

# Why Do Lithium–Oxygen Batteries Fail: Parasitic Chemical Reactions and Their Synergistic Effect

Xiahui Yao<sup>+</sup>, Qi Dong<sup>+</sup>, Qingmei Cheng<sup>+</sup>, and Dunwei Wang<sup>\*</sup>

electrochemistry · energy storage · lithium–oxygen batteries · reactive oxygen species · synergistic effect

**A**s an electrochemical energy-storage technology with the highest theoretical capacity, lithium–oxygen 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 chemical reactions at the anode, electrolyte, and 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 chemical reactions and finds the reactive oxygen species a key chemical mediator that participates in or facilitates nearly all parasitic chemical reactions. 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 lithium–oxygen 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  $\text{Li}_2\text{O}_2$ , aprotic lithium–oxygen batteries hold great promise to meet the societal needs for high-capacity energy storage in areas such as electric vehicles.<sup>[1]</sup> The theoretical specific energy can reach  $3505 \text{ Wh kg}^{-1}$ , much higher than other energy storage systems such as lithium ion (Li-Ion,


$387 \text{ Wh kg}^{-1}$ ) and lithium sulfur (Li-S,  $2567 \text{ Wh kg}^{-1}$ ).<sup>[2]</sup> Even by the more conservative estimates, the specific energy of Li– $\text{O}_2$  batteries on a system level ( $300 \text{ Wh kg}^{-1}$ ) is still higher than state-of-the-art Li-ion batteries (LIB,  $120 \text{ Wh kg}^{-1}$ ) by a large margin.<sup>[3]</sup> Originally reported in 1996,<sup>[4]</sup> this technology gained significant attention since 2006.<sup>[5]</sup> Continued research, nev-

ertheless, has revealed a number of important issues that limit further development of Li– $\text{O}_2$  batteries into a practical technology.<sup>[6,7]</sup> These issues include poor stabilities of all components of the test cells—the anode, the electrolyte and the cathode.<sup>[8–10]</sup> Additionally, much higher recharge potentials than discharge ones are often necessary, limiting the achievable energy efficiencies.<sup>[11]</sup> These issues and their chemical origins have been the topic of numerous recent review articles.<sup>[12–14]</sup> 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).<sup>[15–17]</sup> No stable electrolytes have been identified, although DME (dimethoxyethane), TEGDME (tetraethylene glyco dimethyl ether) and DMSO (dimethylsulfoxide) have been popularly used.<sup>[18–20]</sup> Without a stable solid–electrolyte interface (SEI) layer, Li as an anode material faces critical problems.<sup>[21]</sup> But replacing it with other Li-containing materials will greatly reduce the achievable capacities, undermining the potentials held by Li– $\text{O}_2$  batteries.<sup>[22]</sup> The high overpotentials are responsible for the low round-trip efficiencies. While many

[\*] X. Yao,<sup>[†]</sup> Q. Dong,<sup>[†]</sup> Q. Cheng,<sup>[†]</sup> Prof. Dr. D. Wang  
Department of Chemistry, Boston College  
Merkert Chemistry Center, 2609 Beacon St., Chestnut Hill  
Massachusetts 02467 (USA)  
E-mail: dunwei.wang@bc.edu

[†] These authors contribute equally.

 The ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201601783>.

 © 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial, and no modifications or adaptations are made.

catalytic materials have been studied and have shown promises for reducing the overpotentials, their role in the processes remains the subject of debates.<sup>[7,23–25]</sup> These challenges notwithstanding, intense research has significantly advanced our understanding on the chemical nature of Li–O<sub>2</sub> battery operations. While the parasitic chemical reactions 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 chemical reactions, 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<sub>2</sub> battery research has been frustratingly sluggish. It points to the importance of system approaches in studying Li–O<sub>2</sub> batteries for future breakthroughs.

Key to the synergistic effect discussed in this Minireview is the ubiquitous presence of O<sub>2</sub> and its reactive derivatives. For an ideal Li–O<sub>2</sub> battery, the electrolyte (liquid), the cathode support as well as the Li<sub>2</sub>O<sub>2</sub> product (solid) and O<sub>2</sub> (gas) form a three-phase interface.<sup>[1]</sup> At this interface, oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) take place. O<sub>2</sub> and its reactive derivatives are confined to this three-phase interface.<sup>[26]</sup> In reality, however, the cathode is typically flooded by the electrolyte, through which O<sub>2</sub> 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<sup>+</sup> abound in the electrolyte.<sup>[14,27]</sup> The mixture of the electrolyte, O<sub>2</sub> and various reactive oxygen species provides ample opportunities for chemical feedbacks by chemical reactions that should be separated, creating synergistic effects that are poorly understood to date. For a systematic under-

standing 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 chemical reactions involving the anode and the cathode, respectively. Such a treatment of existing knowledge offers us new insights into the parasitic chemical reactions that limit the development of Li–O<sub>2</sub> batteries, which will be presented at the end of this Minireview.

## 2. Decomposition Pathways of the Electrolytes

Due to the ORR and OER on the cathode and possible reactions between Li and dissolved O<sub>2</sub> (see section 3), reactive oxygen species (e.g., O<sub>2</sub><sup>•-</sup>, Li<sub>2</sub>O<sub>2</sub>, and Li<sub>2-x</sub>O<sub>2</sub>) are expected to co-exist with molecular O<sub>2</sub> in the electrolyte.<sup>[12,28]</sup> Their reactivity toward the electrolyte is a critical reason for the electrolyte decomposition.<sup>[9]</sup> 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.<sup>[29]</sup> 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.

### 2.1. The Role of Oxygen Species in Nucleophilic Attack

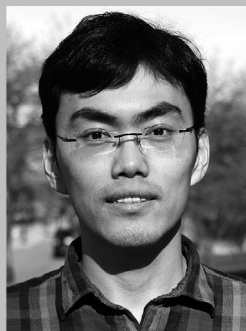
The desired product of O<sub>2</sub> reduction in an aprotic Li–O<sub>2</sub> battery is Li<sub>2</sub>O<sub>2</sub>.<sup>[4]</sup> As a nucleophile, its reactivity toward functional groups such as sulfoxides (S=O) and carbonyls (C=



Xiahui Yao received his bachelor degree in Material Science and Engineering from University of Science and Technology of China in 2012. He is currently a Ph.D. candidate in Chemistry Department at Boston College under the advisement of Prof. Dunwei Wang. His current research interest is the surface functionalization and protection of the electrode materials in energy storage devices.



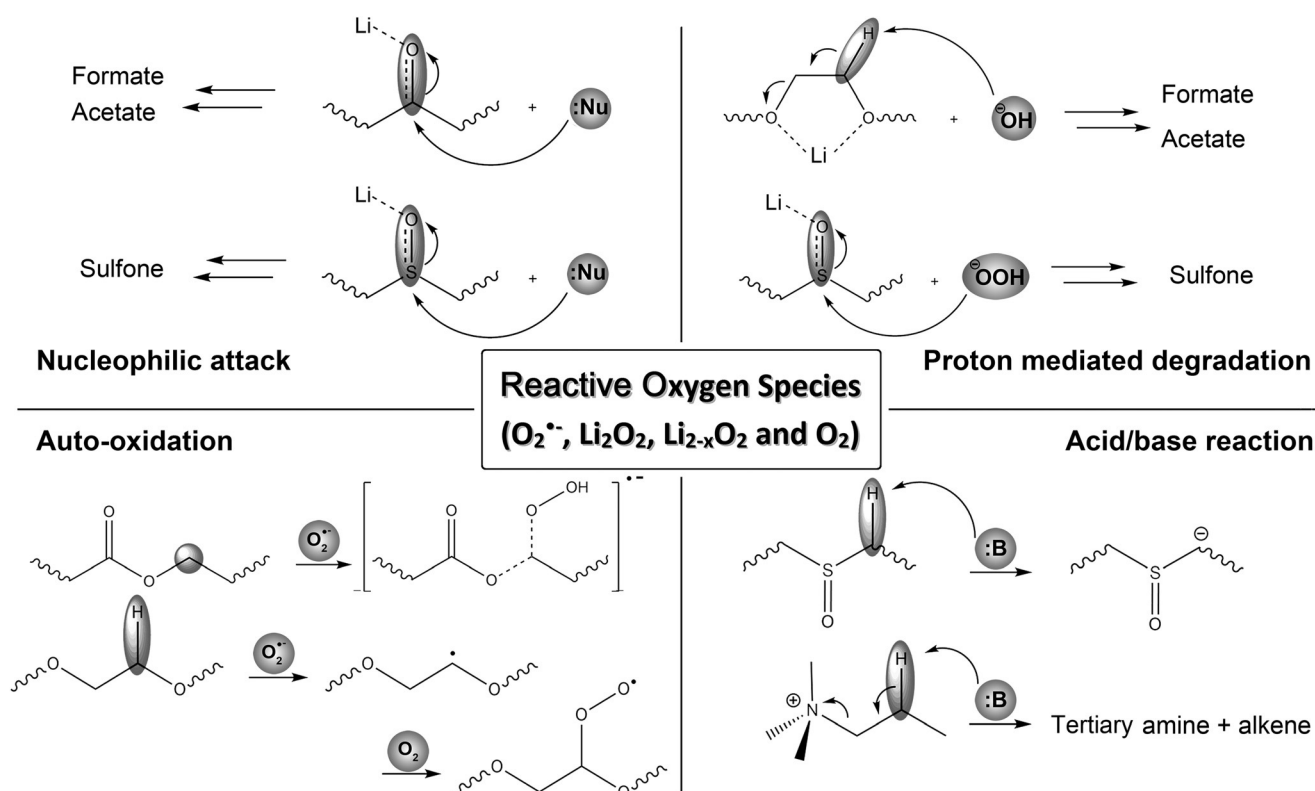
Qingmei Cheng received her B.Sc. in Chemistry from University of Science and Technology of China in 2013. She is currently a Ph.D. candidate in the Chemistry Department at Boston College under the supervision of Prof. Dunwei Wang. Her current research interests include lithium–air battery and solar-powered energy storage devices.



Qi Dong obtained his B.E. and M.E. both in Materials Science and Engineering from Beihang University of China in 2012 and 2014. He studied carbon nanomaterials for fuel cells and polymer composites in the group of Prof. Yan Zhao. He is currently a Ph.D. student in the Chemistry Department at Boston College under the advisement of Prof. Dunwei Wang. His research interests include metal air batteries and photoelectrochemical energy conversion and storage.



Dunwei Wang graduated from Stanford University with a Ph.D. in chemistry in 2005. He has been at Boston College since 2007, where he researches on materials for energy conversion and storage. He has been a recipient of the NSF's CAREER award, a Sloan Fellow and a JSPS Fellow.

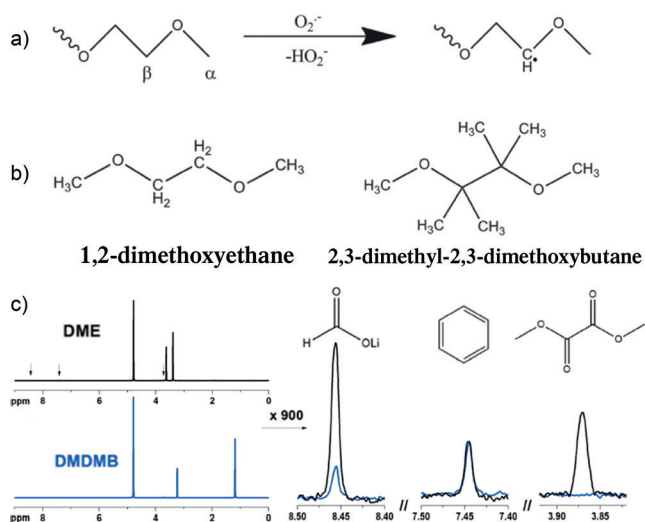


Scheme 1. Pathways of electrolyte decomposition by reactive oxygen species.

O) is known.<sup>[30,31]</sup> A more problematic species toward electrolyte decomposition is  $\text{O}_2^{\cdot-}$ , which is an important intermediate during both ORR and OER.<sup>[32,33]</sup> As an intermediate,  $\text{O}_2^{\cdot-}$  has been found not only at the cathode support where ORR and OER take place,<sup>[27]</sup> but also in the electrolyte as solvated species.<sup>[33,34]</sup> These reactive species serve as a promoter to the electrolyte decomposition. Indeed, carbonates used in early Li– $\text{O}_2$  battery studies were found to decompose severely due to the nucleophilic attacks by  $\text{O}_2^{\cdot-}$  to the C=O groups, producing Li alkyl carbonates and  $\text{Li}_2\text{CO}_3$ .<sup>[35]</sup> Computational studies have shown that other esters face similar issues.<sup>[36]</sup> DMSO has been explored by the Bruce group as an electrolyte for better stability against nucleophilic attacks than carbonates.<sup>[19]</sup> Its high donor numbers were also found to enable low discharge overpotentials and high discharge capacities.<sup>[34]</sup> However, research by Shao-Horn and Aurbach et al. and others revealed that sulfoxide is susceptible to nucleophilic attacks by reduced oxygen species, as well.<sup>[30,32]</sup> Compared to ester and sulfoxide, amide is a weaker electron-withdrawing group and has been studied for this potential as a stable electrolyte toward nucleophilic attacks.<sup>[36–38]</sup> The expectation is supported by computational calculations showing higher free-energy barrier than DMSO and esters.<sup>[36,37]</sup> Experimental results on the stability of amides against nucleophilic attacks, however, are not conclusive.<sup>[39,40]</sup>

## 2.2. The Role of Oxygen Species in Auto-Oxidation

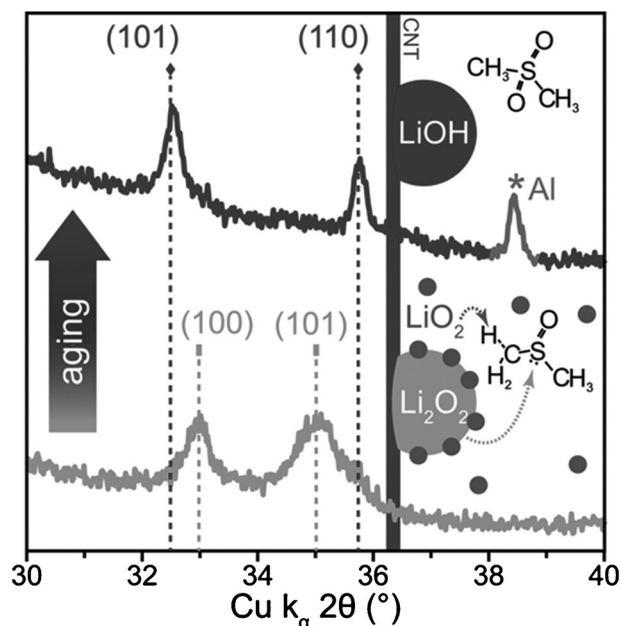
One class of electrolyte, the ethereal-based ones such as DME and TEGDME, is notable for their stability against nucleophiles owing to the lack of electron-withdrawing functional groups in their molecular structures. As a result, they have become the most widely used electrolytes in recent Li– $\text{O}_2$  literatures.<sup>[41]</sup> Their reactivity toward auto-oxidation,<sup>[20]</sup> nevertheless, presents significant problems (Figure 1). For example, the  $\alpha$ -H in ethers has been shown reactive toward superoxide radicals.<sup>[42]</sup> In fact, Shao-Horn and co-workers have shown that simple mixture of ethers with molecular  $\text{O}_2$  leads to auto-oxidation through  $\alpha$ -H abstraction.<sup>[43]</sup> 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.<sup>[44]</sup> 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.<sup>[43]</sup> The auto-oxidation of the  $\alpha$  or  $\beta$  positions also contributes to the decomposition of carbonates.<sup>[35]</sup> It has been predicted by computational studies that auto-oxidation may be a general decomposition pathway,<sup>[37]</sup> presenting a significant challenge in the development of stable electrolyte systems for Li– $\text{O}_2$  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  $\alpha$ - or  $\beta$ -H following an acid–base chemistry mechanism. The reactivity is enhanced by the presence of polarizing functional groups such as sulfoxide or charged atoms.<sup>[45]</sup> Consider DMSO as an example. Its  $\alpha$  position can be readily deprotonated by superoxides and peroxides, including those in their solid forms ( $Li_2O_2$ ,  $Li_{2-x}O_2$ ; see Figure 2).<sup>[30,46]</sup> The resulting anions



**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.

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  $H_2O$  content and possible better 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.<sup>[11]</sup> In those experiments,  $H_2$  was detected as a major gas phase byproduct during discharge, pointing to a  $\beta$ -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.<sup>[47,48]</sup> As a soft acid,  $PYR$  cation interacts favorably with superoxide, which is a soft base, according to the half-soft acid–base (HSAB) theory.<sup>[49]</sup> This interaction helps stabilize superoxide in the electrolyte, promoting OER reactions following a one-electron process. Consequently, low recharge overpotentials are measured.<sup>[53]</sup> The relatively high concentration of superoxide in  $PYR_{14}TFSI$ , nonetheless, also promotes  $\beta$ -H elimination of  $PYR$  cation by the superoxide, leading to the decomposition of the electrolyte.<sup>[33,48]</sup>

### 2.4. The Role of Oxygen Species in Proton-Mediated Degradation

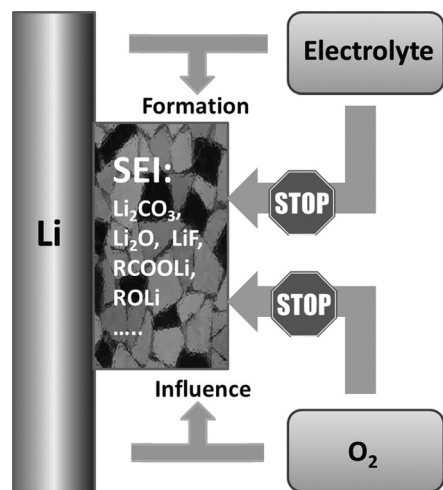
Despite the best efforts to remove  $H_2O$  from the electrolyte,  $H_2O$  has been an inevitable impurity in all electrolytes reported in the literature. It is an important source of protons, which interact strongly with oxygen species such as superoxides and peroxides. These interactions produce protonated 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 species.<sup>[50]</sup> 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.<sup>[51]</sup> Worse, the decomposition reactions liberate more protons to exacerbate the degradation of the electrolyte in a self-accelerating fashion.

### 2.5. The Reduction Susceptibility by Lithium

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 dissolved oxygen species is therefore an important consideration that must be taken into account. The reactivity of Li with oxygen species will be further discussed in Section 3.2. Here we focus our discussions on the direct reactions between Li and the electrolyte. The reactivity originated from the highly reducing nature of Li



leads to the decomposition of most known electrolytes.<sup>[21]</sup> For instance, ethers and carbonates have been shown to be decomposed by Li upon contact, forming insoluble byproducts such as lithium oxides, carbonates, alkyl carbonates and hydroxides.<sup>[21,52]</sup> These byproducts deposit onto Li to form a compact film that prevents further direct contact between Li and the electrolyte, effectively limiting the reactions (Scheme 2). Furthermore, this film is electronically insulating



**Scheme 2.** Spontaneous formation of SEI layer and its protection effect of Li against electrolyte and oxygen. See Section 2.5 for discussions of the SEI formation and functionality.

but allows for diffusion of  $\text{Li}^+$ , serving as a SEI layer.<sup>[53]</sup> Such a feature permits the use of Li anode for  $\text{Li}-\text{O}_2$  test cells. However, no known stable SEI formation has been reported for certain electrolyte systems such as amides or DMSO.<sup>[37]</sup> These electrolytes have attracted attention for their potential resistivity against oxygen species. The reactivity of these electrolytes toward Li is therefore a challenge that must be addressed. Promising results have already been obtained by additives such as  $\text{LiNO}_3$ .<sup>[38,54]</sup> For long-term stability of these electrolytes, however, a highly stable SEI layer on Li with good controls over its properties is needed. This aspect will be further discussed at the end of this article (Section 5).

### 2.6. Summary of Electrolyte Decomposition and Outlook of Future Efforts

Previous reviews have mostly treated the electrolyte systems based on their chemical structures.<sup>[7,9]</sup> The categorization based on the various decomposition pathways as summarized above is new. The knowledge presented here is not limited to the reactive oxygen species, but also applicable to other radicals or anions that might exist in the system, such as redox mediators, dissolution of metal catalysts or electrolyte decomposition intermediates. To facilitate the understanding of the systems, we further list different discussions in Table 1, where the mechanisms and chemical structures are correlated for easy reading. These efforts provide us with new insight into the role of oxygen species on the decomposition

**Table 1:** Electrolytes decomposition pathways.

	$\text{Li}_2\text{O}_2$	$\text{O}_2^{\cdot-}$	Li	$\text{O}_2$
Carbonate	–	B, N, O <sup>[31,35]</sup>	–	–
Ether/polyether	–	O, P <sup>[20,42,44,51]</sup>	–	O <sup>[43]</sup>
DMSO	B, <sup>[32]</sup> N <sup>[30]</sup>	B, <sup>[32]</sup> N, <sup>[30]</sup> P <sup>[46]</sup>	R <sup>[19]</sup>	–
Ionic liquid	–	B <sup>[47,48]</sup>	R <sup>[47]</sup>	–
Amide	–	N <sup>[39,40]</sup>	R <sup>[55]</sup>	–

Notes: N: nucleophilic attack; B: acid–base reaction; O: auto-oxidation; P: proton-mediated process; R: reduction by Li.

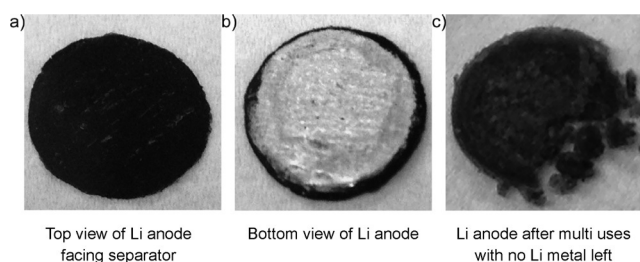
of the electrolytes. It is conceivable that ethers can be stabilized by the substitution of the H on the carbon backbone with inert groups such as  $-\text{CH}_3$ . This hypothesis has been recently verified by experimental efforts by Nazar et al.<sup>[20]</sup> Similarly, the methylation of  $\beta$  positions on PYR cation may improve the stability of the related ionic liquid cation. Nevertheless, the synthesis and purification of modified electrolytes may incur high cost, which can be an issue for practical applications. In addition, the introduction of bulky substitution groups may decrease the oxygen diffusivity, leading to high overpotentials.

### 3. Parasitic Chemical Reactions at the Li Anode

The desired reactions at the anode are the stripping (during discharge) and plating (during recharge) of lithium.<sup>[4]</sup> Lithium is an obvious choice as an anode material. But the high reactivity and low redox potential of Li dictate that complex chemical reactions often take place when Li is in contact with other chemicals.<sup>[21]</sup> In principle, the negative impact of these chemical reactions can be circumvented by replacing Li with other Li-containing compounds, such as the approach employed in commercial LIBs.<sup>[56]</sup> For  $\text{Li}-\text{O}_2$  batteries, however, replacing Li with other materials significantly undermines the achievable capacities.<sup>[22,57–59]</sup> As such, Li is the common anode material in nearly all published studies on  $\text{Li}-\text{O}_2$  batteries. To date, little attention has been paid to the parasitic chemical reactions between Li and other components of the cell, including  $\text{O}_2$ , the electrolytes and the products of the  $\text{O}_2$  reduction and electrolyte decomposition.<sup>[52,60,61]</sup> We will next address this issue by examining three common reactions at the Li anode, namely the reaction between Li and the electrolyte, the reactivity of reduced oxygen species on Li surfaces and the reactions between oxygen species and the SEI layer.

#### 3.1. Corrosion of Lithium by 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.<sup>[53]</sup> These reactions will enable the use of Li as an anode material.<sup>[19]</sup> Nevertheless, it is important to note that these SEI layers are only quasi-stable. Dendritic Li growth during recharge still poses significant challenges.<sup>[62]</sup> Indeed, corrosion

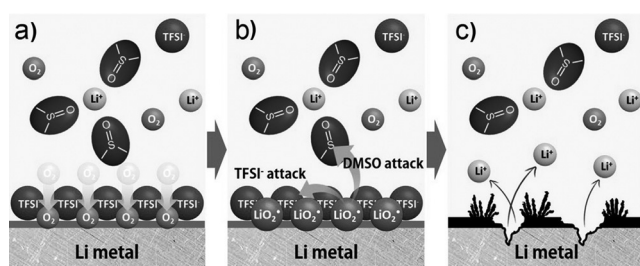


**Figure 3.** Degradation of Li anode in TEGDME electrolyte. a) The side of the Li anode facing the cathode. b) The opposite side. c) Significant decomposition after multiple cycle tests. Reproduced with permission from Ref. [60]. Copyright NPG.

of Li has been observed previously in TEGDME as a result of cycling (Figure 3), although it is unclear to what extent the anode corrosion contributes to the overall cell degradation.<sup>[60]</sup> 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.<sup>[9]</sup> Unless stable artificial SEI layers can be achieved (see Section 5), these electrolytes are incompatible with Li.<sup>[19,54]</sup> Although the problem may be addressed by replacing Li with other Li-containing compounds,<sup>[57,58]</sup> 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<sub>2</sub> batteries.

### 3.2. Reactivity of Reduced Oxygen Species on the Li Surfaces

As discussed in section 1, for most Li–O<sub>2</sub> test cells, the electrolytes are saturated with O<sub>2</sub>. The direct contact between Li and O<sub>2</sub> leads to redox reactions that produce reduced oxygen species such as superoxides (e.g., O<sub>2</sub><sup>•−</sup>, Figure 4).<sup>[52,63]</sup> Under ideal conditions, the final product of these reactions would be Li<sub>2</sub>O. It can serve as an SEI layer to prevent further reactions between Li and O<sub>2</sub>, 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<sub>2</sub> have been found to be continuous during repeated cycling of Li–O<sub>2</sub> test cells.<sup>[52,60,63,64]</sup> It is therefore important to examine how the



**Figure 4.** The existence of reduced oxygen species on the anode surfaces and their reactivity toward Li anode corrosion. 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.

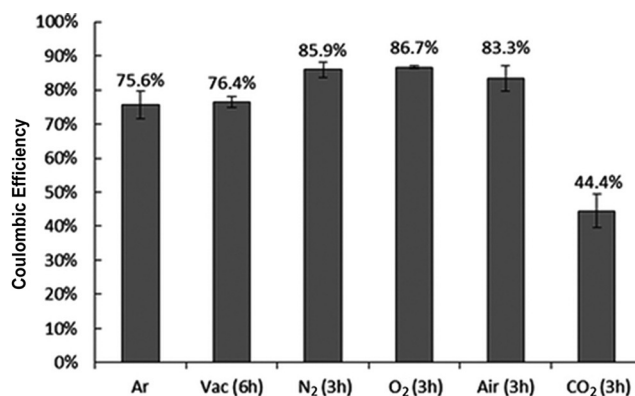
parasitic chemical reactions at the Li anode influence the overall stability of Li–O<sub>2</sub> batteries.

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.<sup>[28]</sup> 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, their influence of promoting the parasitic chemical reactions at the Li anode is profound (Figure 4).

Furthermore, even for thermodynamically more stable products such as Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O, their reactivity with the electrolytes should be examined with great care.<sup>[15,30]</sup> For instance, Li<sub>2</sub>O as a stable final product is strongly basic. It can abstract protons even for solvents normally considered aprotic. It has been shown that soaking Li<sub>2</sub>O and Li<sub>2</sub>O<sub>2</sub> in pure DMSO solution results in the formation of LiOH and severe degradation of DMSO (Figure 2).<sup>[30,45,65]</sup> As a consequence, in the full cell tests, large amount of LiOH was observed on the surface of Li, much more than what can be accounted for by the water impurities in the electrolyte.<sup>[65]</sup>

### 3.3. Synergy between Oxygen and the SEI Formation

The spontaneous SEI formed in the Ar atmosphere usually contains Li<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>O, LiF, RCOOLi, ROLi and some polymeric compounds (Scheme 2). When O<sub>2</sub> 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.<sup>[63,66]</sup> In the case of DMSO, the increase of Li<sub>2</sub>O enhances the formation of LiOH, which lowers the Coulombic efficiency of the Li anode.<sup>[63,65]</sup> In the case of N<sub>1114</sub>TF<sub>2</sub>N ionic liquid, however, more than 10% improvement of the anode Coulombic efficiencies was observed in dry oxygen as compared to Ar atmosphere. It was found that O<sub>2</sub> helps reduce the thickness



**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.

of the SEI layer by up to 67% (Figure 5).<sup>[67]</sup> 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.<sup>[55]</sup> Without  $O_2$ , the protection effect fades quickly due to the consumption of  $LiNO_3$ .<sup>[54]</sup>

### 3.4. Summary of Parasitic Chemical Reactions at the Li Anode

The use of Li as the anode is of great importance to actualizing the full potentials of Li- $O_2$  batteries 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.<sup>[52,60,63,65,68]</sup> 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  $O_2$  generate 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 artificial SEI layer (see Section 5).

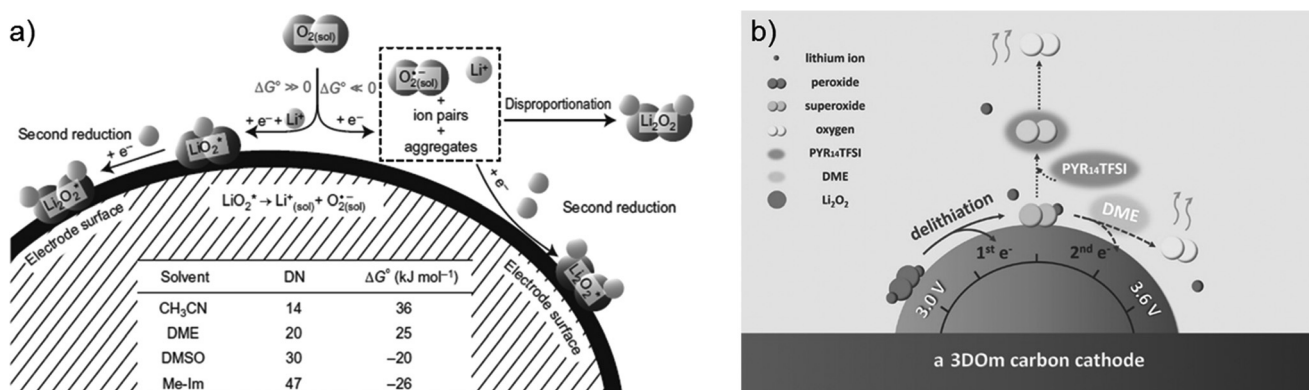
## 4. Synergistic Effects at the Cathodes

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.<sup>[6,12,69-71]</sup> Instead of repeating these discussions, 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 chemical reactions at the cathode and those in the electrolyte have important influences on each other.<sup>[72]</sup> For instance, the reaction mechanisms at the cathode are found to be sensitive to the electrolyte choices. The decomposition chemical reactions on the cathode surface in turn contribute significantly to the electrolyte decomposition.

### 4.1. The 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 chemical reactions. 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 ( $O_2^{\cdot-}$ ). As a soft base,  $O_2^{\cdot-}$  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.<sup>[34]</sup> 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 Figure 6a).<sup>[50]</sup> Johnson et al. demonstrated that electrolytes of high DN favor ORR through the one-electron pathway and enable high capacities and low overpotentials.<sup>[34]</sup> 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.<sup>[73-75]</sup> 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 one-electron recharge pathway (Figure 6b).<sup>[33]</sup> 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 overpoten-



**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); 3D0m carbon electrode = three-dimensionally ordered mesoporous carbon electrode). Reproduced with permission from Refs. [34] and [33]. Copyright NPG and American Chemical Society, respectively.



tials.<sup>[76,77]</sup> More recently, it is reported that with the help of  $\text{H}_2\text{O}$ ,  $\text{LiOH}$  instead of  $\text{Li}_2\text{O}_2$  may act as the discharge product for reversible recharge, which is a fundamentally different chemistry from that involving  $\text{Li}_2\text{O}_2$  as discussed in the rest of this Minireview.<sup>[78]</sup>

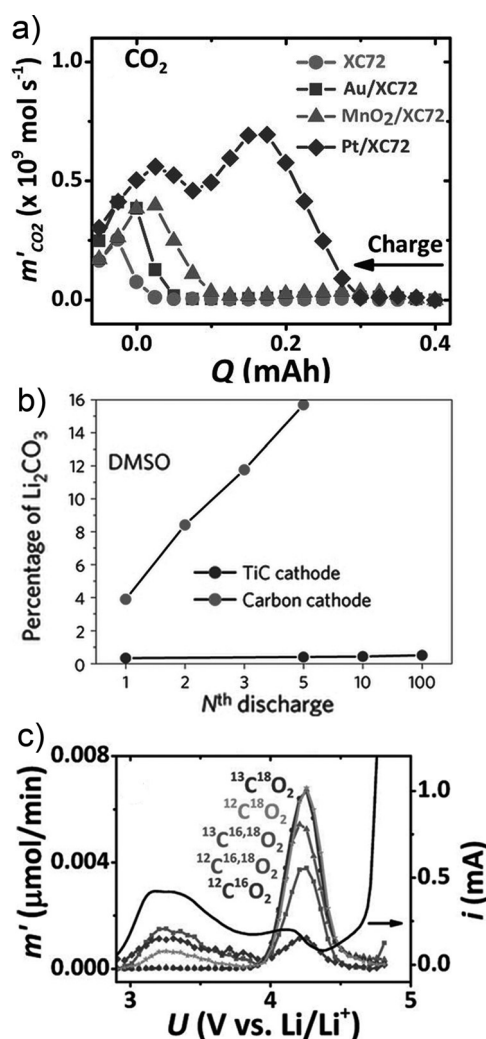
#### 4.2 Synergistic Effect between Carbon Cathode and Electrolyte Degradation

For the purpose of reducing overpotentials, researchers have examined a number of ORR and OER catalysts.<sup>[79,80]</sup> However, studies by McCloskey et al. showed that carbon loaded with catalysts, including Pt,  $\text{MnO}_2$  and Au, would exhibit more  $\text{CO}_2$  evolution than bare carbon, indicating that these catalysts may promote ether-based electrolyte decomposition (Figure 7a).<sup>[25]</sup> The issue of catalyst-promoted elec-

trolyte decomposition should therefore be considered carefully for future studies.<sup>[23,81]</sup>

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 (Figure 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.<sup>[17]</sup> When the carbon is deactivated by  $\text{LiNO}_3$  additives, Kang et al. observed significantly suppressed decomposition of not only the cathode, but also the electrolyte.<sup>[82]</sup> Indeed, greater stability has been consistently measured when carbon-free cathode is employed, either by coating carbon surface with passivation (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}_x$ ) or by using non-carbon materials such as Au,  $\text{TiSi}_2$  and  $\text{TiC}$  (Figure 7b).<sup>[19,83–87]</sup> Lu et al. examined the effect of  $\text{Al}_2\text{O}_3$  coating using DFT calculations and proposed that the protective  $\text{Al}_2\text{O}_3$  coating inhibited electrolyte decomposition on the defect sites.<sup>[83]</sup>

The decomposition of electrolyte has been found to induce carbon decomposition under  $\text{Li-O}_2$  operational conditions, as well.<sup>[72]</sup> By isotope labelling, McCloskey et al. found significant reactions between the electrolyte and the carbon cathode (Figure 7c).<sup>[16]</sup> Their results suggest that the highly reactive species formed as a result of the electrolyte decomposition can diffuse to the cathode surface and react with carbon. This result further highlights the importance of studying the cathode and electrolyte decomposition in a systematic fashion.



**Figure 7.** Synergistic effects between parasitic chemical reactions of the cathode and the electrolyte. a) The electrolyte decomposition is promoted by catalysts on the carbon cathode. b) Electrolyte decomposition is suppressed when non-carbon cathode is used. c) Carbon decomposition is also promoted by the electrolytes. Reproduced with permission from Refs. [25], [87] and [16], respectively. Copyright American Chemical Society and NPG.

## 5. Summary and Outlook

Compared to LIBs,  $\text{Li-O}_2$  batteries feature one additional component,  $\text{O}_2$ , which is highly reactive. This addition complicates the possible chemical reactions considerably, making it difficult to study the parasitic chemical reactions at the anode, the cathode and within the electrolyte that are inherent to  $\text{Li-O}_2$  batteries. But the understanding of these chemical reactions is critical to the actualization of the promise held by  $\text{Li-O}_2$  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. This Minireview is written to fill in the knowledge gap.

We see from the discussions that  $\text{O}_2$  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 phenomenological 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.<sup>[88,89]</sup> The issues connected 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.<sup>[78,90]</sup> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> batteries should benefit tremendously by examining the parasitic chemical reactions systematically.

### Acknowledgements

We thank Boston College and MassCEC for financial support.

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 11344–11353  
*Angew. Chem.* **2016**, *128*, 11514–11524

- [1] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193–2203.
- [2] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.* **2012**, *11*, 19–29.
- [3] K. G. Gallagher, S. Goebel, T. Greszler, M. Mathias, W. Oelerich, D. Eroglu, V. Srinivasan, *Energy Environ. Sci.* **2014**, *7*, 1555–1563.
- [4] K. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1–5.
- [5] J. Read, *J. Electrochem. Soc.* **2006**, *153*, A96.
- [6] A. C. Luntz, B. D. McCloskey, *Chem. Rev.* **2014**, *114*, 11721–11750.
- [7] F. Li, T. Zhang, H. Zhou, *Energy Environ. Sci.* **2013**, *6*, 1125–1141.
- [8] M. D. Bhatt, H. Geaney, M. Nolan, C. O'Dwyer, *Phys. Chem. Chem. Phys.* **2014**, *16*, 12093–12130.
- [9] M. Balaish, A. Kraytsberg, Y. Ein-Eli, *Phys. Chem. Chem. Phys.* **2014**, *16*, 2801–2822.
- [10] Z.-w. Chang, J.-j. Xu, Q.-c. Liu, L. Li, X.-b. Zhang, *Adv. Energy Mater.* **2015**, *5*, 1500633.
- [11] B. D. McCloskey, D. S. Bethune, R. M. Shelby, T. Mori, R. Scheffler, A. Speidel, M. Sherwood, A. C. Luntz, *J. Phys. Chem. Lett.* **2012**, *3*, 3043–3047.
- [12] Y. C. Lu, B. M. Gallant, D. G. Kwabi, J. R. Harding, R. R. Mitchell, M. S. Whittingham, Y. Shao-Horn, *Energy Environ. Sci.* **2013**, *6*, 750–768.
- [13] Z.-L. Wang, D. Xu, J.-J. Xu, X.-B. Zhang, *Chem. Soc. Rev.* **2014**, *43*, 7746–7786.
- [14] B. D. McCloskey, R. Scheffler, A. Speidel, G. Girishkumar, A. C. Luntz, *J. Phys. Chem. C* **2012**, *116*, 23897–23905.
- [15] B. D. McCloskey, A. Valery, A. C. Luntz, S. R. Gowda, G. M. Wallraff, J. M. Garcia, T. Mori, L. E. Krupp, *J. Phys. Chem. Lett.* **2013**, *4*, 2989–2993.
- [16] B. D. McCloskey, A. Speidel, R. Scheffler, D. C. Miller, V. Viswanathan, J. S. Hummelshøj, J. K. Nørskov, A. C. Luntz, *J. Phys. Chem. Lett.* **2012**, *3*, 997–1001.
- [17] M. M. O. Thotiyl, S. A. Freunberger, Z. Q. Peng, P. G. Bruce, *J. Am. Chem. Soc.* **2013**, *135*, 494–500.
- [18] B. D. McCloskey, D. S. Bethune, R. M. Shelby, G. Girishkumar, A. C. Luntz, *J. Phys. Chem. Lett.* **2011**, *2*, 1161–1166.
- [19] Z. Peng, S. A. Freunberger, Y. Chen, P. G. Bruce, *Science* **2012**, *337*, 563–566.
- [20] B. D. Adams, R. Black, Z. Williams, R. Fernandes, M. Cuisinier, E. J. Berg, P. Novak, G. K. Murphy, L. F. Nazar, *Adv. Energy Mater.* **2015**, *5*, 1400867.
- [21] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, J.-G. Zhang, *Energy Environ. Sci.* **2014**, *7*, 513–537.
- [22] M. N. Obrovac, V. L. Chevrier, *Chem. Rev.* **2014**, *114*, 11444–11502.
- [23] F. S. Gittleston, R. C. Sekol, G. Doubek, M. Linardi, A. D. Taylor, *Phys. Chem. Chem. Phys.* **2014**, *16*, 3230–3237.
- [24] R. Black, J.-H. Lee, B. Adams, C. A. Mims, L. F. Nazar, *Angew. Chem. Int. Ed.* **2013**, *52*, 392–396; *Angew. Chem.* **2013**, *125*, 410–414.
- [25] B. D. McCloskey, R. Scheffler, A. Speidel, D. S. Bethune, R. M. Shelby, A. C. Luntz, *J. Am. Chem. Soc.* **2011**, *133*, 18038–18041.
- [26] E. J. Calvo, N. Mozhzhukhina, *Electrochem. Commun.* **2013**, *31*, 56–58.
- [27] J. Yang, D. Zhai, H.-H. Wang, K. C. Lau, J. A. Schlueter, P. Du, D. J. Myers, Y.-K. Sun, L. A. Curtiss, K. Amine, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3764–3771.
- [28] R. Black, S. H. Oh, J. H. Lee, T. Yim, B. Adams, L. F. Nazar, *J. Am. Chem. Soc.* **2012**, *134*, 2902–2905.
- [29] P. Du, J. Lu, K. C. Lau, X. Luo, J. Bareno, X. Zhang, Y. Ren, Z. Zhang, L. A. Curtiss, Y. K. Sun, K. Amine, *Phys. Chem. Chem. Phys.* **2013**, *15*, 5572–5581.
- [30] D. G. Kwabi, T. P. Batcho, C. V. Amanchukwu, N. Ortiz-Vitoriano, P. Hammond, C. V. Thompson, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2014**, *5*, 2850–2856.
- [31] W. Xu, K. Xu, V. V. Viswanathan, S. A. Towne, J. S. Hardy, J. Xiao, Z. Nie, D. Hu, D. Wang, J.-G. Zhang, *J. Power Sources* **2011**, *196*, 9631–9639.
- [32] D. Sharon, M. Afri, M. Noked, A. Garsuch, A. A. Frimer, D. Aurbach, *J. Phys. Chem. Lett.* **2013**, *4*, 3115–3119.
- [33] J. Xie, Q. Dong, I. Madden, X. Yao, Q. Cheng, P. Dornath, W. Fan, D. Wang, *Nano Lett.* **2015**, *15*, 8371–8376.
- [34] L. Johnson, C. Li, Z. Liu, Y. Chen, S. A. Freunberger, P. C. Ashok, B. B. Praveen, K. Dholakia, J.-M. Tarascon, P. G. Bruce, *Nat. Chem.* **2014**, *6*, 1091–1099.
- [35] S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Bardé, P. Novák, P. G. Bruce, *J. Am. Chem. Soc.* **2011**, *133*, 8040–8047.
- [36] V. S. Bryantsev, V. Giordani, W. Walker, M. Blanco, S. Zecevic, K. Sasaki, J. Uddin, D. Addison, G. V. Chase, *J. Phys. Chem. A* **2011**, *115*, 12399–12409.
- [37] V. S. Bryantsev, J. Uddin, V. Giordani, W. Walker, D. Addison, G. V. Chase, *J. Electrochem. Soc.* **2013**, *160*, A160–A171.
- [38] W. Walker, V. Giordani, J. Uddin, V. S. Bryantsev, G. V. Chase, D. Addison, *J. Am. Chem. Soc.* **2013**, *135*, 2076–2079.
- [39] Y. Chen, S. A. Freunberger, Z. Peng, F. Bardé, P. G. Bruce, *J. Am. Chem. Soc.* **2012**, *134*, 7952–7957.
- [40] D. Sharon, D. Hirsberg, M. Afri, A. Garsuch, A. A. Frimer, D. Aurbach, *J. Phys. Chem. C* **2014**, *118*, 15207–15213.

- [41] H. G. Jung, J. Hassoun, J. B. Park, Y. K. Sun, B. Scrosati, *Nat. Chem.* **2012**, *4*, 579–585.
- [42] V. S. Bryantsev, F. Faglion, *J. Phys. Chem. A* **2012**, *116*, 7128–7138.
- [43] J. R. Harding, C. V. Amanchukwu, P. T. Hammond, Y. Shao-Horn, *J. Phys. Chem. C* **2015**, *119*, 6947–6955.
- [44] S. A. Freunberger, Y. Chen, N. E. Drewett, L. J. Hardwick, F. Bardé, P. G. Bruce, *Angew. Chem. Int. Ed.* **2011**, *50*, 8609–8613; *Angew. Chem.* **2011**, *123*, 8768–8772.
- [45] A. Khetan, H. Pitsch, V. Viswanathan, *J. Phys. Chem. Lett.* **2014**, *5*, 2419–2424.
- [46] N. Mozhzhukhina, L. P. M. De Leo, E. J. Calvo, *J. Phys. Chem. C* **2013**, *117*, 18375–18380.
- [47] M. Piana, J. Wandt, S. Meini, I. Buchberger, N. Tsiouvaras, H. A. Gasteiger, *J. Electrochem. Soc.* **2014**, *161*, A1992–A2001.
- [48] K. U. Schwenke, J. Herranz, H. A. Gasteiger, M. Piana, *J. Electrochem. Soc.* **2015**, *162*, A905–A914.
- [49] C. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, M. A. Hendrickson, *J. Phys. Chem. C* **2010**, *114*, 9178–9186.
- [50] N. B. Aetukuri, B. D. McCloskey, J. M. García, L. E. Krupp, V. Viswanathan, A. C. Luntz, *Nat. Chem.* **2015**, *7*, 50–56.
- [51] J. M. García, H. W. Horn, J. E. Rice, *J. Phys. Chem. Lett.* **2015**, *6*, 1795–1799.
- [52] R. S. Assary, J. Lu, P. Du, X. Luo, X. Zhang, Y. Ren, L. A. Curtiss, K. Amine, *ChemSusChem* **2013**, *6*, 51–55.
- [53] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, *Adv. Sci.* **2016**, *3*, 1500213.
- [54] J. Uddin, V. S. Bryantsev, V. Giordani, W. Walker, G. V. Chase, D. Addison, *J. Phys. Chem. Lett.* **2013**, *4*, 3760–3765.
- [55] V. Giordani, W. Walker, V. S. Bryantsev, J. Uddin, G. V. Chase, D. Addison, *J. Electrochem. Soc.* **2013**, *160*, A1544–A1550.
- [56] V. Etacheri, R. Marom, R. Elazari, G. Salitra, D. Aurbach, *Energy Environ. Sci.* **2011**, *4*, 3243–3262.
- [57] J. Hassoun, H. G. Jung, D. J. Lee, J. B. Park, K. Amine, Y. K. Sun, B. Scrosati, *Nano Lett.* **2012**, *12*, 5775–5779.
- [58] Z. Guo, X. Dong, Y. Wang, Y. Xia, *Chem. Commun.* **2015**, *51*, 676–678.
- [59] G. A. Elia, D. Bresser, J. Reiter, P. Oberhumer, Y.-K. Sun, B. Scrosati, S. Passerini, J. Hassoun, *ACS Appl. Mater. Interfaces* **2015**, *7*, 22638–22643.
- [60] J.-L. Shui, J. S. Okasinski, P. Kenesei, H. A. Dobbs, D. Zhao, J. D. Almer, D.-J. Liu, *Nat. Commun.* **2013**, *4*, 2255.
- [61] R. Younesi, M. Hahlin, M. Roberts, K. Edström, *J. Power Sources* **2013**, *225*, 40–45.
- [62] M. S. Park, S. B. Ma, D. J. Lee, D. Im, S.-G. Doo, O. Yamamoto, *Sci. Rep.* **2014**, *4*, 3815.
- [63] H. Lee, D. J. Lee, J.-N. Lee, J. Song, Y. Lee, M.-H. Ryou, J.-K. Park, Y. M. Lee, *Electrochim. Acta* **2014**, *123*, 419–425.
- [64] R. S. Assary, J. Lu, X. Luo, X. Zhang, Y. Ren, H. Wu, H. M. Albishri, D. A. El-Hady, A. S. Al-Bogami, L. A. Curtiss, K. Amine, *ChemPhysChem* **2014**, *15*, 2077–2083.
- [65] M. Marinaro, P. Balasubramanian, E. Gucciardi, S. Theil, L. Jörissen, M. Wohlfahrt-Mehrens, *ChemSusChem* **2015**, *8*, 3139–3145.
- [66] N. Togasaki, T. Momma, T. Osaka, *J. Power Sources* **2015**, *294*, 588–592.
- [67] J. K. Stark, Y. Ding, P. A. Kohl, *J. Phys. Chem. C* **2013**, *117*, 4980–4985.
- [68] D. J. Lee, H. Lee, Y.-J. Kim, J.-K. Park, H.-T. Kim, *Adv. Mater.* **2016**, *28*, 857–863.
- [69] Y. Shao, F. Ding, J. Xiao, J. Zhang, W. Xu, S. Park, J.-G. Zhang, Y. Wang, J. Liu, *Adv. Funct. Mater.* **2013**, *23*, 987–1004.
- [70] J. Lu, L. Li, J.-B. Park, Y.-K. Sun, F. Wu, K. Amine, *Chem. Rev.* **2014**, *114*, 5611–5640.
- [71] J. Wang, Y. Li, X. Sun, *Nano Energy* **2013**, *2*, 443–467.
- [72] M. A. Schroeder, A. J. Pearse, A. C. Kozen, X. Chen, K. Gregorczyk, X. Han, A. Cao, L. Hu, S. B. Lee, G. W. Rubloff, M. Noked, *Chem. Mater.* **2015**, *27*, 5305–5313.
- [73] A. Khetan, A. Luntz, V. Viswanathan, *J. Phys. Chem. Lett.* **2015**, *6*, 1254–1259.
- [74] C. M. Burke, V. Pande, A. Khetan, V. Viswanathan, B. D. McCloskey, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 9293–9298.
- [75] B. D. McCloskey, C. M. Burke, J. E. Nichols, S. E. Renfrew, *Chem. Commun.* **2015**, *51*, 12701–12715.
- [76] S. Meini, S. Solchenbach, M. Piana, H. A. Gasteiger, *J. Electrochem. Soc.* **2014**, *161*, A1306–A1314.
- [77] F. Li, S. Wu, D. Li, T. Zhang, P. He, A. Yamada, H. Zhou, *Nat. Commun.* **2015**, *6*, 7843.
- [78] T. Liu, M. Leskes, W. Yu, A. J. Moore, L. Zhou, P. M. Bayley, G. Kim, C. P. Grey, *Science* **2015**, *350*, 530–533.
- [79] Y. Shao, S. Park, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, *ACS Catal.* **2012**, *2*, 844–857.
- [80] J. R. Harding, Y. C. Lu, Y. Tsukada, Y. Shao-Horn, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10540–10546.
- [81] S. Ma, Y. Wu, J. Wang, Y. Zhang, Y. Zhang, X. Yan, Y. Wei, P. Liu, J. Wang, K. Jiang, S. Fan, Y. Xu, Z. Peng, *Nano Lett.* **2015**, *15*, 8084–8090.
- [82] S. J. Kang, T. Mori, S. Narizuka, W. Wilcke, H.-C. Kim, *Nat. Commun.* **2014**, *5*, 3937.
- [83] J. Lu, Y. Lei, K. C. Lau, X. Y. Luo, P. Du, J. G. Wen, R. S. Assary, U. Das, D. J. Miller, J. W. Elam, H. M. Albishri, D. Abd El-Hady, Y. K. Sun, L. A. Curtiss, K. Amine, *Nat. Commun.* **2013**, *4*, 2383.
- [84] J. Xie, X. Yao, Q. Cheng, I. P. Madden, P. Dornath, C.-C. Chang, W. Fan, D. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*, 4299–4303; *Angew. Chem.* **2015**, *127*, 4373–4377.
- [85] J. Xie, X. Yao, I. P. Madden, D.-E. Jiang, L.-Y. Chou, C.-K. Tsung, D. Wang, *J. Am. Chem. Soc.* **2014**, *136*, 8903–8906.
- [86] X. Yao, Q. Cheng, J. Xie, Q. Dong, D. Wang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 21948–21955.
- [87] M. M. O. Thotiyil, S. A. Freunberger, Z. Peng, Y. Chen, Z. Liu, P. G. Bruce, *Nat. Mater.* **2013**, *12*, 1050–1056.
- [88] A. C. Kozen, C.-F. Lin, A. J. Pearse, M. A. Schroeder, X. Han, L. Hu, S. B. Lee, G. W. Rubloff, M. Noked, *ACS Nano* **2015**, *9*, 5884–5892.
- [89] S. Visco, V. Nimon, A. Petrov, K. Pridatko, N. Goncharenko, E. Nimon, L. De Jonghe, Y. Volkovich, D. Bograchev, *J. Solid State Electrochem.* **2014**, *18*, 1443–1456.
- [90] J. Lu, Y. J. Lee, X. Luo, K. C. Lau, M. Asadi, H.-H. Wang, S. Brombosz, J. Wen, D. Zhai, Z. Chen, D. J. Miller, Y. S. Jeong, J.-B. Park, Z. Z. Fang, B. Kumar, A. Salehi-Khojin, Y.-K. Sun, L. A. Curtiss, K. Amine, *Nature* **2016**, *529*, 377–382.

Received: February 19, 2016

Revised: April 12, 2016

Published online: July 6, 2016