlooked~~ (Fig. 4).

Figure 4. The existence of reduced oxygen species on the anode surfaces and their reactivity toward Li anode corrosion.~~Electrolyte decomposition promoted by reduced oxygen species at the anode surfaces.~~ (a) Generation of superoxide species on Li surface. (b) Superoxide species attack the electrolyte. (c) The reaction leads to etching of the Li anode. Reproduced with permission from Ref. [63]. Copyright Elsevier.

Furthermore, even for thermodynamically more stable products such as Li$_2$O$_2$ and Li$_2$O, their reactivity with the electrolytes should be examined with great care.[15,30] For instance, Li$_2$O as a stable final product is strongly basic. It can abstract protons even for solvents normally considered aprotic. It has been 235 0 0 3580 (even 2 (e.) (n /TT5 1 Tf ( ) Tj ET

3.3. Synergy between oxygen and the SEI formation

The spontanous SEI formed in the Ar atomosphere usually contains Li_2CO_3, Li_2O, LiF, RCOOLi, ROLi and some polymeric compounds (Scheme 2). When O_2 is introduced to the system, compositional and morphological changes are often observed. Both positive and negative impacts to the cell stability due to these changes have been reported.[63,66] In the case of DMSO, the increase of Li_2O enhances the formation of LiOH, which lowers the Coulombic efficiency of the Li anode.[63,65] In the case of $N_{1114}TF_2N$ ionic liquid, however, >10% improvement of the anode Coulombic efficiecies was observed in dry oxygen as compared to Ar atomsphere. It was found that O_2 helps reduce the thickness of the SEI layer by up to 67% (Fig. 5).[67] In another example, O_2 was discovered to help regenerate $LiNO_3$ ($LiNO_2+O_2 \rightarrow LiNO_3$), which has been shown to react with Li to form Li_2O as a reasonably stable SEI in DMA.[55] Without O_2, the protection effect fades quickly due to the consumption of $LiNO_3$.[54]
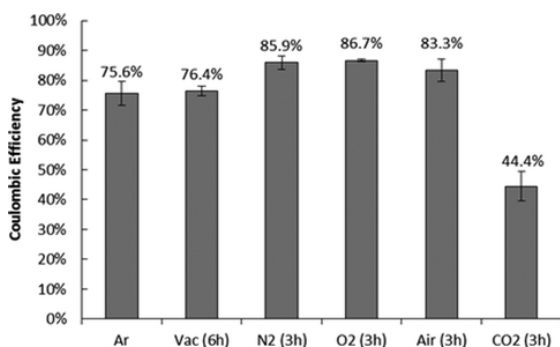
Figure 5 Effects of oxygen invasion to the anode. The Coulombic efficiencies are sensitive to the atmosphere in which the SEI is formed. Reproduced with permission from Ref. [67]. Copyright American Chemical Society.

3.4 Summary of parasitic chemistries at the Li anode

The utilization of Li as the anode is of great importance to actualizing the full potentials of Li-O_2 battereis as a high energy density energy storage technology. The reactivity of Li with the electrolyte and O_2 is therefore a critical issue that has received underwhelming attention previously overlooked.[52,60,63,65,68] We see from the above discussions that the presence of O_2 has a profound impact on the SEI layer, both its formation and the compositional changes. The direct reactions between Li and O_2 genreate reactive oxygen species that may contribute to the degradation of the electrolyte. Additionally, the reductive nature of Li further limits the electrolyte choices. These issues call for a solution that may be met by a stable articifical artificial SEI layer (see Section 5).

4. Synergistic effects at the cathode

As the primary site for Li_2O_2 formation and decomposition, the cathode is the most studied component in Li-O_2 batteries. It has also been the subject of numerous reviews.[6,12,69-71] Instead of repeating these disucssions, here we focus on the synergistic effect between the cathode and the electrolyte, an aspect that has received underwhelming attention previously. It is shown here that the parasitic chemistries at the cathode and those in the electrolyte have important influences on each other.[72] For instance, the reaction mechanisms at the cathode are found to be sensitive to the electrolyte choices. The decomposition chemistries on the cathode surface in turn contribute significantly to the electrolyte decomposition.

4.1 The influence of the electrolyte on tThe cathode reaction pathways influenced by the electrolyte

The reactions taking place at the cathode (both ORR during discharge and OER during recharge) generate reactive oxygen species that promote parasitic chemistries. The detailed mechanisms by which these reactions proceed are highly sensitive to the nature of the electrolyte, as well. Below we discuss how the choice of electrolyte influences the reaction pathways at the cathode. The most representative pathway of the ORR involves the electrochemical reduction of an oxygen molecule to a superoxide anion ($O_2^{\cdot -}$ O_2^-). As a soft base, $O_2^{\cdot -}$ O_2^- interacts strongly with Li^+, which is a hard acid, to disproportionate into Li_2O_2 and O_2. The one-electron electrochemical reaction features low overpotentials. Alternatively, LiO_2 may receive a second electron to be reduced to Li_2O_2, which corresponds to a 2-electron electrochemical reaction that features relatively high overpotentials.[34] Recent studies suggest that ORR favors the one-electron pathway when electrolytes with either high donor number (DN) or acceptor number (AN) are employed. For example, Aetukuri et al. found that the inclusion of trace amount of H_2O promotes the solution-based mechanism due to the strong Lewis acidity of H_2O (AN=54.8; see Fig. 6a).[50] Johnson et al. demonstrated that electrolytes of high DNs favour ORR via the 1-electron pathway and enable high capacities and low overpotentials.[34] Nevertheless, the enhanced solubility of LiO_2 may increase the presence of superoxide species, which negatively impacts the stability of the electrolyte and the cathode following mechanisms as discussed in Section 2.[73-75] This effect has not been experimentally studied in the literature.

Similar influence by the electrolyte on the OER pathways during recharge has been recently observed, as well. For instance, ionic liquid ($PYR_{14}TFSI$) is found to help solvate superoxide species to favor the 1-electron recharge pathway (Fig. 6b).[33] Correspondingly, low recharge overpotentials are measured. As far as overpotentials are concerned, it has been shown that H_2O in the electrolyte may serve as a mediator to facilitate charge transfer for low overpotentials.[76,77] More recently, it is reported that with the help of H_2O, LiOH instead of Li_2O_2 may act as the discharge product for reversible recharge, which is a fundamentally different chemistry from that involving Li_2O_2 as discussed in the rest of this Minireview.[78]

Figure 6. Schemes of the influence of electrolytes on the reaction pathways for the (a) Oxygen Reduction Reaction (ORR) and (b) Oxygen Evolution Reaction (OER). Reproduced with permission from Ref. [50] and [33]. Copyright NPG and American Chemical Society, respectively.

4.2 Synergistic effect between carbon cathode and electrolyte degradation

For the purpose of reducing overpotentials, researchers have examined a number of ORR and OER catalysts.[79,80] However, studies by McCloskey et. al. showed that carbon loaded with catalysts, including Pt, MnO_2 and Au, would exhibit more CO_2 evolution than bare carbon, indicating that these catalysts may promote ether-based electrolyte decomposition (Fig. 7a).[25] The issue of catalyst-promoted electrolyte decomposition should therefore be considered carefully for future studies.[23,81]

As a popularly used cathode material, porous carbon often features functional groups and defect sites that interact strongly with superoxide species following mechanisms as discussed in Section 2. The reactivity of carbon may also induce electrolyte decomposition (Fig. 7b). For example, Bruce et. al. observed that the extent of cathode and electrolyte decomposition is more severe for hydrophilic carbon than hydrophobic one due to the more abundant surface defects on the former.[17] When the carbon is deactivated by $LiNO_3$ additives, Kang et al. observed significantly supressed decomposition of not only the cathode, but also the electrolyte.[82] Indeed, greater stability has been consistently measured when carbon-free cathode is employed, either by coating carbon surface with passivation (e.g., Al_2O_3, FeO_x) or by using non-carbon materials such as Au, $TiSi_2$ and TiC (Fig. 7b)

5 Summary and outlook

Compared to LIBs, Li-O_2 batteries feature one additional component, O_2, which is highly reactive. This addition complicates the possible chemistries considerably, making it difficult to study the parasitic chemistries at the anode, the cathode and within the electrolyte that are inherent to Li-O_2 batteries. But the understanding of these chemistries is critical to the actualization of the promise held by Li-O_2 batteries. While the parasitic cathode degradation and electrolyte decomposition have been reviewed separately previously, their possible synergistic effects are rarely discussed in a systematic fashion previously. This Minireview is written to fill in the knowledge gap.

We see from the discussions that O_2 and reactive oxygen species play important roles in promoting various undesired side reactions in nearly all components of a test cell. For the anode, oxygen species react with Li to initiate a number of reactions that contribute to the degradation of the anode. In addition, Li often exhibits reactivity toward the electrolyte, particularly those with resistance against oxidation (e.g., DMA and DMSO). While the formation of spontaneous SEI layer helps protect Li to some extent, the effect is highly phenomological and lacks control. Moving forward, the strategy of forming a stable SEI is expected to address this issue. Solid-state electrolytes that can be grown as ultra-thin, uniform layers can serve as an artificial SEI layer and have received some research attention lately.[88,89] The issues connect to the reactivity of carbon surfaces may be mitigated by coating the cathode with passivation layers. But such an approach also makes it difficult to take advantage of the good ORR activity of carbon, which may increase the discharge overpotentials. To solve the problem, researchers have started looking into the possibility of promoting one-electron reaction pathways by choosing appropriate electrolytes. Additionally, researchers have studied the possibilities of controlling the reaction pathways by altering the carbon surfaces and morphologies.[78,90] Before these approaches can be widely implemented, nevertheless, careful studies must be performed to evaluate how the new reaction pathways impact the stability of various components of the test cells. With regard to the electrolyte, no known compounds are stable enough for the operation of Li-O_2 batteries. It is by far the most challenging problem that requires significant research attention. While the modification of known compounds for better stability without sacrificing their properties in terms of salt solubility and O_2 diffusivity appears promising, the performance metrics by these derivatives remain subpar. In addition, the increased cost as a result of the modifications must be taken into account for practical applications. Most importantly, we see from the discussions presented here that future studies of Li-O_2 batteries should benefit tremendously by examining the parasitic chemistries systematically.

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MINIREVIEW

Literature reports on the parasitic chemistries of Li-O$_2$ battery are examined in this minireview. The reactive oxygen species are found a key chemical mediator that participates in or facilitates nearly all parasitic chemistries at the anode, cathode and electrolyte. Understanding of their synergistic effect will enable more rational designs for future Li-O$_2$ batteries.

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