Lithium-Oxygen Batteries and Related Systems: Potential, Status and Future

Won-Jin Kwak[a,b,ψ], Rosy [c,d,ψ], Daniel Sharon[e], Chun Xia[f], Hun Kim[a], Lee R. Johnson[g], Peter G. Bruce[h,*], Linda F. Nazar[f,*], Yang-Kook Sun[a,i,*], Aryeh A. Frimer[c], Malachi Noked[c,d], Stefan A. Freunberger[j,k] and Doron Aurbach[c,d,*]

(a) Department of Energy Engineering, Hanyang University, Seoul 04763, Republic of Korea
(b) Energy & Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, USA
(c) Department of Chemistry, Bar-Ilan University, Ramat Gan, 5290002, Israel
(d) Bar-Ilan Institute of Nanotechnology and Advanced Materials, Ramat Gan, 5290002, Israel
(e) Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, USA
(f) Department of Chemistry and the Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
(g) School of Chemistry and GSK Carbon Neutral Laboratory for Sustainable Chemistry, University of Nottingham, NG7 2TU, UK
(h) Departments of Materials and Chemistry, Parks Road, University of Oxford, OX1 3PH, UK

(i) Department of Chemical Engineering, Hanyang University, Seoul 04763, Republic of Korea
(j) Institute for Chemistry and Technology of Materials, Graz University of Technology, 8010 Graz, Austria
(k) IST Austria (Institute of Science and Technology Austria), 3400 Klosterneuburg, Austria

CONTENTS

ABSTRACT

The goal of limiting Global Warming to 1.5 °C requires a drastic reduction in CO_2 emissions across many sectors of the world economy. Batteries are vital to this endeavour, whether used in electric vehicles, to store renewable electricity or in aviation. Present lithium-ion technologies are preparing the public for this inevitable change, but their maximum theoretical specific capacity presents a limitation. Their high cost is another concern for commercial viability. Metal-air batteries have the highest theoretical energy density of all possible secondary battery technologies and could yield step changes in energy storage - if their practical difficulties could be overcome. The scope of this review is to provide an objective, comprehensive and authoritative assessment of the intensive work invested in non-aqueous rechargeable metal-air batteries over the last few years, which identified the key problems and guides directions to solve them. We focus primarily on the challenges and outlook for $Li-O_2$ cells, but include $Na-O_2$, $K-O_2$ and $Mg-O_2$ cells for comparison. Our review highlights the interdisciplinary nature of this field that involves a combination of materials chemistry, electrochemistry, computation, microscopy, spectroscopy, and surface science. The mechanisms of O_2 reduction and evolution are considered in the light of recent findings, along with developments in positive and negative electrodes, electrolytes, electro-catalysis on surfaces and in solution, and the degradative effect of singlet oxygen, which is typically formed in $Li-O_2$ cells.

1. INTRODUCTION
1.1. Contemporary Energy Needs

Over the last decades, the intensive use of fossil fuels and electricity has dramatically increased the standard of living. Energy, particularly electrical energy, is core to a modern society. Presently, over 70% of the world's energy requirement is met by fossil fuels including coal, oil and natural gas, but this is damaging our environment. Serious issues like global warming and air pollution make it extremely clear that it is imperative to reduce our dependence on fossil fuels to meet our energy requirements. In order to implement the necessary changes scientific advances and technological solutions are urgently required.

Electrochemical power sources and energy storage systems will play a vital role in shifting the paradigm of the future energy network towards clean, renewable sources. This is because such systems form a vital bridge between dispatchable energy generation, and intermittent supply from renewable sources such as wind and solar power.[1,2] The most impressive scientific and applicative successes of modern electrochemistry are lithium-ion batteries (LIBs), which today power most of our mobile electronic devices. Building on this progress, the scientific community has set ambitious targets in the hope of substantially reducing fossil fuel use in the near future and promote the propulsion of ground transportation by electric power. It is well known that in powering the 3Cs - computers, communication devices and consumer electronics - LIBs have deeply penetrated every corner of our daily lives.[1,3] Despite LIBs successful history so far, there has been a continuous call to improve their capabilities and performance, primarily driven by their inability to meet society's emerging needs.[2] For example, the present LIBs, with a maximum specific energy of ca. 250 Wh kg^{-1} (at the cell level), do not possess sufficient energy, rate, durability or affordability to match the performance of traditional automotive gasoline/internal combustion engines (Figure 1).[2] In addition, detrimental climatic change has hastened the need to electrify transport and develop reliable energy storage systems. These urgent requirements drive the scientific

community to further increase the energy and power density of electrochemical power sources and not least the ecological footprint beyond the limits of LIBs.

Relying on recent research efforts from both academia and industry, it is believed that further advancements in LIB technology and composition will eventually push their specific energy to ~300 Wh kg^{-1} $_{cell}$.[1–4] With such an upper limit, advanced LIBs can meet the requirement of mid-sized passenger or light goods electric vehicles. Nevertheless, for the realization of full-electric vehicles (EVs) with long driving range (500 miles), and especially for long range small vehicles and heavy goods vehicles (HGVs), new electrochemical couples and chemistries, with a targeted specific energy of 500 Wh kg^{-1}$_{cell}$ and beyond, need to be developed. In addition, the low reserves (0.0017 wt.%) of Li in the earth's crust has spurred extensive research in innovative battery platforms exploiting other active metals such as Na, Mg or K.
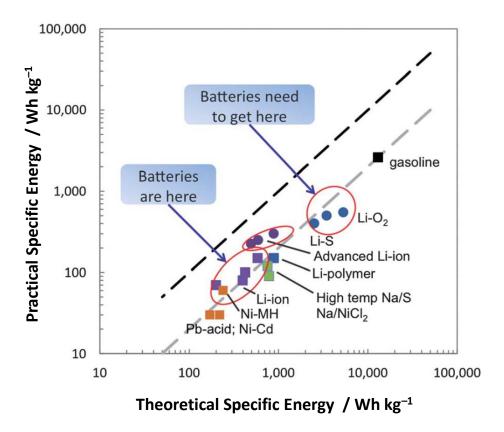

Figure 1. The graph shows the present position of various batteries on a plot of practical specific energy versus theoretical energy density. This illustrates the enormous challenge of increasing the practical energy density of advanced batteries beyond that of present state-of-

the-art LIBs if they have to compete with the energy stored and delivered by fossil fuels like gasoline. Reproduced with permission from ref [2]. Copyright 2012 Royal Society of Chemistry.

1.2. Brief overview of electrochemical energy storage

The electrification of many technologies has motivated researchers to develop advanced batteries replete with innovation. Currently, the development of Li-ion batteries is a topic of prime importance. Significant progress has been achieved with the discovery and development of some high energy layered cathode materials of the general formula $Li_{1+x}Ni_zCo_wMn_yO_2$, denoted as Li and Mn-rich NMC compounds ($x > 0$, $y > 0.5$, $x+y+z+w = 1$). These cathodes can deliver a specific capacity > 260 mAh g^{-1}, almost twice that of conventional layered, spinel, or olivine type cathode materials.[3–8] Unfortunately, these high specific capacity cathode materials require high charging potentials > 4.6 V, which challenge the stability of most relevant electrolyte solutions. Also, they suffer from stability problems, plagued by both capacity and average voltage fading during their cycling due to their complex structure and operation mechanism.[6,9,10] Another approach to boost the energy densities of the LIBs is to use layered transition metal oxide cathodes with a high nickel content, denoted as Ni-rich NMC cathode materials ($LiNi_xCo_yMn_zO_2$, $x > 0.8$)[8,11–13] As the Ni content approaches 100%, their specific capacity can reach 240 mAh g^{-1}, with a maximal charging potential < 4.3 V. These materials also suffer from capacity fading problems upon cycling; however, those issues can be mitigated by using judicious doping and coating.[7,10,14–18] Using high voltage cathode materials (> 4.7 V) like $LiCoPO_4$ (olivine) and $LiNi_{0.5}Mn_{1.5}O_4$ may also be attractive for some applications; however, the relatively low specific capacity of these cathodes (practically < 140 mAh g^{-1}) weakens their importance.[19–21] Since LIBs use graphite anodes (with a theoretical capacity of 372 mAh g^{-1}) it is possible to increase their energy density by moving to high capacity Si based anodes (theoretically > 3000 mAh g^{-1}).[22–25] However, Si based anodes suffer from intrinsic instability issues related to SEI formation.[23,24] Nonetheless, since the limiting factor is the cathode side, changing the anodes in LIBs cannot drastically

increase their energy density. The durability and cycle life of LIBs depends on complex interfacial interactions between the electrodes and the electrolyte solution and development of passivation phenomena on the electrode surfaces.[26,27] Thereby, much attention has been devoted to developing suitable electrolyte solutions for LIBs.[28,29] The success in developing commercial LIBs which currently conquer the markets and the fear about a possible shortage in lithium if the electro-mobility revolution succeeds, promotes development of more battery technologies based on other active metals. An excellent example are the intensive efforts to develop Na-ion batteries in recent years.[30–33] Hence, despite the constant progress in LIBs performance, and encouraged by their success, worldwide efforts are underway to find new types of even more promising redox couples.[22,34,35] Relying on the benefits of metallic anodes, the choice of sulfur and oxygen as the cathode is based on their high specific capacity (1168 mAh g^{-1} for Li_2O_2). Yet, the practical performance of batteries based on these redox couples lags significantly behind their theoretical promise. Nevertheless, metal-sulfur and metal-oxygen batteries may outperform all other possible choices from a cost perspective and have attracted global attention from both academia and industries. This is because of their 3-5 fold higher specific energy, as seen in Figure 2.[22,36–38] The key determinant in the advancement of these batteries relies on combating parasitic reactions that take a toll in terms of efficiency, cyclability and safety.[2] There is much research activity ongoing in the field of Li-S batteries,[39,40] but this topic is beyond the scope of this review, which focuses on the alluring lithium-oxygen (Li-O_2) batteries, based on their formal specific energy of 3500 Wh kg^{-1}. First, however, we introduce the reader to metal-air batteries in the next section.
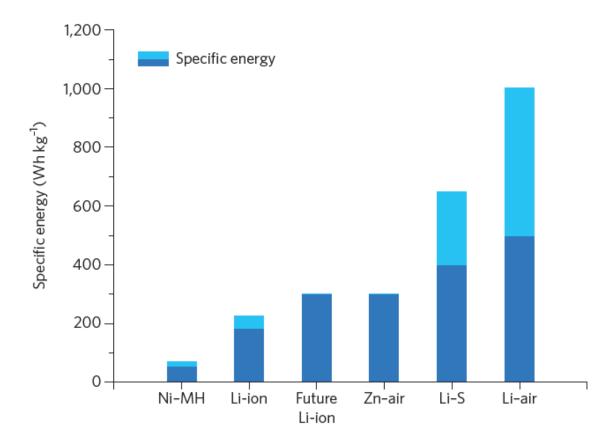
Figure 2. Bar graph demonstrating the practical specific energies in the battery world. These are reduced from the theoretical values by current collectors, cell packaging and system overheads. Light blue boxes indicate the range of specific energies. Reproduced with permission from ref [37]. Copyright 2016 Springer Nature.

1.3. Metal-air batteries

Metal-air batteries[36,41] promise a higher specific energy in comparison to the state of art LIBs and thus have arguably gained the most attention under the topic of "*post Li-ion batteries*". Based on the pairing of a metal anode and an oxygen/air electrode (called as anode and cathode respectively in this paper), metal-air batteries present a hybrid architecture combining the features of both batteries and fuel cells. To date, several metal-air batteries using alkali metals (Li, Na and K), alkaline earth metal (Mg), and first row transition metals (Fe, Zn) or Al as the anode have been reported and their formal specific energies are presented in Figure 3. At this point it is important to note that, despite being the motivation for the research, there is lots of ambiguity with what energy metal-O_2 batteries could potentially store. The problem arises from confusing *formal capacity* (1168 mAh·g^{-1}, 2500 mAh·cm^{-3} Li_2O_2) with *theoretical*

capacity (Li_2O_2 including the minimum electron and ion conductor to allow the storage process $O_2 + 2\ e^- + 2\ Li^+ \leftrightarrow Li_2O_2$ to take place) [Ref 136, 185]. As broadly discussed in Section 3, Li_2O_2 can by far not be cycled in pure substance which cuts the theoretical well below formal capacity. Yet there is no theoretical barrier for the Li-O$_2$ cathode to achieve higher true capacity than LIB cathodes (see Section 3.4(c)).
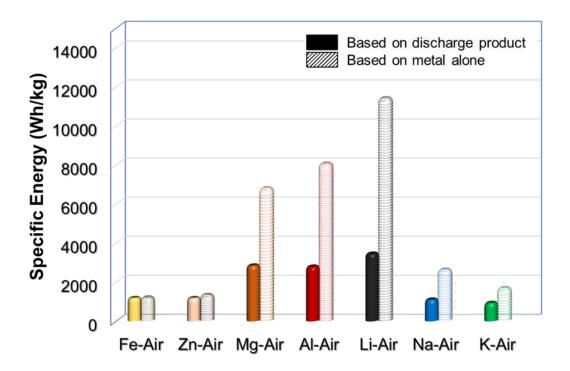
Figure 3. Specific energies of metal-air batteries. Solid colored bars represent specific energies densities based on the discharge product and one equivalent of the metal anode whereas patterned bars are based on the formal specific energies taking only metal into account. Reproduced with permission from ref[42]. Copyright 2017 American Chemical Society.

The non-aqueous systems have gained recent attention specifically due to the high formal specific energy of Li-O$_2$ batteries. However, aqueous electrolyte solution-based configurations have been researched since the early 1900's.[43] The commercialization of metal-air batteries commenced with the primary Zn-air battery in 1932.[44] Later, other aqueous systems like Al-air[45,46] and Mg-air[47] came into existence in 1960s. Amongst the aqueous counterparts, the aluminium–air battery was considered to be an attractive candidate as a power source for electric vehicles (EVs) because of its high formal energy density (2800 Wh kg^{-1}).

Notably, in 2016, an Al–air battery weighing 100 kg was fabricated by Alcoa and Phinergy Co. Ltd. and shown to be capable of running a car on air for more than 1000 miles.[45] Unfortunately, most of the aqueous metal-air cells, including the Al-air battery, function as primary cells and can only be mechanically charged by replacing the used metal anodes and the electrolyte solution. Additionally, corrosion of metallic anodes in presence of water, high self-discharge rate, sluggish discharge kinetics, and short shelf life render these systems inappropriate for demanding applications like full EV vehicles.

On the other hand, non-aqueous metal air systems[48] are comparatively new but offer rechargeability with extremely high theoretical capacity. In 1996, Abraham et al.[49] reported the first rechargeable non-aqueous lithium-O_2 battery, which opened up a completely new field for researchers that led to development of other analogous systems such as Na-O_2 and K-O_2 batteries. Amongst these, the Li-O_2 battery is the most attractive since it offers the highest operational voltage (~2.96 V) with a formal specific energy of ~3500 Wh kg^{-1} (based on formation of Li_2O_2 on discharge). The societal need for energy storage that exceeds Li-ion and the possibility that Li-air could deliver the step-change required has convinced the research community of its importance. Significant effort was devoted a decade ago to commercialize Li-air, which failed, but prompted research aimed at a deeper understanding of the poorly understood underpinning chemistry and electrochemistry, including the processes of degradation.

1.4. Scope of this review article

In the past, diverse aspects of metal-air batteries, in general and the most promising Li-O_2 batteries in particular, have been reviewed by various leading research groups.[37,48,50–56] Detailed reviews with emphasis on the strategies towards a stable metal anode,[57–59] methodologies for mechanistic studies,[60–62] effect of contaminants,[63–65] stability of the electrolyte solutions[66] and the role of redox mediators on the performance of Li-O_2 batteries

[54,67] have appeared. Even overviews questioning the practical reality of metal air batteries have been published recently.[42,68,69] The intensive work in this area over the last decade has identified the key problems and guided directions to solve them. Thus, the preparation of a comprehensive report covering the challenges, possible solutions and recent developments associated with the progress of these batteries is called for. It is hoped that such a review will give the interested and educated reader a clear picture of the potential prospects of Li-O$_2$ and related batteries.

This review has four major goals:

(1) To clearly describe the current status of Li-O$_2$ batteries with respect to: new mechanistic insights; the stability and degradation of the electrolyte solutions and the electrodes in the presence of reactive oxygen species (ROS), singlet oxygen and other contaminants; and the catalytic ability of anchored and mobile catalysts (redox mediators) to address the problematic oxygen reduction and evolution reactions.

(2) To extend the knowledge gained by in-depth research in the field of Li-O$_2$ batteries to analogous systems like Na-O$_2$, K-O$_2$ and Mg-O$_2$ batteries which are still in their infancy.

(3) To introduce novel electrolyte solutions and electrode architectures which stabilize extremely reactive systems without compromising their promising energy density.

(4) To present a critical, yet realistic overview of the accumulated knowledge in this rapidly expanding field in order to overcome the gap between breakthroughs and commercialization. We have, therefore, tried avoiding redundant areas while carefully maintaining the comprehensive nature of the review to keep it relevant for readers of broad interest.

2. LITHIUM-OXYGEN BATTERIES: DIVERSITY AND EVOLUTION

2.1. Configuration of Li-O$_2$ cells

The Li-O$_2$ battery - composed of a metallic lithium as the negative electrode, namely the anode, air/O$_2$ as the cathode active mass and a Li$^+$ containing electrolyte solution - is one of the most studied class of metal-air batteries. The cathode in these systems is a composite electronically conducting porous matrix that enables the electrochemical contact between oxygen gas and Li ions in the electrolyte solution phase. It primarily functions with the dissolution/deposition of lithium metal at the anode and an oxygen reduction reaction (ORR)/ oxygen evolution reaction (OER) at the cathode,[55] as schematically outlined in Figure 4.

Figure 4. Schematic presentation of Li-O$_2$ battery.

There are currently four categories of Li-O$_2$ systems under investigation, referred to as aprotic, aqueous, hybrid and solid-state batteries. The four types differ from each other with regard to the electrolyte species involved. The latter, in turn, determines the specific

electrochemical reactions during energy storage and release. A schematic illustration of these four types of batteries is provided in Figure 5.[56]

The "aprotic LOB" [49,70] consists of a lithium anode, a porous air cathode, and an electrolyte composed of a lithium salt dissolved in non-aqueous, organic solvent. Electrochemical reaction pathways for this type of LOB were proposed by Abraham et al.,[70-72] and not surprisingly, involve the reduction of molecular oxygen to lithium superoxide (LiO_2) via one electron transfer, as depicted in eq. 1:

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \qquad (1)$$

This reduction is followed by either disproportionation (eq. 2) or receipt of a second electron (eq. 3) – both pathways forming lithium peroxide (Li_2O_2) as the main discharge product.

$$2LiO_2 \rightarrow Li_2O_2 + O_2 \qquad (2)$$

$$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \qquad (3)$$

The resulting lithium peroxide is insoluble in the aprotic solvents[73] and thus deposits on the cathode either as an insulating thin film, or crystallizes in the shape of large toroidal precipitates. Consequently, the capacity of this battery is limited by the thickness of the Li_2O_2 film ($\sim$ 7 nm for this insulating solid) in case of an electrolyte solution that forms a Li_2O_2 film, and by the volume of the porosity of the cathode if the product is toroidal particles. During charge, the deposited Li_2O_2 undergoes oxidation at the positive electrode surface, regenerating molecular oxygen.
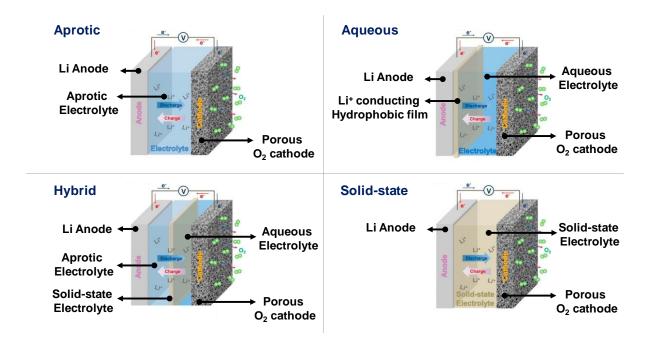
Figure 5. Schematic configuration of all types of Li-O$_2$ cells. Reproduced with permission from ref[56]. Copyright 2017 Elsevier.

Researchers at the PolyPlus Battery Company eliminated the solid, insoluble discharge product of Aprotic LOB by replacing the non-aqueous solvent with an aqueous solution, and employing an Ohara glass Li-ion conducting membrane to protect the Li anode from corrosion.[74] In 2004, such a cell was reported by Visco et al (see Figure 5).[50,75] The use of an aqueous electrolyte resulted in the formation of soluble lithium hydroxide (LiOH) as the discharge product, in contrast to solid Li$_2$O$_2$. This system has not yet become a commercial reality.

Another attempt to implement an aqueous system brought the "Hybrid LOB" into existence.[73,76–78] In the proposed design, the anode side of the battery was filled with an aprotic solvent, whereas the air electrode was in contact with an aqueous electrolyte. The two electrolyte solutions were de-coupled by a solid electrolyte membrane. The hybrid LOB avoided direct contact between the lithium and the solid electrolyte membrane, and indeed resulted in improved lithium ion conductivity. However, the design leads to added complications and different diffusion kinetics in the two solutions.

"Solid-state LOBs" were also developed which do not use any liquid electrolytes, as shown in Figure 5. The development and application of solid-state lithium ion conducting materials for use in LOBs gained pace around 2010.[79] However, a truly all-solid-state LOB is challenged by how much Li_2O_2 can be stored in the cathode.

Since only the aprotic configuration of a LOB has shown a considerable rechargeability, it has attracted the largest effort worldwide. Consequently, in the following section, we will focus our discussion on this configuration.

2.2. The History and Early-Stage Research on Aprotic Li-O₂ Batteries

A Li and O_2 electrochemical couple for batteries was proposed in early 1970s; however, the first experimental observation was made in 1996 by Abraham et al.[49] – and that in a serendipitous manner.[70] During the in-situ investigation of the electrochemical intercalation of graphite in a Li/graphite cell with a polymer electrolyte, O_2 was accidentally injected while collecting the evolved gases for infrared spectroscopy. On resuming the experiment, a higher OCV and increased capacity was observed which was attributed to the formation of Li_2O_2 and other products as a result of reaction between Li and O_2. These unexpected conclusions led them to build the first Li-air cell and study this hybrid fuel cell. The field took off a decade later to unravel many electrochemical and mechanistic details. In 2002, Read et al. [80–82] illustrated that the discharge capacity, rate performance and cyclability of Li-O_2 cells depends largely on the electrolyte solution and the air cathode formulation. In 2006, Ogasawara et al.,[83] demonstrated for the first time that Li_2O_2 could be oxidized electrochemically, using mass spectrometry to prove O_2 evolution. Many of these early pioneering studies used carbonate electrolytes and manganese dioxide as the electrocatalyst, which have since been shown to be unstable.[84,85] Overall, it can be said unequivocally that by 2008, the pioneering work of the research groups of Abraham, Read and Bruce laid the foundation which attracted immense attention to Li-O_2 systems.

3. CURRENT STATUS

3.1. A short introduction on important aspects of non-aqueous electrochemistry

As already noted, the use of Li metal anodes in Li-O$_2$ batteries is mandatory to achieve high energy density. This dictates the use of cell components that can enable safe and controllable operation of anodes comprising this reactive alkali metal. It is very likely that a Li anode protected by a solid electrolyte membrane will be required as the criteria for a liquid electrolyte in direct contact with Li metal is a major challenge. We can summarize a few of the criteria that are relevant to any chosen system:

1) The polarity of the solvent should be sufficient to enable facile dissolution of salts.

2) The overall physical properties (polarity, viscosity) should enable high ionic conductivity.

3) The electrochemical window available must be wide enough to allow the full operation of the battery.

4) The systems must be stable against side reactions (e.g. via development of effective passivation phenomena).

5) The components must be of high purity, due to possible undesirable side reactions with contaminants such as atmospheric species, acidic moieties etc.

6) The electrolyte should exhibit appropriate safety features (e.g. low volatility, flammability, and opportunity for thermal run-away routes).

While many possible combinations of aprotic solvents and lithium salts answer the first and second criteria, only a few candidates at best can fit criteria 3 - 6. In fact, all electrolyte solutions are only metastable toward the electroactive species and working potentials of standard lithium-oxygen batteries. The empirical physical and chemical properties of various aprotic solvents and lithium salts that affect (or even determine) the mechanisms of oxygen electrochemistry in them, became more and more understood, thanks to systematic studies

during the last decade. We note, however, that non-aqueous electrolyte solutions that are truly suitable alone for controllable Li-O_2 electrochemistry have yet to be found. Nevertheless, the insights and fundamental knowledge gleaned over the last decade attests to the great progress made in understanding the limitations of many types of electrolytes examined to date in Li-O_2 cells and hence, inform the properties required from suitable systems.

3.2. Mechanistic aspects of non-aqueous oxygen electrochemistry:
3.2.1. Li$_2$O$_2$ formation on discharge

Studies of oxygen electrochemistry in non-aqueous electrolyte solutions took place much before the appearance of the Li-O_2 battery concept.[86,87] These studies were conducted with the aim of understanding the behavior of reactive oxygen species (ROS) in the absence of proton donors such as water. It was found (even by simple voltammetric measurements) that oxygen electrochemistry is very dependent on the nature of polar aprotic solvent and the electrolyte salt (especially the identity of the cation). In some cases, oxygen exhibited reversible redox behavior, while in others the response was more complex (irreversible in many cases). Therefore, to properly describe the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), one must consider the media in which the reaction is taking place.[88]

The important parameters that govern the mechanism of O_2 reduction to Li$_2$O$_2$ are:

1) The donor number (DN) of the solvent and salt. These are critically important as they determine the solubility and dissociation of LiO$_2$ and hence whether Li$_2$O$_2$ grows on the electrode (low DN) or in solution (high DN).

2) The Lewis acidity of the solvated lithium cation.

3) Contaminants and additives in the electrolyte solution.

4) The stability of the solvent toward the reduced oxygen species generated and toward possible formation of very a reactive molecular oxygen state (as discussed further below).

The above parameters can have a synergetic effect; therefore, the second and third two parameters must be described together. The stability of various aprotic solvents is described in the next section of this review.

The first step in O_2 reduction is the one electron reduction to form the superoxide radical ($O_2^{-\cdot}$) as confirmed by early experiments in nonaqueous solutions with solvents such as DMSO.[86,87] The subsequent fate of the superoxide is dependent on the nature of the counter cation. With large cations such as K^+ and tetrabutylammonium (TBA^+) the metal peroxides are less stable compared to Na_2O_2 and Li_2O_2 (the latter being the most stabilized peroxide). The level of stability of the metal peroxide affects the lifetime of superoxide intermediates in these systems. Hence, with cations like TBA^+ or Na^+ it is possible to observe reversible reduction of oxygen to superoxide moieties, while with the lithium cation such a reversible behaviour is not seen. Using methods such as Raman and UV spectroscopy coupled with electrochemical measurements, it was demonstrated that the superoxide does form in lithium containing solutions (Eq. 1 above).[89,90] However, this unstable radical quickly disproportionates to form lithium peroxide, Li_2O_2 (Eq. 2 above). While the superoxide is somewhat soluble and can diffuse in the electrolyte solution, the peroxide moieties are insoluble in aprotic solvents (if their DN are not high enough).[72,71]

The mechanisms of O_2 reduction in different aprotic solvents that vary in their donor numbers were extensively studied in recent years. The mechanism of O_2 reduction to form Li_2O_2 is summarised in Figure 6. In all solvents of high donor number (DN), following reduction of O_2 to O_2^- at the electrode surface, the O_2^- is present in solution due to the strong solvation of the Li^+ ion by coordination by the solvent molecules. In other words, in a high DN solvent, LiO_2 does not exist and is instead present as solvated ions. However, as Li_2O_2 is more stable than LiO_2, disproportionation occurs for LiO_2 to grow relatively large toroidal Li_2O_2 particles directly from solution. In contrast, when the DN is sufficiently low, Li^+ is not

strongly solvated and LiO_2 (ion coupled electron transfer) forms on the electrode surface. Either rapid disproportionation or a second electron transfer forms Li_2O_2 that grows as a film on the electrode. This understanding of the role of the DN in determining whether LiO_2 will dissolve in solution or will deposit on the electrode surface following the first electron transfer, was a milestone in understanding the Li-O_2 cell. It showed that high DN electrolyte solutions will promote growth of Li_2O_2 from solution, thus forming large toroidal particles in the pores of the electrode that do not passivate the electrode. This results in relatively high rates and capacities of ORR in high DN solvents, whereas, low DN electrolyte solutions, like ethers, lead to Li_2O_2 film growth and consequently low rates and capacities.

Given the important role of LiO_2 solvation/stabilization and the importance of the interactions of the solvent molecules with the Li ions, the effective DN and acceptor number (AN) of the solutions determines whether Li_2O_2 forms via a solution or surface mediated pathways. High DN and AN additives were shown to favour solution pathways. Considering first the DN, the counter-anion can strongly tune the DN of the electrolyte solution. The degree in which the anion can interact with the solvated Li cation can be quantified by the association strength of the salt. Strongly dissociated salts such as LiTFSI form solvated complexes where the Li cation hardly interacts with the TFSI anion. In weakly dissociated or associated salts such as LiTf and $LiNO_3$, the negatively charged functional groups of the anions interact with the Li cations in complexes such as NO_3^---Li^+--Solvent, are strongly solvated. The stabilization of the Li cations by the anion will promote LiO_2 in solution. We note that the effect of the anion was shown to be relevant only for lower DN solvents, such as polyethers (reference 37 and discussions therein).

A

Solution mechanism

$$Li^+_{(sol)} + e^- + O_2{}_{(sol)} = Li^+_{(sol)} + O_2{}^-_{(sol)}$$

$$2(Li^+_{(sol)} + O_2{}^-_{(sol)}) = Li_2O_2 + O_2$$

$$2Li^+_{(sol)} + O_2{}^-_{(sol)} + e^- = Li_2O_2$$

Surface mechanism

$$Li^+ + e^- + O_2{}_{(sol)} = LiO_2{}^\star$$

$$Li^+ + LiO_2{}^\star + e^- = Li_2O_2{}^\star$$

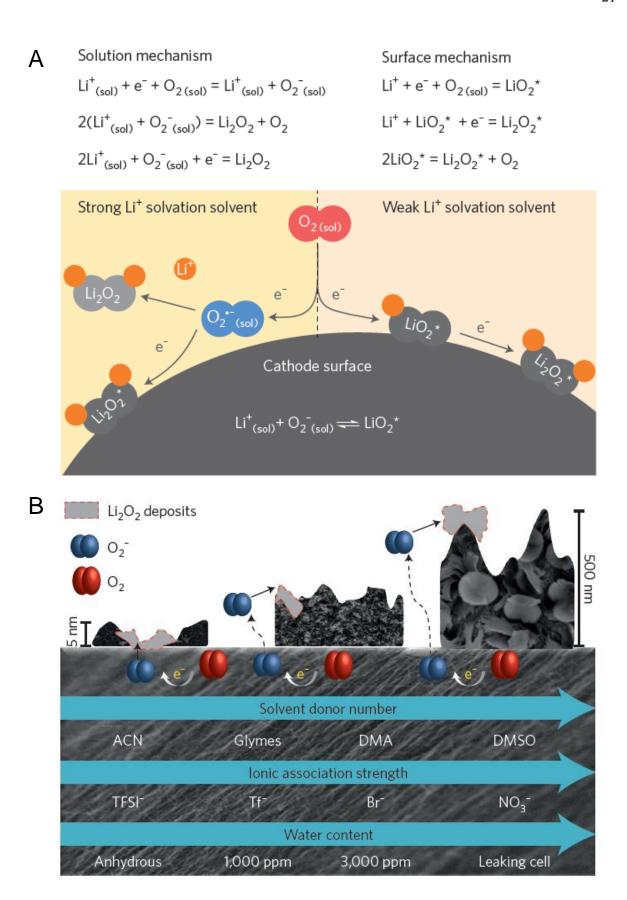$$2LiO_2{}^\star = Li_2O_2{}^\star + O_2$$

Figure 6. (A) Oxygen reduction mechanistic pathways in non-aqueous Li-O₂ batteries. Reproduced with permission from ref[90]. Copyright 2014 Springer Nature. (B) The influence of

solvents, counter anions and water content on the Li_2O_2 growth mechanism during ORR. Reproduced with permission from ref[37]. Copyright 2016 Springer Nature.

In the solution mediated mechanism, after the initial nucleation of Li_2O_2 seeds, the growth of Li_2O_2 particles can proceed from solution and therefore leave behind an active cathode interface. It is the avoidance of a passivating surface film of Li_2O_2 that leads to high rates and high capacities in high DN electrolyte solutions.

High AN additives, particularly protic ones, were further found to favour large discharge capacities with big toroidal Li_2O_2 particles. The most common protic additive/contaminant is water. The reaction of water (if in large concentration) with a superoxide species can lead to the formation of insoluble LiOH deposits on the cathode interface. However, it was demonstrated that with small to medium amounts of water, the main discharge product can still be Li_2O_2. By the addition of 0.01 to 1% water into a polyether-based electrolyte solution the discharge capacity increased by more than 25-fold. In addition, the yield and size of Li_2O_2 particles increased with added water.[94] However, Aetukuri et al. reported that discharge capacity increased 4-fold with 4000 ppm of water with increasing size of Li_2O_2 particles but the number (yield) of Li_2O_2 particles decreased.[94]

The mechanism by which water induces the formation of large toroidal shaped particles is still unclear. One proposed explanation is that protic molecules increase the effective AN of the electrolyte and improve solvation of superoxide much more efficiently than aprotic solvents. This can lead to Li_2O_2 growth by a solution-based mechanism. Alternatively, protonation of O_2^- to form HO_2 can occur, which diffuses from the electrode surface and forms Li_2O_2 in solution.[95–97] The presence of water can also influence the oxidation of Li_2O_2 during the OER. Li et al. suggested that the addition of water to a Li-O_2 cell can significantly reduce the OER overpotential.[98] They found that some Li_2O_2 was converted to LiOH during the cathode discharge (Figure 7A). However, it is not clear that LiOH can be oxidized to molecular

oxygen, even catalytically, as suggested in the mechanism of Figure 7B. In order to avoid the consumption of water by Li_2O_2, MnO_2 was introduced to regenerate water by catalysing the reduction of H_2O_2. However, as described below, these catalysts are known to induce decomposition reactions in the battery. A similar regenerative process was described in $Li-O_2$ systems that include water impurities and LiI salt.[99–101] Therefore, the influence of water in $Li-O_2$ cells should be examined very carefully to avoid any misperceptions that may rise from the chemical complexity of this kind of system.
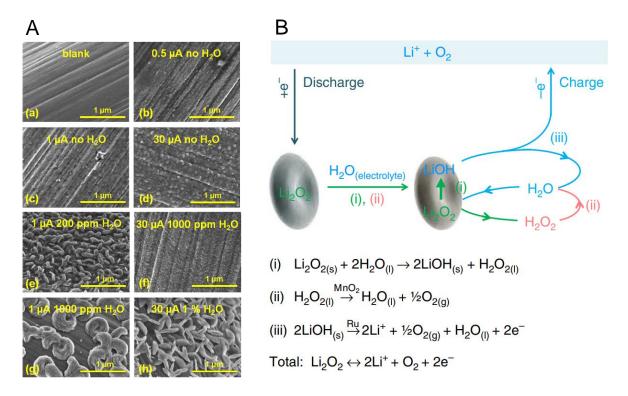
Figure 7. (A) SEM images of the carbon cathodes of $Li-O_2$ cell after discharged in the presence of water at different concentrations. Reproduced with permission from ref [96]. Copyright 2015 The Electrochemical Society. (B) the ORR and OER mechanistic scheme in a non-aqueous $Li-O_2$ cell in the presence of added water. Reproduced with permission from ref[98]. Copyright 2015 Springer Nature.

3.2.2. Li_2O_2 oxidation mechanism on charge

In contrast to the steady discharge voltage plateau during the formation of Li_2O_2, the oxidation curve of Li_2O_2 is seemingly comprised of multiple voltage steps. A fundamental hysteresis exists because while disproportionation of LiO_2 to form Li_2O_2 dominates on

discharge, the reverse process (comproportionation) cannot occur on charge. Charge usually initiates around 3.2 V and can continue up to 4.5 V in many Li-O$_2$ systems. In an early study, it was suggested that the different slopes in the OER voltage curve might be associated first with the oxidation of surface Li$_2$O$_2$, and subsequently with bulk Li$_2$O$_2$. Using operando X-ray diffraction, Ganapathy et al. found that ORR forms both crystalline and amorphous Li$_2$O$_2$ products.[102] They proposed that initially the amorphous phase starts to oxidize at low overpotentials, while the toroidal Li$_2$O$_2$ crystalline aggregates, depending on their size, begin to decompose at much higher overpotentials. The enhanced charge transport of the amorphous phase was later confirmed by charging very pure chemically synthesized amorphous Li$_2$O$_2$.[103] It was suggested that the higher mobility of Li ions, and increased superoxide concentration within the amorphous Li$_2$O$_2$, lead to relatively lower overpotentials. Enhancement in the local Li ion mobility was also observed in mechanically induced defects of nanocrystalline Li$_2$O$_2$.[104] In practice, the OER overpotential required for complete removal of the Li$_2$O$_2$ layer is more than 1 V. During investigation of OER mechanisms it became clear that during oxidation of Li$_2$O$_2$, different parasitic reactions take place with the electrolyte and carbon to form organic decomposition products and Li$_2$CO$_3$. Potentials greater than 4 V vs Li/Li$^+$ are needed to remove those species.[105] Online electrochemical mass spectroscopy (OEMS) studies showed that the oxidation reaction required more than 2e$^-$ per O$_2$, which implies that some ROS to react with cell components in an irreversible manner. A very important recent result from several groups is the recognition that the instability of the electrolyte and carbon is associated with the formation of singlet oxygen (^{1}O$_2$) during the OER.[106–109] By operando Electron paramagnetic resonance (EPR) spectroscopy, Wandt et al. suggested that at potentials of around 3.5 V, approximately 0.5 % of highly reactive ^{1}O$_2$ is evolved.[107] Subsequently, ^{1}O$_2$ has also been shown to evolve both on discharge and from the onset of charge.[108] Its generation is intimately tied to the ORR and OER through superoxide disproportionation steps which generates 1O2.[109]

$^1O_2$ is the key to the degradation mechanism of Li-O$_2$ batteries, and thus it is discussed in detail in the following section.

Recent studies visualized the decomposition of Li$_2$O$_2$ deposits by in situ atomic force microscopy (AFM) and vibrational spectroscopy of sum frequency generation (SFG) measurement during the OER.[110,111,112] They concluded that at relatively low potentials (< 3.7 V), a thin film of Li$_2$O$_2$ which is in direct contact with the cathode surface is oxidized to produce superoxide radicals. As the surface layer oxidizes, the upper Li$_2$O$_2$ layer is detached from the cathode surface.[112] This disconnected product layer was found to be oxidized only at potentials above 4.5 V, which is above the oxidation potentials of most aprotic solvents - thus leading to instability. In general, the mechanisms described above clearly implies that properties such as size, morphology and crystallinity of the Li$_2$O$_2$ deposited during the ORR should govern the efficiency of the OER and are controlled by the choice of electrolyte solutions.

Recently, a comprehensive unified model for Li$_2$O$_2$ oxidation was introduced by Lu et al. that shows, analogously to discharge, the solvent DN to govern the oxidation mechanism (Figure 8).[113] They used a thin film rotating ring-disc electrode (RRDE) to show that in high DN solvents the superoxide intermediate forms as soluble LiO$_{2(sol)}$, while in low DN solvents the intermediate is not soluble, Figure 8B. Using X-ray absorption near edge structure (XANES) they showed surface LiO$_2$ formation upon charging in high DN solvents but its absence in low DN solvents. As for charge, the solvent directs the Li$_2$O$_2$ decomposition pathway to pass either via soluble superoxide species or Li-deficient Li$_2$O$_2$.[90,114,115] The unified reaction mechanism is illustrated in Figure 8C and commences with delithiation:

$$Li_2O_2 \rightarrow Li_{2-x}O_2 + x\ Li^+ + x\ e^- \qquad (4)$$

The Li$_{2-x}$O$_2$ formed in low DN solvents was suggested to undergo a second oxidation:

$$Li_{2-x}O_2 \rightarrow O_2 + (2-x)\ Li^+ + (2-x)\ e^- \qquad (5)$$

At the same time, disproportionation of these solid superoxide intermediates cannot be strictly excluded, however, a plausible mechanism for such a solid state reaction is hard to suggest.[116] In contrast, $Li_{2-x}O_2$ to dissolve to $LiO_{2(sol)}$ in high DN solvents and releases then O_2 by disproportionation:

$$2\ LiO_{2(sol)} \rightarrow Li_2O_2 + O_2 \qquad (2)$$

Lu et al. used SEM imaging to elegantly prove that disproportionation of soluble LiO2(sol) does happen in high DN solvents since upon partial charge, large particles of chemically synthesized Li_2O_2 recrystallized to layered structures as typically observed on discharge in high DN such as DMSO and methyl-imidazole (Me-Im) (Figure 8A). Since superoxide disproportionation is now recognised as the principal rout to $^1O_2$, its prevalence as the O_2 releasing step has a major impact on parasitic chemistry as further discussed in the following Section.
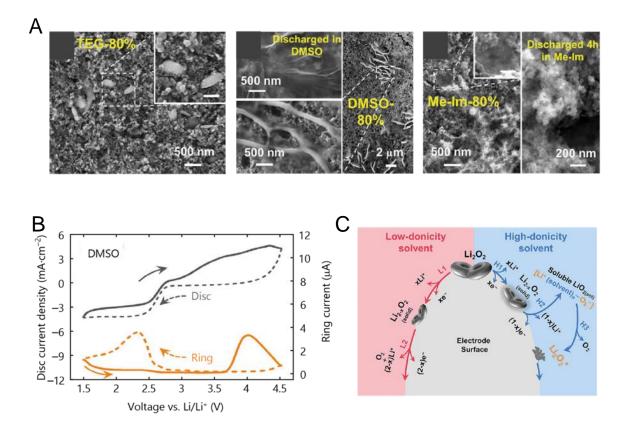
Figure 8. The solvent controlled charge mechanism of Li_2O_2. (A) SEM images of Li_2O_2-packed electrodes after 80% recharge in different solvents containing 1 M LiTFSI. The inserts show recrystallization of Li_2O_2 into lamellar structures due to disproportionation in DMSO and Me-Im. (B) RRDE measurement of oxygen reduction/evolution in O_2 saturated DMSO with 0.2 M LiTFSI. The ring current indicates the superoxide reduction during both discharge and charge and hence $LiO_{2(sol)}$ to be present. (C) Scheme of the charge mechanism via surface or solution mechanism in low or high DN solvents, respectively. Reproduced from Ref.[113] with permission from Elsevier.

3.3. Parasitic chemistry

Parasitic chemistry at the cathode is the prime obstacle for reversible operation of Li-O_2 cells and hence understanding the mechanisms underpinning parasitic reactions is the most pressing research need in the field. Current understanding has resulted in a unified mechanism of parasitic chemistry across the alkali metal-O_2 cells (M = Li, Na, K) and will hence be treated together.[109] Metal-O_2 chemistries typically consume close to the ideal number of electrons per O_2 upon discharge according to:

$$O_2 + x\,e^- + x\,M^+ \leftrightarrow M_xO_2 \qquad (6)$$

The products that typically form are Li_2O_2, Na_2O_2, NaO_2, or KO_2.[37,117–120] However, for Li-O_2 cells, significant amounts of side products such as Li_2CO_3, Li formate and Li acetate were found and the Li_2O_2 yield was significantly lower than expected from the charge passed.[84,121–123] Similarly, on charge the amount of O_2 evolved falls below the expected amount and more side products form. Na-O_2 cells have been recognized to be more reversible if superoxide (NaO_2) is the product, but things are much worse with Na_2O_2 as the product.[124] K-O_2 cells perform best in all cases.[120] (Su)peroxide yields on discharge and O_2 yields on recharge (based on charge passed) from a wide range of studies that give quantitative values are summarized in Table 1. The general trend is that irreversibility becomes worse when moving from K to Na and Li, which goes along with the peroxide rather than the superoxide being the product.

Table 1 Typical M_xO_2 yields on discharge and O_2 yields on recharge of M-O_2 cells (M = Li, Na, K). Data are compiled from Refs.[96,109,118,120,123,125–133] Definitions of reversibility and means to quantify them have been summarized in detail in Refs.[134,135]

Product	Li-O_2	Na-O_2	K-O_2
Superoxide		90 - 95%	99 – 100 %
Peroxide	50 - 93%	< 50%	

The parasitic reactions have traditionally been ascribed to the direct reactivity of electrolyte or carbon with superoxides and peroxides.[37,118,123,127,128,130,132,133] However, the extent of side reactions would suggest the reactivity to seemingly severely grow in the order $KO_2 < NaO_2 < LiO_2$, and peroxides to be much more reactive than superoxide. In the following section we summarize the current knowledge about these reactivities and the recognition that the highly reactive singlet oxygen ($^1O_2$) forms in metal-O_2 cells, which conclusively explains the pattern of irreversibility and guides pathways to counteract the problem.

3.3.1. Reactivity of reduced O₂ species and O₂

Reduced reactive oxygen species (RROS) have for long been known for their reactivity with many organic substrates owing to their nucleophilicity, basicity and radical nature and are

recognized as a reactant or source of parasitic chemistries[37,136,137]. The primary species are O_2^-, O_2^{2-}, HOO•, HOO$^-$, and HO• that may react via nucleophilic substitutions, H$^+$ and H-atom abstraction. Superoxide is furthermore an electron transfer agent and molecular oxygen may equally react via H-atom abstraction in auto-reactions.

Salt solubility in non-aqueous media for use as electrolyte is introduced via polarity by means of heteroatoms, which however makes the solvents susceptible to the mentioned reactions, particularly at C and H atoms adjacent to the heteroatom. Along this line, nucleophilic attack has for long been considered the primary source of side reactions in metal-O_2 cells, which is certainly true for carbonates.[84,137,138] Since also all so far investigated classes of organic solvents have shown a certain degree of decomposition, superoxide's reactivity has equally been made responsible for the reactions. Bryantsev et al.[138–142] pioneered Density functional theory (DFT) calculations to understand the reactivity of electrolyte solvents with reduced O_2 species and O_2 with the aim to possibly predict more stable ones. Table 2 summarizes their data and those of several other groups for activation energies for reactions of superoxide, peroxide, and molecular oxygen with various classes of organic solvents via nucleophilic substitution, H-atom and H$^+$ abstraction.

Table 2 Reactions of organic electrolytes with reduced oxygen species and molecular oxygen and their calculated activation energy barriers. ROR' is generically used for organic moieties with polarizing heteroatoms and reactions may accordingly be translated to, e.g., N or S containing solvents. Adapted with permission from Ref. [135] - Published by The Royal Society of Chemistry.

Reactant	Type of reaction	Reaction	E^{act} (kJ·mol⁻¹)	References
O_2^-	nucleophilic substitution	$ROR' + O_2^- \rightarrow RO^- + ROO^\bullet$ (7)	121–144[1], 105[2], 65–95[3]	140,141,143,144
	H-atom abstraction	$RH + O_2^- \rightarrow R^\bullet + HOO^-$ (8)	129–180[4], 191[5]	140,143,145,146
	H⁺ abstraction	$RH + O_2^- \rightarrow R^- + HOO^\bullet$ (9)	pKa > 30 stable[6]	139,147
Li_2O_2	nucleophilic substitution	$ROR' + Li_2O_2 \rightarrow RO^-Li^+ + R'OO^-Li^+$ (10)	134–192[1]	148
	H-atom abstraction	$RH + Li_2O_2 \rightarrow R^\bullet + [Li_2O_2 - H^\bullet]$ (11)	96–112[1]	148
	H⁺ abstraction	$RH + Li_2O_2 \rightarrow R^-Li^+ + HOO^-Li^+$ (12)	116–311[1]	144,148
O_2	H-atom abstraction	$RH + O_2 \rightarrow R^\bullet + HOO^\bullet$ (13)	163-183[7], 138–161[8]	140

A striking feature is that for all considered reactions the activation energies are too high to explain major reactivity. Solvent stability screening experiments with KO₂ as the superoxide source have shown that reactions with activation energies >100 kJ·mol⁻¹ can be considered not to contribute noticeably.[141] All pathways with ethers, for example, require high activation energy and are strongly endothermic. Only one study found H-abstraction by Li₂O₂ clusters to be slightly exothermic with E^{act} < 100 kJ·mol⁻¹.[148] Generally, Li⁺ coordinated solvents were reported to be more stable against H-abstraction by O₂⁻ and O₂ than the free molecules.[140,146]

As reviewed in Section 3.2, protic additives have recently been proposed to have a certain positive effect on discharge capacity despite reports of increased parasitic chemistry.[94,96] However, in presence of proton sources HOO•, HOO⁻, and HO• may form, which are potentially more reactive than the non-protonated species[139]. The HOO⁻ species may more easily abstract H⁺ as it is a stronger base than superoxide. HO• readily abstracts H-atoms and forms C-centred radicals which initiate favourable chain reactions in the presence of O₂ akin to combustion reactions[84,140]. Nevertheless, the described reactivity of reduced reactive oxygen species including the protonated species cannot consistently explain the observed pattern of parasitic chemistry shown in Table 1. For example, much stronger side reactions on charge compared to discharge directly oppose superoxide's reactivity as an explanation. Very

reversible cyclability of KO_2 in DMSO for thousands of cycles further forcefully demonstrates that the direct reactivity of reduced O_2 species with cell components is not the prime source of side reactions[120].

3.3.2. Singlet oxygen in metal-O_2 cells

3.3.2(a) Evidence for singlet oxygen as the main culprit for parasitic chemistry

Chemical oxidation of peroxides is recognized as a source of the highly reactive singlet oxygen ($^1O_2$)[149]. Similarly, electrochemical oxidation of Li_2O_2 was hypothesized in 2011 to possibly evolve singlet oxygen in Li-O_2 cells.[150] Singlet oxygen is the first excited state of ground state triplet oxygen and has an energy difference of ~1 eV. Considering energy, charging of Li_2O_2 beyond 3.5 to 3.9 V vs Li/Li$^+$ was hypothesized to potentially form $^1O_2$.[106,131,150] Furthermore, disproportionation of HOO• has been considered as a source of $^1O_2$ although it is now recognized to negligibly form it.[109,151–153] Since $^1O_2$ is difficult to detect, this idea was only discussed in a few reports but not proven except for a seminal study by Wandt et al.[106] who used operando EPR to prove a small degree of $^1O_2$ evolution upon charging between 3.55 and 3.75 V. The process was explained via direct 2 e$^-$ oxidation according to $Li_2O_2 \rightarrow O_2 + 2\,Li^+ + 2\,e^-$ [92,106,153]. However, measurements during discharge and higher charge voltages were not possible with the used spin trap. $^1O_2$ forming above ~3.5 V helped explain parasitic chemistry at high charge potentials. However, it left parasitic chemistry on discharge unexplained and particularly also why significant amounts of side products form at the onset of charge, where always less than 1 mol O_2 evolved per 1 mole of Li_2O_2 oxidized.[105,123,154]

To investigate involvement of $^1O_2$ more comprehensively, Freunberger et al. developed a set of methods to sensitively and quantitatively detect $^1O_2$ over the entire relevant voltage range during discharge and charge of metal-O_2 cells.[108] As direct unambiguous proof they detected the characteristic 1270 nm emission when $^1O_2$ transits from the singlet to the triplet

state. The process has a low quantum yield since this phosphorescent radiative decay is forbidden and is strongly influenced by the environment and is hence insensitive. Nevertheless, in-situ measurements have shown unequivocal proof for $^1O_2$ from the onset of charge, Figure 9A[108]. As a more sensitive and quantifiable method, 9,10-dimethylanthracene (DMA) was identified as a suitable $^1O_2$ trap, which fulfils all requirements for the cell environment. DMA forms selectively and rapidly its endoperoxide form (DMA-O_2) in the presence of $^1O_2$; both DMA and DMA-O_2 are electrochemically stable in the relevant voltage range between 2 and ~4 V vs Li/Li$^+$; and importantly DMA does not form DMA-O_2 in contact with superoxide and peroxide alone, which otherwise could falsely indicate $^1O_2$ formation. Further, DMA-O_2 forms only with $^1O_2$ but not with other possibly reactive O-containing species like Li_2CO_3, O_2, or CO_2. DMA-to-DMA-O_2 can be probed in various ways such as ex-situ HPLC of electrolyte extracted from cells or in-situ fluorescence of DMA (Figure 9B).

These studies proved that $^1O_2$ forms both during discharge and from the onset of charge and with growing rate as the charge voltage rises, Figure 9B. The rates of $^1O_2$ formation resemble the rates at which parasitic reactions occur in Li-O_2 cells.[155] Further, it was proven that $^1O_2$ accounts for the majority of parasitic reaction products on discharge and charge. Thus $^1O_2$ arises as the biggest obstacle for cycling of the Li-O_2 cell by reversible formation/decomposition of Li_2O_2. The first report suggested up two possible means to counter $^1O_2$-related side reactions. First, the $^1O_2$ probe DMA, which acts by trapping $^1O_2$, was shown to reduce parasitic products during both discharge and charge if large concentrations were used. However, at the rate of $^1O_2$ formation, DMA is consumed within a few cycles. Second, they introduced the $^1O_2$ quencher 1,4-diazabicyclo[2.2.2]octane (DABCO) into Li-O_2 cells and have shown that it even more strongly reduced parasitic chemistry by physically deactivating $^1O_2$ to $^3O_2$ without consumption of the quencher itself. DABCO is, however, not electrochemically stable above 3.6 V and hence does not allow for full recharge, which requires more oxidation-

stable quenchers as described below. Singlet oxygen was also shown to form on discharge and

charge in Na-O$_2$ cells where NaO$_2$ forms as the discharge product.[107]
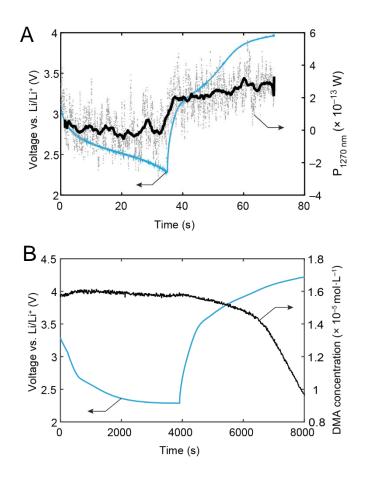

Figure 9. Singlet oxygen formation in Li-O$_2$ cells. (A) Operando detection of ^{1}O$_2$ by detecting the near infra-red (NIR) emission at 1270 nm during galvanostatic cycling of an Au grid electrode in O$_2$ saturated deuterated acetonitrile containing 0.1 M LiClO$_4$ and 1000 pm D$_2$O. The black trace is the moving average of the raw data in grey. (B) Voltage profile and DMA concentration during galvanostatic cycling of a carbon black electrode at 25 µA·cm^{-2} in O$_2$ saturated tetraethylene glycol dimethyl ether (TEGDME) containing 0.1 M LiClO$_4$ and 1000 ppm water. DMA consumption indicates ^{1}O$_2$ formation. Adapted from Ref. [108] with permission from Springer Nature.

^{1}O$_2$ is not only responsible for electrolyte and carbon decomposition but has also been

shown to be the prime source of redox mediator decomposition (see section 3.5 for a further

discussion on the use of redox mediators). Kwak et al. studied the deactivation of two

representative redox mediators by O$_2$, superoxide, peroxide, and ^{1}O$_2$ and found ^{1}O$_2$ to dominate

decomposition by far.[156] Its reactivity could conclusively be explained by electrophilic addition

of $^1O_2$ to electron rich moieties. In turn, DABCO, as mentioned above, has shown to preserve the mediator.[157]

3.3.2(b) Pathways towards singlet oxygen

A direct two-electron oxidation step along $Li_2O_2 \rightarrow O_2 + 2\ Li^+ + 2\ e^-$ was initially suggested by Hassoun et al.[150] and Wandt et al.[106] to possibly form $^1O_2$ above 3.9 V or ~3.55 V. However, more recent insights into the Li_2O_2 oxidation mechanism suggest no direct two-electron process to exist as discussed above in Figure 8. Instead, superoxide disproportionation is now accepted to be involved on discharge and charge of the peroxides.[37,90,102,113,114,116,117,158–160] Based on this recognition, recently, a unified mechanism for $^1O_2$ generation in metal-O_2 cells was established,[109] which links the Lewis acidity of cations in the electrolyte with the production of $^1O_2$. Whether the initial one-electron reduction product superoxide reacts further to peroxide is governed by the relative thermodynamic stability of peroxide and superoxide with the respective cation as illustrated in Figure 10A, which also gives rise to the favoured products in Table 1. Strong Lewis acids such as Li^+ or Na^+ favour the peroxide, albeit only slightly for sodium.[119,124,128,160–162] K^+ and even weaker Lewis acids (e.g., quaternary amines like tetrabutylammonium (TBA$^+$) and imidazolium favour the superoxide.[125,159,163,164] The latter constitute often-used ionic liquid electrolytes.
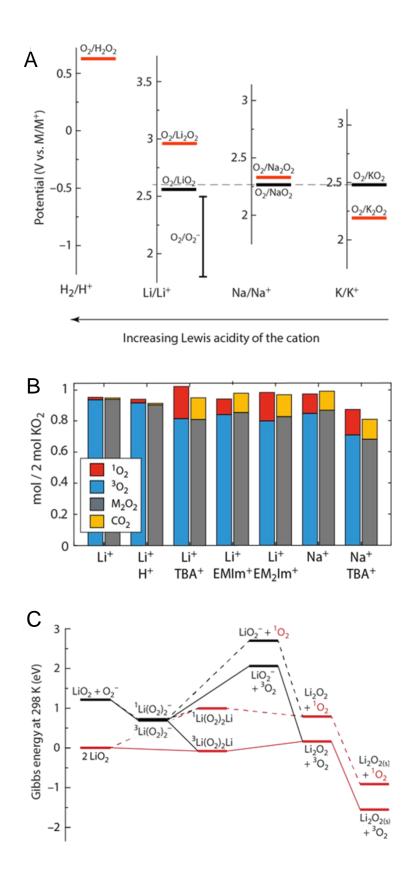
Figure 10. Singlet oxygen formation mechanism. (A) Thermodynamics of alkali peroxides and superoxides and the Lewis acidity of the involved cations. Standard potentials of the O_2/MO_2 and O_2/M_2O_2 redox couples on the M/M^+ scales with M = Li, Na, K as well as for the O_2/H_2O_2 couple. The scales are brought to a common scale based on their M/M^+ standard potentials.

The dashed horizontal line indicates the O_2/KO_2 couple. The O_2/LiO_2 potential is adopted from Ref. [165], but also values between 2.29 and 2.46 V vs. Li/Li$^+$ have been reported.[114,128] O_2/O_2^- denotes the potential range reported for O_2 reduction in TBA$^+$ electrolytes.[90,158,159,165,166] (B) $^1O_2$ from superoxide disproportionation in presence of various cations. Obtained O_2, $^1O_2$, and Li_2O_2 (or Na_2O_2) upon reacting KO_2 in TEGDME that contained equimolar 18-crown-6, 30 mM DMA, 0.5 M Li$^+$ (or Na$^+$), and either no additive, 0.1 M TBA$^+$, EMIm$^+$, or EM$_2$Im$^+$, or F$_3$CCOOH. Ideally 1 mol O_2 and 1 mol M_2O_2 would form according to 2 KO_2 + 2 M^+ → M_2O_2 + O_2 + 2K$^+$. (C) Reaction free energy profiles for LiO_2 disproportionation with itself or O_2^- to Li_2O_2 and molecular oxygen. Pathways to release $^3O_2$ and $^1O_2$ are indicated by full and dashed lines, respectively. Adapted from Ref. [109] - Published by The Royal Society of Chemistry.

Generally, the disproportionation reaction:

$$2\,O_2^- \rightarrow O_2^{2-} + x\,^3O_2 + (1-x)\,^1O_2 \qquad (14)$$

in presence of the alkali metal cations, H$^+$ or weakly Lewis acidic cations was found to cause varying fractions of $^1O_2$ as shown in Figure 10B. According to Figure 10A, the overall reaction is driven by the stability of peroxide and thus favoured by stronger Lewis acidic cations H$^+$, Li$^+$, and Na$^+$. However, the $^1O_2$ fraction grows with decreasing Lewis acidity of the cation, giving rise to insignificant $^1O_2$ with H$^+$ and strongly growing $^1O_2$ fractions with Li$^+$ and Na$^+$. Importantly and surprisingly, weakly Lewis acidic cations such as TBA$^+$ alone do not drive disproportionation, but, when combined with strong Lewis acids, cause substantially larger fractions of $^1O_2$. This is generally true for prototypical motifs of cations used in ionic liquid electrolytes such as quaternary ammonium and imidazolium. How weak Lewis acids act to favour $^1O_2$ can be explained by DFT calculations as shown in Figure. 10C. $^1O_2$ release from LiO_2 disproportionation faces a barrier of ~ 1eV (red path with dashed lines). However, when a weak Lewis acid is present next to Li$^+$ in the electrolyte, asymmetric pairs of LiO_2 and, e.g, $TBAO_2$ will disproportionate. $TBAO_2$ may be seen as a free solvated O_2^- anion. Triplet and singlet paths pass via $^3Li(O_2)_2^-$ and $^1Li(O_2)_2^-$ dimers that are stabilized versus LiO_2 + O_2^- by ~0.5 eV. Ongoing pathways are much more facile than for symmetric LiO_2 pairs: the $Li(O_2)_2^-$

dimers exchange TBA^+ for Li^+ and go on to the symmetric $Li(O_2)_2Li$ pathways. Crucially, the weak Lewis acid curbs the largest barrier towards $^1O_2$, the endergonicity to the $^1Li(O_2)_2Li$ dimer, from ~1 eV to only 0.27 eV. Overall, weak Lewis acids allow for pathways that bypass the most unfavourable reaction steps und hence strongly facilitate $^1O_2$ evolution. Moreover, TBA^+ arises as a probe for disproportionation steps. If the presence of TBA^+ increases the $^1O_2$ yield, then disproportionation must be involved.

This insight was used to probe $^1O_2$ formation during discharge and charge. Larger $^1O_2$ yields in mixed Li^+/TBA^+ electrolytes as compared to pure Li^+ electrolytes verified that the described pathways are active both on discharge and charge. Strong sensitivity of the $^1O_2$ yield towards the presence of TBA^+ confirms discharge to significantly occur via disproportionation, although possible second one-electron reduction of the LiO_2 intermediate is not ruled out. On charge, the initial charging step forms a LiO_2-like surface species as discussed above[113–115,167] and its disproportionation forms $^1O_2$ analogously. This pathway is active from the onset of charge. Another possible pathway is a second one-electron oxidation of the superoxide intermediate that could give $^1O_2$ above ~3.5 V.

Electrochemical oxidation of Li_2CO_3 has recently been revealed as another pathway towards $^1O_2$. Li_2CO_3 is a common side product on discharge and charge[105,154] and its formation known to contribute to the ever increasing voltage on charge because of its high oxidation potential[84,85,105,123,131,168,169]. The burden of Li_2CO_3 formation was seemingly harnessed in in rechargeable metal-O_2/CO_2 batteries based on the observation that Li_2CO_3 can be electrochemically decomposed.[84,166,170,171] For long, the fate of the third O-atom in CO_3^{2-} has led to various theories, since no O_2 evolves as expected from the formal oxidation reaction:[84,171–173]

$$2\ Li_2CO_3 \rightarrow 4\ Li^+ + 4\ e^- + 2\ CO_2 + O_2 \qquad E^0 = 3.82\ \text{V vs. } Li/Li^+ \quad (15)$$

To explain the absence of O_2, the formation of superoxide or "nascent oxygen" was proposed, which could react with cell components[173] (without, however, definite proof for these mechanisms). Mahne et al. provided evidence that the electrochemical oxidation of Li_2CO_3 forms $^1O_2$, which, through the parasitic reaction of $^1O_2$ with battery components, explains the absence of O_2 evolution.[174] Since Li_2CO_3 is also a common residual component on transition metal oxide (TMO) cathode materials,[172] $^1O_2$ from Li_2CO_3 oxidation has far-reaching implications for the surface reactivity of TMO cathodes that operate beyond 3.8 V and couples parasitic reactions upon recharging metal-O_2 and metal-O_2/CO_2 batteries.

$^1O_2$ generation upon oxidation of Li_2CO_3 was probed by charging cells with Li_2CO_3-packed working electrodes in presence of DMA. High-performance liquid chromatography (HPLC) analysis of the extracted electrolyte (Figure 11A) shows that DMA-O_2 is formed from 3.8 V onwards and hence from the onset of Li_2CO_3 oxidation. In quantitative terms, the amount of $^1O_2$ shows that the majority of the "missing O_2" from the electrochemical Li_2CO_3 oxidation forms $^1O_2$, explaining its absence in the gas phase. Absent O_2 evolution implies that the formed $^1O_2$ reacts with cell components rather than being, even in part, deactivated to $^3O_2$. In presence of the $^1O_2$ quencher DABCO, O_2 evolution started together with CO_2 evolution at ~3.8 V with a similarly growing rate as the voltage rose (Figure 11B). Hence, with a suitable quencher Li_2CO_3 could potentially be oxidized without the detrimental effects of $^1O_2$ formation. The $^1O_2$ formation mechanism was suggested to occur via a peroxodicarbonate intermediate that forms from two Li_2CO_3 moieties via two $LiO_2CO\bullet$ moieties, which combine to LiO_2COOCO_2Li. Its further oxidation and decarboxylation to yield $LiCO_4$ could in turn yield $^1O_2$.
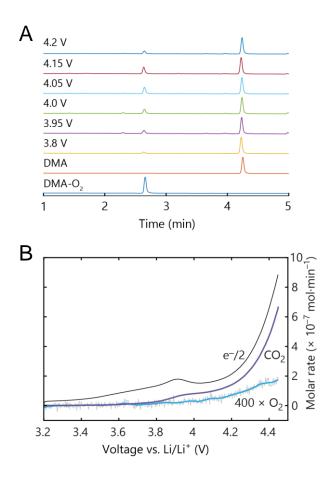
Figure 11. Singlet oxygen from Li_2CO_3 oxidation. (A) HPLC determination of DMA-O_2 upon polarizing Li_2CO_3-packed electrodes at different potentials in 1,2-dimethoxyethane (DME) containing 0.1 M LiTFSI and 30 mM DMA. (B) CO_2 and O_2 evolution during electrochemical oxidation of Li_2CO_3 in presence of the quencher DABCO. Adapted from adapted from Ref. [174] with permission from Wiley-VCH.

3.3.2(c) Quenching singlet oxygen

While superoxide disproportionation is now known to be the source of $^1O_2$ via Eq. 15, it is also known to readily deactivate it via quenching.[175]

$$O_2^- + {}^1O_2 \rightarrow {}^3O_2 + O_2^- \qquad (16)$$

The net formation of singlet oxygen will hence not simply scale with the superoxide concentration. It will rather depend on the relative kinetics of all superoxide sources and sinks with $^1O_2$ being involved in both. Many factors may influence the kinetics, which may be governed by electrolyte, electrodes, current or potential, for example.

Since cell-inherent quenching by superoxide is too inefficient to deactivate $^1O_2$, quenchers may be added. Early work has shown that DABCO significantly reduces $^1O_2$-related side reactions on discharge and charge. However, its oxidation stability of 3.6 V is too low for recharge[108]. Physical quenchers deactivate $^1O_2$ to $^3O_2$ without quencher consumption and no new products accumulate. Radiationless physical quenching converts the excess energy of $^1O_2$ into heat via three mechanisms[175]: electronic-to-vibrational (e-v) energy transfer ($^1O_2$ quenching by solvents, slow), charge transfer (CT) induced quenching (~10^7 times faster than e-v), and electronic energy transfer (faster yet, unsuitable for electrochemical systems because of too low oxidation stability). Suitable quenchers for electrochemical systems use the CT mechanism which passes via a singlet encounter complex $^1(Q^1\Delta)_{EC}$ and a singlet charge transfer complex $^1(Q^1\Delta)_{CT}$, where electronic charge is partially transferred to the oxygen. Intersystem crossing (isc) to the triplet ground state complex $^3(Q^3\Sigma)_{CT}$ releases energy. The latter dissociates to Q and $^3O_2$

$$Q + {}^1O_2 \rightleftarrows {}^1(Q^1\,\Delta)_{EC} \rightleftarrows {}^1(Q^1\,\Delta)_{CT} \xrightarrow[\text{isc}]{} {}^3(Q^3\,\Sigma)_{CT} \rightleftarrows Q + {}^3O_2 \qquad (17)$$

This mechanism was first suggested for DABCO and has generally been shown to be applicable for electron-rich quenchers such as amines. The partial charge transfer causes the quenching efficiency to correlate logarithmically with the ionization potential and hence oxidation potential.[175] A suitable, sufficiently oxidation-stable quencher should therefore allow for high concentrations to balance for the inevitably lower molar activity.

Monoalkylating DABCO to form the DABCOnium salt has recently been shown to shift its oxidation stability to ~4.2 V vs. Li/Li$^+$ while still quenching effectively.[176] Previously known quenchers are strongly Lewis basic amines with too low an oxidative stability. DABCOnium is a cation of a non-volatile ionic liquid, highly soluble in electrolytes, stable against superoxide and peroxide, and compatible with lithium metal. The electrochemical

stability covers the required range for metal-O_2 batteries and greatly reduces $^1O_2$ related parasitic chemistry as demonstrated for the Li-O_2 cell. DABCOnium was shown to drastically reduce the amount of side products during discharge and charge. Its effect was especially clear during charge, where O_2 evolved at the ideal rate of 2 e^-/O_2 up to the oxidative stability limit of ~4.2 V, which proves that all electrons are extracted from Li_2O_2 rather than partly from side products.

Given the stellar importance of $^1O_2$ for the reversibility of metal-O_2 cells, further research into ways to prevent its formation appear highly appropriate. Recognizing that $^1O_2$ formation is deeply rooted in the way current metal-O_2 cells operate has serious consequences for aspects to avoid and on directions that should be taken. First, caution must be exercised with weak Lewis acids as electrolytes or additives. Given that ionic liquid cations suitable for electrolytes are most typically weak Lewis acids, the effect can likely be generalized. Favored $^1O_2$ formation explains why quantitative studies of metal-O_2 chemistry with a broad variety of ionic liquids have shown worse parasitic chemistry on discharge and charge than molecular electrolytes.[131,177,178] Second, protic additives drive $^1O_2$ formation insignificantly but may drive parasitic chemistry in other ways. Third, reversible chemistry based on alkali metal carbonate formation/decomposition (metal-O_2/CO_2 cells) is questionable based on the involvement of $^1O_2$ and other reactive species.[174–176,179] The most prominent consequence is that reactions involving superoxide disproportionation must be avoided. Cells based on metastable LiO_2 or NaO_2 as target products lack the practically required tolerance to slow discharge and rest periods as the superoxides gradually convert to peroxide and side products.[107,116,118,132,161,162,180] Peroxide products are preferred as they are much higher in energy density and are the thermodynamically stable products[124,128,181]. Cycling them highly reversibly requires finding routes to form and decompose them without superoxide disproportionation steps. It is not yet clear whether $^1O_2$ -related parasitic chemistry can be completely avoided but practical

realization of aprotic Li-O_2 and Na-O_2 batteries will, in our opinion, stand or fall with mastering $^1O_2$ formation.

3.4. Cell components
3.4.1. Electrolytes

In this section, we will divide our discussion into two categories: (1) aprotic solvents; and (2) Li- salts. As an initial note it must be stated that the vast majority of work described in this section was published before recognizing the importance of $^1O_2$ in parasitic chemistry (see the previous section). Therefore, proposed side reactions and mitigation strategies were based on the assumption that the nucleophilicity, basicity, or radical nature of reduced O_2 species governed reactivity.

3.4.1(a) Aprotic Solvents

As noted previously, early research on Li-O_2 batteries utilized organic carbonates as the solvents, following their dominance in Li-ion batteries.[81] In 2006, Ogasawara et al.[83] demonstrated a rechargeable Li-O_2 battery with ~50 cycles using alkyl carbonates. Importantly, they also demonstrated for the first time that Li_2O_2 can be electrochemically oxidized to O_2. A few years later, Mizuno et al.[182] demonstrated a Li-O_2 battery that was discharged and recharged for 100 cycles - with almost 60% capacity retention. To explain the large voltage hysteresis of over 1.4 V, they suggested the formation of significant quantities of Li_2CO_3, as well as Li_2O_2, as the discharge products, the former originating from the decomposition of carbonates.[182] Later, Freunberger et al. illustrated the cathodic decomposition pathways of carbonates in oxygen environment specifically in the presence of the superoxide radical.[84] Proposing the degradation mechanism during the discharge and charge shown in Figure 12, they showed that the prolonged cyclability of Li-O_2 cells containing alkyl carbonate-based electrolyte solutions was attributed to the irreversible decomposition and oxidation of Li_2CO_3 along with other species, namely $C_3H_6(OCOOLi)_2$, CH_3COOLi, $HCOOLi$, CO_2 and H_2O with no evidence of reversible oxygen reduction to Li_2O_2. Furthermore, they reported the

accumulation of side products on the cathode in a polymer like film, resulting in increased over-potential, capacity fading and ultimately cell failure. The dramatic instability of organic carbonates in the highly reactive environment of $Li-O_2$ led to studies of other solvents and catalyzed the search for better and more stable solvents.

Figure 12. Graphical representation of charge –discharge of $Li-O_2$ cell with 1 M $LiPF_6$ in PC. Reproduced with permission from ref[84]. Copyright 2011 American Chemical Society.

Building on their initial experience[82] with the carbonate instability, Read et al.[80] investigated the use of ethers as electrolyte solvents. Using DME (dimethoxyethane) and DOL (1,3-dioxolane), they described a $Li-O_2$ cell showing both good stability and excellent rate capability. They attributed these properties to the high oxygen solubility and low viscosity which results in facilitated oxygen transport in the $Li-O_2$ cell. Later McCloskey et al.[183] studied the fundamental chemistry, in particular, the discharge product during the recharging of $Li-O_2$ cells. They confirmed that in DME-based solvents, Li_2O_2 is the major discharge product; however, DME undergoes oxidative degradation during recharge in the presence of Li_2O_2. Sharon et al and Freunberger et al.[121,184] further confirmed the degradation of DME and other ether-based solvents and proposed the formation of CO_2, HCOOLi, CH_3COOLi, LiOCOOLi, $LiOCH_2CH_2OLi$ following the mechanisms shown in Scheme 1. Compared to the carbonates, ether-based electrolytes are relatively more stable - attributable to the ether solvents' greater

resistance to nucleophilic attack and higher cathodic stability.[183] Hence, they are considered to

be the best compromise for such active systems. Indeed, progress[185,186] in Li-O$_2$ batteries would

not have been possible without glyme based electrolyte solutions. It is important to note that

various glymes differ in their reactivity towards the oxygen species formed in Li-O$_2$ cells. In a

study summarized in Figure 13 it was clearly found that diglyme is the most stable glyme

solvent in Li-O$_2$ cells. The reason for that may relate to the nature of the active sites in the poly-

ether molecules. This depends on the chain length, number of oxygens, the steric conformations

and the interactions of the oxygen atoms with the Li ions.

Scheme 1. Proposed mechanism for the decomposition of ether based solvents during the oxygen reduction reactions in Li-O$_2$ batteries. Reproduced with permission from ref[121]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 13. The performance of Li-O₂ cells with glyme based electrolyte solutions and the relative stability of glymes solvents: (A) Galvanostatic voltage profiles and (B) corresponding cycling trend of the lithium oxygen batteries using the TEGDME–LiTFSI (1 mol kg⁻¹) electrolyte and the N₂@MWCNT (multi-walled carbon nanotubes) electrode. Reproduced with permission from ref[186]. Copyright 2018 American Chemical Society. Cycling behavior of Li-O₂ cells in different glymes containing (C) 0.2 M LiTFSI, (D) 1 M LiTFSI (E) 0.2 M LiNO₃, and (F) 1 M LiNO₃ electrolyte solutions. Reproduced with permission from ref[185]. Copyright 2017 Royal Society of Chemistry.

While the glyme polyether solvents were found indeed to be more stable than the carbonates, there was a lack of unanimity on the extent of this stability. Their relatively non-polar nature also keeps the concentration of Li salts rather low. Crucially, they resulted in cells that exhibited low rates and capacities, which we now understand is because they promote the formation of Li_2O_2 films on the electrode surface on discharge, which are insulating and limited to approx. 7 nm[187] as discussed in the section describing the mechanism of O_2/Li_2O_2 above. This low rate and capacity promoted examination of other solvents including higher DN solvents such as dimethyl sulfoxide (DMSO). Peng et al. reported on Li-O_2 cells with DMSO as the solvent, with a porous gold electrode, exhibiting ~ 95% capacity retention for 100 cycles (Figure 14A).[188] Subsequently, several other groups reported excellent reversibility of Li-O_2 cells, with Li_2O_2 as the discharge product.[189,190] However, the capacity of the Au electrode was intrinsically low due the limited pore volume. Investigation with larger pore volume carbon electrodes revealed significant degradation of DMSO, attributed to the susceptibility of DMSO to nucleophilic attack by reduced oxygen species, forming sulfone, and dimethyl sulfone - following the mechanism outlined in Figure 14B.[191] It should, however, be noted that excellent cyclability of KO_2 in DMSO has been reported recently,[120] which casts doubt at the major influence of direct reactivity of superoxide.

Nevertheless, Liu et al. have recently reported a super-concentrated salt/DMSO based Li-O_2 cell which showed excellent stability and reversibility even with an unprotected Li anode. Since DMSO molecules are corrosive to the Li metal anode and unstable to $O_2^{\bullet-}$ attack, the better performance of the super-concentrated solutions can be attributed to the absence of free DMSO solvent molecules and existence of only $TFSI^--Li^+-(DMSO)_3$ complexes.[192]
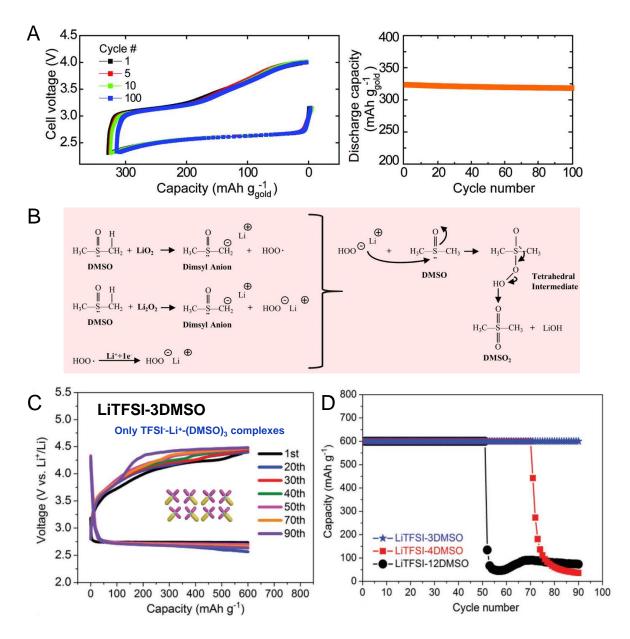
Figure 14. On the stability of DMSO: (A) Performance of Li-O_2 battery with DMSO as solvent and a porous gold cathode. Reproduced with permission from ref[188]. Copyright 2012 The American Association for the Advancement of Science. (B) proposed mechanism of degradation of DMSO. Reproduced with permission from ref[191]. Copyright 2013 American Chemical Society. Voltage profiles for (C) LiTFSI–3DMSO electrolyte and (D) cycling stability of the three electrolytes with different concentration. Reproduced with permission from ref[192]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The unsatisfactory stability of DMSO spurred further search of new solvent candidates showing stability toward ROS. Amide-based solvents like N,N-dimethylacetamide, dimethylformamide (DMF), and N-methyl-2-pyrrolidone (NMP) were next investigated because of their presumed stability towards the superoxide radical. However, the amines do

have facile reactivity toward lithium metal. To minimize the latter issue, Uddin et al.[193] proposed the use of $LiNO_3$ as a passivation agent for metallic lithium. Similarly, exploiting these passivating properties of the $LiNO_3$, Walker et al.[194] showed reversible cycling of a Li-O_2 battery for more than 2000 h in N,N-dimethylacetamide, with Li_2O_2 as the main discharge product. Unfortunately, this amide-based solvent cycling stability was found to be unsuitable for oxygen reduction applications. As outlined in Scheme 2, studies by Chen et al.[195] and Sharon et al.[196] demonstrated the oxidative cleavage of amides and their further degradation to various species including dimethylamine, acetate, carbonate, and various N−O species. Although the stability results of amide-based solvents are debatable, it may be concluded that amide stability toward reduced oxygen species is not sufficient for rechargeable aprotic Li-O_2 cells. Another popular polar solvent, acetonitrile,[131] also showed some success owing to its stability towards superoxide; however, because of its high volatility and high reactivity toward lithium metal, it was not extensively explored for Li-O_2 batteries.

Scheme 2. Proposed mechanism for degradation of dimethylacetamide during oxygen reduction reactions. Reproduced with permission from ref[195]. Copyright 2012 American Chemical Society.
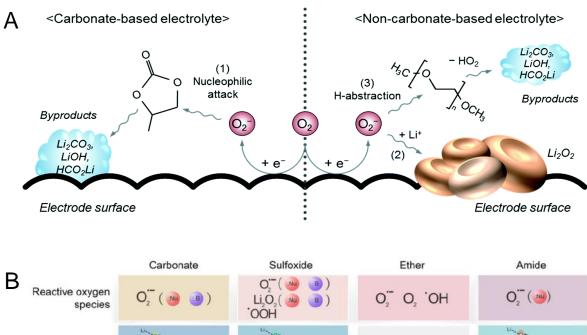
$$O_2 \xrightarrow[(1)]{e^-} O_2^{\cdot-} \xrightarrow[(2)]{Li^+} LiO_2 \xrightarrow{(3)} \tfrac{1}{2} Li_2O_2 + \tfrac{1}{2} O_2$$

$$2 O_2^{\cdot-} + 2 CO_2 \longrightarrow C_2O_6^{2-} + O_2 \qquad (12)$$

$$C_2O_6^{2-} + 2 O_2^{\cdot-} + 4 Li^+ \longrightarrow 2 Li_2CO_3 + 2 O_2 \qquad (13)$$

In summary, almost all the available aprotic solvents degrade to a greater or lesser extent under the highly reactive environment of Li-O_2 batteries. Four modes of degradation mechanisms can be listed: nucleophilic attack, H-atom abstraction, acid/base reactions, and reductive degradation at the metallic lithium anodes. The strongly nucleophilic superoxide anion (O_2^-) readily attacks the electron deficient sites of polar solvents such as carbonyl or sulfoxides groups. These include carbonates, amides, as well as sulfoxides (like DMSO) which undergo degradation via nucleophilic attacks. In other modes of action, superoxide can mediate α-hydrogen atom and/or β-proton abstraction via acid/base reactions leading to solvent deprotonation and decomposition. Ethers, which are generally stable to nucleophilic attack, can undergo some autoxidative decomposition in the presence of these reactive oxygen species. Hence, the ethers solvents are proven to be the most appropriate class of solvents (among the available options) for Li-O_2 batteries.

It is important to emphasize here that the extent of degradation also depends on the possible stabilization of reduced oxygen species by the electrolyte solutions (nature of the solvent, salt anions, additives). Such a stabilization leads to prolonged exposure of electrolyte solution to the reactive species thereby enhancing the probability of nucleophilic attack, H-abstraction etc. This leads to the conundrum in which solutions that promote a top-down growth of the Li_2O_2 during discharge - leading to enhanced discharge capacity – may be also exposed to accelerated decomposition (stabilization of reduced oxygen species increase their retention time, thus their ability to attach solution species). The various degradation pathways utilized by the various families of solvents are listed in Figure 15.[66] New solvents continue to be synthesized and tested for use in Li-O_2 batteries – as discussed in the next section.
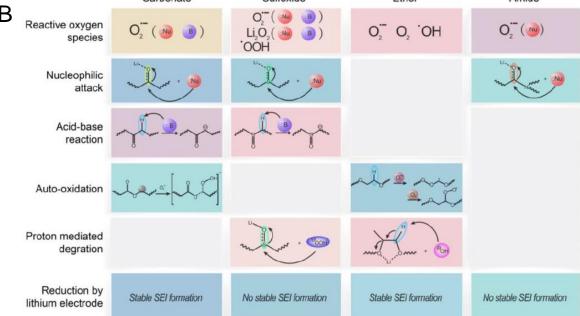
Figure 15. (A) Schematic illustration of possible discharge reactions involving oxygen radicals in different electrolyte systems. (1) Nucleophilic attack of an oxygen radical in a carbonate-based electrolyte and the subsequently produced byproducts. (2) Reaction between oxygen radicals and Li ions to produce Li_2O_2 in a non-carbonate-based electrolyte. (3) H-abstraction reaction induced by oxygen radicals and the subsequently produced byproducts in a non-carbonate-based electrolyte. Reproduced with permission from ref.[197] Copyright 2017 Royal Society of Chemistry. (B) Possible degradation pathways of the solvents. Reproduced with permission from ref [66]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.4.1(b) Salts

Li salts are an indispensable component of the electrolyte solutions which strongly

influence the course of ORR/OER. As already pointed out, the donor number of the solvents

as well as the counter anion (as expressed in the ionic association/dissociation level of the salt) play important roles in guiding the discharge product, especially in terms of its morphology.

$LiNO_3$ is one of the most explored salts in Li-O_2 batteries. In addition to promoting solution mediated growth, $LiNO_3$ also exhibits a bi-functional role. It catalyzes the OER[198,199] and passivates the carbon electrode against oxidative damage.[200] A myriad of other salts have also been employed in Li-O_2 battery electrolyte solutions and their discharge voltage profiles are presented in Figure 16A. Distinct discharge capacity and voltage plateaus are observed for each of the different anions. LiTFSI exhibited the maximum discharge capacity followed by LiTf, and $LiPF_6$. LiTFSI is also among the most frequently salts reported for Li-O_2 batteries because of its good chemical and electrochemical stability and considerable ionic conductivity. However, it also undergoes partial decomposition to form LiF on the cathode surface, similar to LiTf and $LiPF_6$.[201]

Using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), Nasybulin et al.[201] studied various salts in Li-O_2 batteries and showed that almost every salt undergoes at least partial decomposition, reacting with the in situ generated reactive oxygen species. $LiBF_4$ and LiBOB suffered from complete decomposition to LiF, boron-oxygen compounds,[66,201] and Li_2CO_3 on the cathode surface. The degradation of $LiBF_4$ and LiBOB is reflected in the abnormally high discharge plateaus seen in Figure 16A. By contrast, LiTFSI, $LiNO_3$, $LiClO_4$, and LiBr showed relatively stable performance. The beneficial role of LiBr and LiI as redox mediators has also been reported recently, and is discussed further below.[202,203] This emphasizes that in describing the performance of Li-O_2 battery chemistry, the involvement of the salts holds an equal importance to the stability of the solvents. Consequently, this aspect should be comprehensively investigated in order to come up with stable electrolyte solutions.
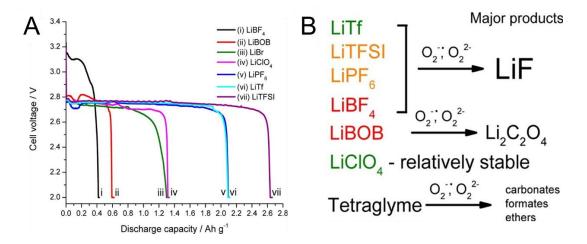
Figure 16. (A) Discharge profiles of Li-O$_2$ battery with various anions of Li-salt dissolved in TEGDME, (B) Decomposition products of Li-salts in the presence of reactive oxygen species. Reproduced with permission from ref[201], copyright American Chemical Society, 2013.

3.4.2. Development of new solvents for Li-oxygen batteries.

From the discussion above, the importance of finding appropriate solvents is crucial for the development of durable Li-O$_2$ batteries. As shown in Figure 17, the various characteristics of solvents that can be suitable for Li-O$_2$ batteries have to be considered.
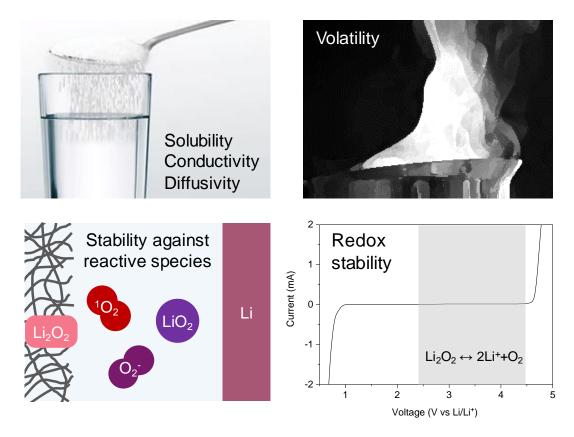
Figure 17. Important parameters for promising solvents for Li-O$_2$ batteries.

The solubility of the Li salt must be considered, since the solution must be capable of ion transfer. In addition, the solubility of O_2 gas should also be considered because the O_2 gas is the cathode's active mass which should be dissolved in the electrolyte solution in order to react electrochemically. The conductivity and diffusivity, which are critical properties of any electrolyte solution, can also be controlled by the nature of the solvent, and thereby should be taken into account. The volatility of the solvents is also a factor that should be considered for long-term operation. Non-volatile solvents like tetraglyme are indeed widely used in these systems.

It is also important to have enough redox stability to prevent decomposition during discharge and charge, but it should be noted that practical lithium-air batteries would aim to operate below 3.5 V, and significant anodic stability isn't requisite. However, when the stability window of the electrolyte is exceeded, decomposition of the solvent occurs and such side reactions not only interfere with the desired decomposition of Li_2O_2, but also decreases the cyclability of the batteries due to the accumulation of byproducts on the cathode.

Hence, in general, the reversibility of Li-O_2 cells is very poor if the solvent is decomposed by possible reactions with O_2^-, LiO_2, or the recently reported $^1O_2$ - produced by the formation and decomposition of Li_2O_2. Since Li_2O_2 is an indispensable product of the battery reaction, stability of solvents against Li_2O_2 must be ensured. Therefore, the stability of any solvent examined for Li-O_2 batteries to ROS should be first verified. Several candidate solvents that have been reported as more stable than glyme solvents in Li-O_2 cells are summarized in Figure 18 below.
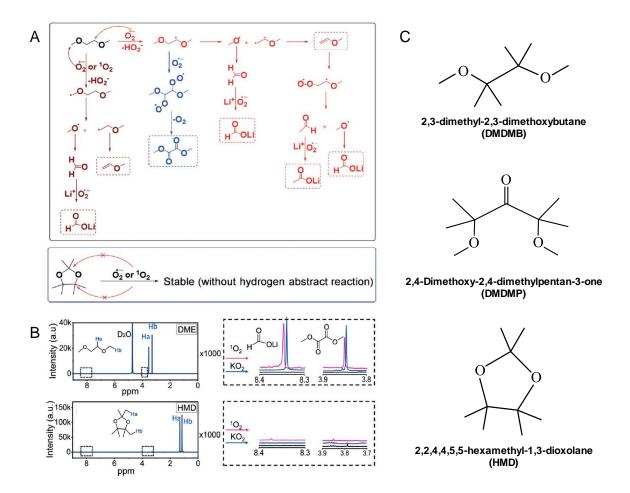
Figure 18. (A) Possible decomposition mechanism of DME (top) and HMD (down). (B) ^{1}H NMR spectra (left) with magnified views (right) for checking stability of DME (top) and HMD (down) against $^1O_2$ and KO_2. (C) Proposed candidates as stable solvents in Li-O_2 batteries in previous articles.[133,204,205] Reproduced with permission from ref.[205]. Copyright 2019 John Wiley & Sons, Inc.

Adams et al.[133] synthesized 2,3-dimethyl-2,3-dimethyoxybutane (DMDMB). In this compound, the internal β-hydrogens of DME (1,2-dimethoxyethane) are replaced with methyl groups. As shown in Figure 18A, this prevents facile elimination by preventing abstraction of these hydrogens. In their paper, DMDMB reduced the amount of generated CO_2 by 10 fold and did not form byproducts such as lithium formate compared to DME.

Sharon et al.[204] synthesized 2,4-dimethoxy-2,4-dimethylpentan-3-one (DMDMP) by replacing the acidic hydrogens alpha to the carbonyl of 1,3-dimethoxyacetone with methyl groups. The DMDMP is stable to nucleophilic attacks and H-abstraction by reduced oxygen species.

Huang et al.[205] proposed 2,2,4,4,5,5-hexamethyl-1,3-dioxolane (HMD), which does not have any hydrogen atoms on the alpha-carbon, also preventing H-abstraction by superoxide. Compared to DMDMB and DMDMP, nuclear magnetic resonance (NMR) data demonstrated that HMD is stable to both reduced oxygen species and singlet oxygen.

The common strategy in all the above studies is to substitute labile hydrogens, which are the starting point for solvent decomposition, with methyl or methoxy groups, generating structures more stable to ROS. However, since only a few examples of such compounds appear in the literature, more examples are required. Furthermore, in addition to improving the stability by using steric hindrance, various other properties such as solubility, conductivity, and volatility of these solvents must be examined.

It is expected that stable and reliable solvents, which can improve the actual performance, can be found as substitutes for polyethers (glymes), which were predominantly used until now as the best compromised family of solvents. However, the development of a suitable solvent that meets all conditions may be difficult in practice.

Strategies that can compensate for instability of solvents should be considered, such a high concentration of electrolytes (the concept of solvent in salt). Liu et al.[146,192] proposed highly-concentrated solutions as more stable electrolytes. These include 3 M solutions of LiTFSI in DME and highly-concentrated LiTFSI-DMSO (1/3 n/n) which in either case contain no free solvent molecules and which could in comparison to less concentrated solutions demonstrate improved stability toward Li-metal anodes and air cathodes.

Dong et al.[206] have also seemingly solved the problem of parasitic reactions in Li-O_2 cells by replacing the organic solvent with super-concentrated LiTFSI (21 m) in H_2O. Li_2O_2 was confirmed as the only discharge product, with no LiOH formation, although H_2O is used as the solvent in this system.

Zhao et al.[207] mixed tetraglyme with 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) in a 1: 1 volume ratio. This was done in order to improve the electrochemical stability, as well as to increase the ionic conductivity and wettability, reduce viscosity, and flammability. In addition, the stability of the Li metal anodes in the cells were improved due to formation of passivating surface films, thanks to the presence of the fluorinated co-solvent. In summary, this section definitely shows some light at the end of the tunnel, demonstrating interesting attempts to develop new solvents in light of understanding the mechanisms of side reactions. Also, the use of super-concentrated solutions can also help to stabilize $Li-O_2$ batteries.

3.4.3. Cathode materials and their stability in $Li-O_2$ cells.

In contrast to lithium-ion batteries, in lithium-air batteries the full mass of the storage material Li_2O_2 is fully formed and decomposed in every cycle. The role of the cathode is to provide a framework within which this can occur. The cathode must possess high electronic conductivity, high open porosity to allow for Li_2O_2 storage and O_2 and Li^+ transport. The accessible surface area governs the true surface area discharge current and impacts the ORR; larger current densities form thinner deposits, which calls for properly balancing inner surface area and pore space. This must be accomplished while introducing minimal additional mass and volume to the battery.[208,181] Perhaps most importantly, and yet rarely acknowledged, is the need to fill large fractions of the cathode volume with Li_2O_2 during discharge (ORR).[208,53] In our opinion the cathodes should be able to host Li_2O_2 deposits after discharge that fill at least half of their volume while not impeding battery performance, to achieve the ambitious performance targets envisaged for the lithium-air battery. Unfortunately, most work in the field fails to consider this requirement and it is common practice to measure the capacity per unit mass of the cathode material.
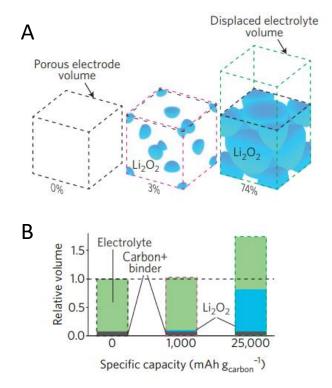
Figure 19. (A) Space filling of spherical Li_2O_2 particles inside a porous electrode and the displaced electrolyte volume at discharge capacities of 0, 1,000, and 25,000 mAh g^{-1}_{carbon}. (B) Volumes of the electrode components at these capacities normalized to the full electrode volume in the delithiated state. Reproduced with permission from ref[181]. Copyright 2017 Springer Nature.

In too many publications, the mass and volume of all other non-active components (electrolyte solution, displaced volume, binder, accumulated lithium peroxide etc.) are commonly disregarded in the calculations of specific capacity or energy. As shown in Figure 19 and the excellent perspective article from Freunberger,[181] such calculations mislead the true evaluation of the metrics of Li-O$_2$ cells. Below we attempt to review advances in cathodes in the context of their true electrochemical performance in lithium-air batteries.

3.4.3(a) Carbon cathodes and their stability

Carbon cathodes are ubiquitous in Li-O$_2$ batteries due to their high conductivity, low weight, low cost, and flexible structure. Typically, carbons have been selected to provide a large surface area and pore volume in which the Li_2O_2 ORR product can be hosted. Early work in the lithium-air field employed carbon blacks such as Super P, Vulcan XC 72R and Ketjen black.[83,209,153] These materials, while having relatively moderate surface area, possess

reasonably high specific pore volume. Consequently, calculating specific discharge capacity of such carbons in cathodes of Li-O_2 cells may provide capacities >2000 mAh g^{-1}$_{carbon}$.[210] Ding et al. used silica templates to form a series of hierarchical carbons with varying pore sizes and showed that a general correlation exists between the pore volume and the discharge capacity.[211] However, they also showed that pores of ultra-high surface area mesoporous carbons are not accessible for Li_2O_2 storage.[211] Nie et al. demonstrated the importance of large macropores that remain open and able to delivery oxygen through the cathode.[212] Graphene-based carbons have been reported to offer capacities in excess of 10,000 mAh g^{-1}$_{carbon}$,[213] but there is also an unanswered question regarding the long-term stability of graphene-based cathodes. However, graphene based-materials should not be dismissed, as rigid, free standing graphene foams and papers meet many of the requirement for housing Li_2O_2 deposits (Figure 20).[214] In addition, the lack of a binder may increase stability.
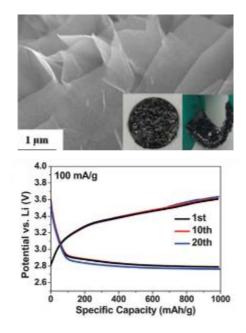
Figure 20. SEM image of a graphene foam cathode (inset optical images) and the resulting cycling profile of Li-O_2 cells when it is used as the cathode. Reproduced with permission from ref[214]. Copyright 2013 Royal Society of Chemistry.

Unfortunately, most studies have failed to account for the mass of Li_2O_2. When additional considerations of the electrolyte solution are included in the volume of highly porous cathodes

few, if any, reported cathodes offer suitable performance for viable lithium-air batteries (in terms of attractive specific capacity). This is exemplified by a laudable contribution from Mitchell et al. (Figure 21)[215] where the capacity per mass of carbon only and per mass of carbon + Li_2O_2 is provided for a lithium-O_2 cell containing a CNT cathode. The CNT cathode capacities are 4720 mAh g^{-1}_{carbon} versus 944 mAh $g^{-1}_{carbon+Li2O2}$, demonstrating the fallacy of measuring capacity as a function of carbon mass only. Zhao et al[216] calculated the capacity of a graphene cathode to be ca. 1000 mAh $g^{-1}_{carbon+Li2O2}$. These variations in performance metrics have resulted in a move towards presenting real capacities and the use of fibrous carbon gas diffusion electrodes previously used in fuel cells.[217] These materials are not practical due to their large mass. But they do offer physical properties similar to those presumably required in a practical lithium-air cathode, i.e. large porous volume, large pores for O_2 delivery, reasonable surface area, and a rigid and robust 3D structure. Thus, they offer a suitable testbed. With the advent of redox mediators able to direct significant discharge via a solution route, Gao et al[208] have presented discharge capacity as a volume fraction, which provides a more robust measure of improvement, and paves the way for meaningful comparisons of cathode performance.
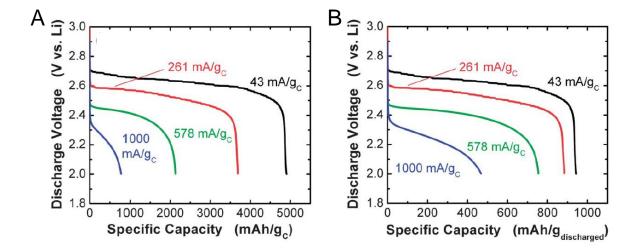
Figure 21. First-discharge profiles of Li-O_2 cells containing CNF electrodes with the capacity normalized to (A) the weight of the carbon and (B) to the carbon + Li_2O_2. Reproduced with permission from ref[215]. Copyright 2011 Royal Society of Chemistry.

Stability is the Achilles' heel of carbon cathodes. Gallant et al. reported the formation of lithium carbonate at the interface between Li_2O_2 and carbon.[218] XANES spectra of discharged cathodes showed significant amounts of lithium carbonate after discharge to low capacities, which gives way to predominantly lithium peroxide as the discharge capacity increases (Figure 22). Moreover, the surface of carbon was found to be oxidized. They interpreted this as a reaction between the lithium peroxide in close proximity with the carbon followed by growth of higher purity lithium peroxide on the outer layer (Figure 22C). During subsequent cycling, they identified an accumulation of lithium carbonate, accompanied by a shift to higher charging voltages due to oxidation of lithium carbonate.
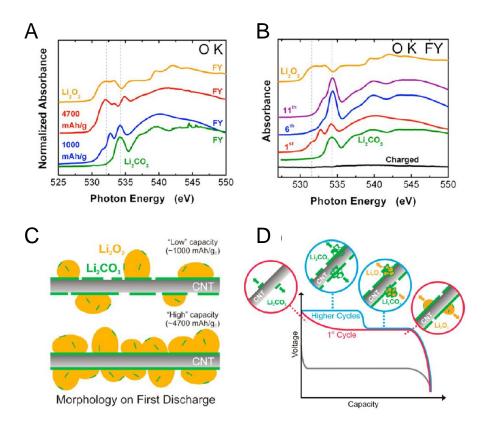
Figure 22. O K-edge FY spectra of Li-O_2 electrodes (A) discharged to 1000 (at 250) and 4700 mAh g^{-1}_C (at 100 mA g^{-1}_C) on the 1st discharge and (B) cycled electrodes ending on the 1st, 6th, or 11th discharge. (C) Schematic of discharge products formed at low and high capacity on carbon on the 1st discharge and (D) during 1st and higher cycle numbers and the corresponding influence on the charging voltage. Reproduced with permission from ref[218]. Copyright 2012 American Chemical Society.

Thotiyl et al. demonstrated the evolution of $^{13}CO_2$ when charging a lithium-O_2 battery containing a cathode containing ^{13}C, conclusively demonstrating carbon decomposition in this battery (Figure 23).[154] Analysis of the cathode at various states of discharge and charge showed that carbon decomposition predominantly occurred during charging and at high voltages. Oxidation of Li_2CO_3 and CO_2 evolution was shown to occur below 4 V in accord with other studies.[84,174] Analysis over successive cycles indicated that Li_2CO_3 from carbon decomposition accumulates in the cell. Comparison of hydrophobic and hydrophilic carbons showed that the latter offers higher stability due to the lack of reactive surface groups.[154] The preferential reactivity of functional groups on carbons has been observed also by others and is also relevant during the discharge processes.[219,220]
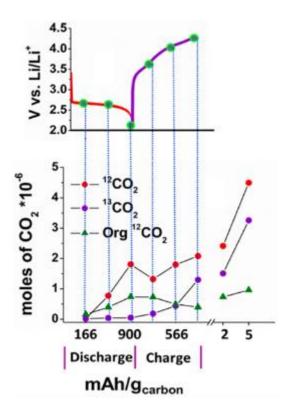
Figure 23. (upper) Discharge−charge curves on the first cycle for Li-O_2 cells containing a tetraglyme-based electrolyte and a ^{13}C cathode. (lower) Moles of CO_2 evolved during chemical treatment of the removed cathodes due to decomposition of (red) the electrolyte, (purple) the cathode, and (green) electrolyte (organic fragments) during cycling to the point indicated by the markers on the plot. Reproduced with permission from ref[154]. Copyright 2012 American Chemical Society.

Summarizing the above results, it seemed that carbonaceous materials, despite all their promising attributes, suffered instability in lithium-air batteries. This led to a search for alternative stable materials (reviewed below). However, when using redox mediators for the charging processes of Li-O_2 batteries, a significant decrease in degradation of the battery components is observed.[221] Gao et al. demonstrated a dual mediator cell with both discharge and charge mediators, including cathodes containing ^{13}C, and showed that the use of redox mediators increase the stability of the carbon cathodes.[208] This is shown in Figure 24 where the Li_2CO_3 content of discharged cathodes was analyzed ex situ. Li_2CO_3 rapidly accumulates in standard cells, but cells using dual mediators showed markedly less decomposition and accumulation.

The authors assigned this improved stability to three factors: 1) when using soluble discharge redox mediators, the products forms in solution and lacks intermediate contact with the carbon thus lowering the propensity for decomposition; 2) the redox mediators force the cells to undergo charging at 3.6 V, thus avoiding the highly positive potentials that drive carbon oxidation; 3) the redox mediators are less affected by surface area loss from passivation by Li_2CO_3 that would otherwise increase the OER overpotentials. These recent results using redox mediators rekindle the possibility of using carbon in the lithium-air cell.
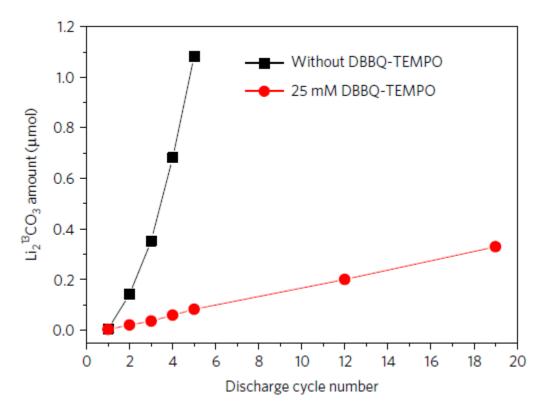
Figure 24. Amounts of $Li_2{}^{13}CO_3$ at the end of discharge of successive cycles of cells contain ^{13}C cathodes, with and without duel mediators. Reproduced with permission from ref [208]. Copyright 2017 Springer Nature.

3.4.3(b) Non-carbon cathodes

Alternative stable cathode materials have been sought to replace carbon. As proof of concept, Peng et al.[188] showed that a cell containing an Au cathode could deliver improved cycling efficiency. In the absence of carbon, the evolution of CO_2 upon charge was much reduced, indicating less decomposition. A search for more practical alternatives identified metal carbides as promising cathode materials, in particular TiC.[222] These studies showed that the surface of TiC forms an oxide layer, which is stable during cycling. This was supported by theoretical work showing that a TiC surface in contact with Li_2O_2 would lead to termination with a stable oxide layer.[223] Adams et al. showed that the thickness of these surface oxide layers is critically important. A complete oxide coverage can passivate the cathode and stop the charge reaction.[224] However, TiC is one of the few metal carbides identified that is stable during cycling.[225]
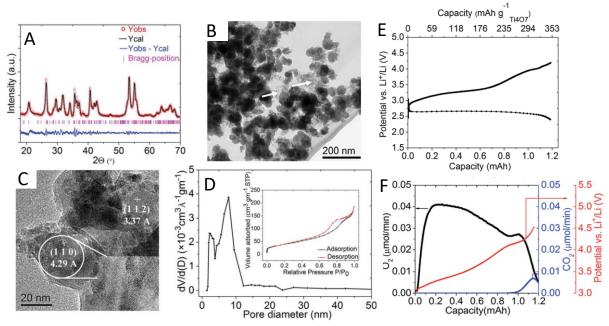
Figure 25. Characterization of a Magneli phase Ti_4O_7 cathode material including (A) XRD pattern, (B,C) TEM images and (D) pore size analysis and the (E) cycling profiles for Li-O_2 cells containing magneli phase Ti_4O_7 cathode and (F) gas analysis during cycling of the cell during charge. Reproduced with permission from ref [226]. Copyright 2015 Royal Society of Chemistry.

The surface of metal carbides during cycling is predominantly oxide based, suggesting that conducting metal oxides may be considered as viable cathode materials. Kundu et al. reported the use of Magneli phase Ti_4O_7 as a cathode in the lithium-O_2 battery (Figure 25).[226] The Ti_4O_7 was synthesized with a particle size of 80-100 nm consisting of smaller 10-20 nm crystallites with 2-10 nm pores. The cycling performance and accompanying on-line electrochemical mass spectrometry on charge is shown in Figures 25E and F. The overpotential during charge was below 3.5 V for the bulk of the charge process, and CO_2 release is greatly reduced. The e⁻/O_2 ratio was shown to be 2.6, which is an improvement compared to what is measured with Vulcan carbon cathodes (indicating much less side reactions). A number of other metal oxides have been used in the Li-O_2 cells, such as MnO_2,[227] Co_3O_4,[228] Mn_3O_4,[229] and Al_2O_3.[230] However, without careful analysis, similar to those described above, it is difficult to judge the efficacy of these materials. Other materials considered include precious metal

catalysts and metal sulfide materials, but in this review, we consider these in the context of heterogeneous catalysis.

3.4.3(c) On the stability of polymeric binders in the cathodes

The stability of polymers as binders in the cathodes was evaluated by Amanchukwu et al.[231] by checking their reactivity with Li_2O_2. The polymeric binders PAN, PVC, PVdF, PVdF-HFP, and PVP were found to be unstable to Li_2O_2, in agreement with previous studies revealing the instability of PVdF.[232] In contrast, PMMA, PTFE, and Nafion polymers were found to be chemically stable under these conditions. PEO is generally stable; however, some cross-linking can occur. The instability of polymeric binders like PVdF may complicate the analysis of composite cathodes. For instance, the side products formed by the decomposition of PVDF show Raman spectroscopic absorptions which resemble those of LiO_2 moieties; this in turn, can lead to a severe misunderstanding of the results.[233] Hence, it is important to note that the use of unstable materials may cause errors in the interpretation of the cathodes' reaction mechanisms. This is on top of the poor stability that could obviously lead to poor electrochemical performance.

3.4.4. Negative electrodes

As mentioned above, the Li-O_2 battery has generated much interest because of its 4 to 5-fold higher theoretical specific energy compared to conventional LIBs. This high energy density depends primarily on the use of metallic lithium as the anode, which has a very high theoretical specific capacity ($\sim$ 3860 mAh g^{-1}) and the most negative reduction potential (-3.040 V versus the standard hydrogen electrode). To date, numerous efforts have been invested in introducing lithium as a practical anode in order to meet the progressing demand of advanced, lightweight, high-energy batteries. But unfortunately, all the impressive traits of this metallic anode come at the cost of three important factors, namely, reactivity, efficiency, and safety, which impede its successful application in rechargeable energy storage devices.

The high Fermi energy level and negative reduction potential of lithium, on the one hand, offers the benefits of high operational voltage. However, these factors also make the lithium electrode extremely chemically reactive towards almost all liquid electrolyte solutions. Undesirable parasitic reactions occur as soon as the electrolyte solution is exposed to a lithium surface. These spontaneous reactions result in the formation of a fragile solid electrolyte interphase (SEI) that temporarily passivates the lithium from further reaction. The oxygen environment of the $Li-O_2$ system complicates matters further, as the presence of reactive oxygen species (ROS) promote parallel degradation pathways proceeding towards the accumulation of insulating by-products (Li_2O/Li_2O_2, Li_2CO_3, and various types of insoluble ionic Li compounds) on the anode surface. Additionally, during cycling, the crossover of CO_2, trace levels of H_2O (arising from electrolyte decomposition), and redox mediators (used for catalysing OER/ORR), from the cathode to the negative electrode, have a detrimental effect on the performance of Li metal electrode by direct reactions. These species also affect the composition and morphology of the SEI at the lithium/electrolyte solution interface. Recently, the effect of O_2 crossover on SEI formation has been investigated in ether-based solvents.[64] With the help of in-situ XRD and computational studies, Assary et al.[64] have revealed the formation of LiOH, aldehydes, and carbonates at the anode. These impede the migration of lithium ions, leading to increased charge transfer resistance and failure of the electrode (Figure 26).
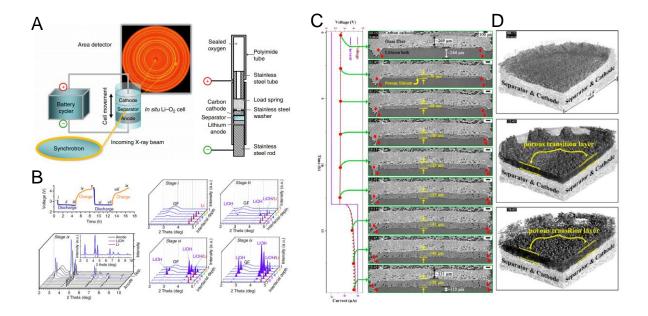
Figure 26. Observation of Li metal degradation in Li-O$_2$ batteries. (A) The experimental set-up for operando XRD and schematic design of the cell. (B) The change of lithium anode during discharge–charge cycling in Li-O$_2$ batteries. XRD patterns exhibit LiOH formation during cycling tests. (C) Electrochemical and morphological results of cell during discharge and recharge process in situ measured at energy dispersive diffraction (EDDI) beamline. (D) Selected 3D demonstrations of the reconstructed data sets shown in C with time stamps (top) 00:15, (middle) 12:45, and (bottom) 19:45. Reproduced with permission (A, B) from ref. [234], copyright Springer, 2013. (C) from ref. [235]. Copyright 2019 American Chemical Society.

In general, the formation of the SEI and other side reactions between lithium metal and crossover contaminants, irreversibly consumes lithium and the electrolyte solution - which results in limited coulombic efficiency (CE). If the formed SEI is self-limiting and stable throughout the cycle life, the CE of the Li-anode will be greatly improved after the first cycle. But, unfortunately, with repeated stripping/plating, the morphology of the lithium surface changes and the natural SEI undergoes repeated rupture and repair cycles. This leads to both undesirable electrolyte solution consumption, and inhomogeneous and uncontrolled deposition of Li as sharp needles or in branch like patterns commonly known as dendrites. These severely reduce the CE as illustrated in Figure 27. These dendrites act as hotspots and in further cycles, become the preferred site for Li-ion deposition because of fast reaction kinetics and shorter diffusion lengths. This results in their continuous growth, which not only leads to large volumetric and morphological changes, but also creates a safety issue by short circuiting the

cell. This poses a threat of thermal runaway and explosion. To deal with the low CE of the lithium anode, and dendritic growth at high current densities, researchers typically carry out experiments using a large mass of lithium. Consequently, technical breakthroughs focusing on the use of a massive excess of lithium or its complete replacement by a stable substitute, ignore the consequences of the proposed protocols in a full practical Li-O_2 cells and are of less practical merit. It is important to emphasize that to attain practical goals, a protected Li anode is needed for Li-O_2 and many other Li metal batteries.

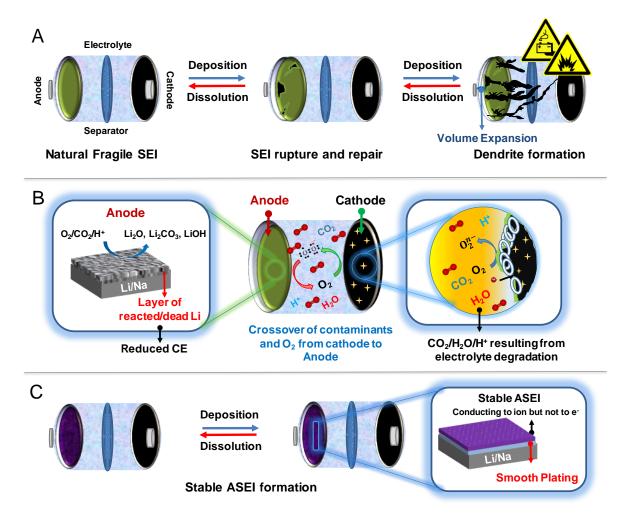**Figure 27.** Graphic representation of the mechanistic issues associated with the use of metallic anodes. The figure illustrates: (A) dendrite formation and concomitant safety issues originating from the rupture and repair of the fragile solid electrolyte interface (SEI); (B) effect of O_2 crossover on the columbic efficiency (CE); and, (C) the benefits of an artificial SEI (ASEI) in stabilizing the metal anode.

Nevertheless, despite the formidable challenges associated with metallic lithium, the recent development of the Li-O_2/air battery has undoubtedly hastened the possible discovery of practical solutions to surmount these challenges. Specifically, in the field of Li-O_2/air batteries, where metallic lithium is an indispensable component, researchers have utilized three approaches to mitigate the various issues: (1) Stabilizing the SEI - either by designing the anode/electrolyte interface (artificial SEI) and/or by optimizing the salt-solvent coordination. The latter can be accomplished by using super concentrated electrolyte solutions with fewer free solvent molecules, and an ionic liquid-like bulk nature; (2) developing selective membranes to restrict the crossover of O_2, CO_2, redox mediators, and other contaminants; and, (3) engineering the metallic Li anode structure to overcome morphology and volume changes.

The first approach relies predominantly on controlling the composition of the SEI which can, in turn, stabilize the lithium metal by suppressing the parasitic side reactions, and, by controlling the metal ion flux.[236–241] Many kinds of approaches have been studied for direct coating of Li metal anodes by artificial protective layers to avoid contact of Li metal with reactive electrolyte solutions. Among these, liquid or gas treatments have been reported.[242–244] In addition, the use of electrolyte solution additives or co-solvents like FEC were adapted for elaborating a stable artificial SEI on Li metal electrodes.[245]

It is now well known that a smartly designed interface can ensure uniform metal deposition and high coulombic efficiency by reducing rupture/repair of reinforced interfaces. Recently, Kozen et al.[246] experimentally demonstrated the success of this approach by designing a hybrid organic/inorganic artificial SEI on a lithium surface, which exhibited stable cycling over 110 cycles at a current density as high as 2 mA cm^{-2}. Additionally, by optimizing the electrolyte composition, the solubility and diffusion of ions, gases, and other contaminants can be controlled. This is accomplished by exploiting the different solubility of reaction intermediates/discharge products in the different solvents or salts depending on their Guttman

number and ionic strength. This can be clearly inferred from the stabilizing ability of super concentrated electrolyte solutions based on LiTFSI-DMSO (1:3 molar ratio)[192], 3 M LiTFSI-DME[146], and 4 M LiNO$_3$-DMSO.[247] With the above compositions, it has been demonstrated that Li-O$_2$ batteries with super concentrated solutions exhibit significantly enhanced cycle life with a CE > 90. Enhanced reversibility of Li-O$_2$ batteries containing an advanced Li salt, LiTNFSI, for formation of a stable SEI layer, was also reported by Tong et al.[248] The use of gel or solid electrolytes instead of standard liquid solutions are also known to help in eliminating side reactions and suppressing dendrites formation (Figure 28). However, solid electrolytes are associated with low migration kinetics of the Li ions.

Another way to prolong the cycle life of the negative electrode is to utilize membranes with selective permeability, or functionalized separators.[59,249–251] These can create barriers to the crossover of contaminants that accelerate the deterioration responsible for lithium instability. By restricting the gases and radical species reaching the lithium surface, such membranes can attenuate the multiple degradation pathways and accumulation of side products on the metal interface. This approach is particularly important for the Li-air system, where the cathode's active mass forms highly reactive moieties on reduction. In these systems, it is important to protect the Li anode from all other active atmospheric contaminants like N$_2$, CO$_2$ and moisture that can instantly corrode the negative electrode and shorten the battery life. The use of bi-compartment cells in which the Li anodes and the carbon cathodes can operate in the most appropriate liquid electrolyte solutions (relevant for them) separated by a membrane (ceramic or polymeric) which can transport only Li ions from side to side were proposed in order to limit the cross-talk. The bi-compartment configuration (Figure 28 B) fully prevents detrimental crossover of reactive products between the reactive electrodes. While such a configuration may not be practical due to the relatively low specific energy of these cells, nevertheless, it is excellent for systematic studies of the behavior of components in Li-O$_2$ cells

without interference of side reactions. For instance, with such cells it was possible to study separately the effectiveness of redox mediators at the cathode side and effective ways to stabilize the Li metal anode.[252] Alternatively, functional polymer membranes that fully block detrimental crossover between the electrodes can be used in similar bi-compartment Li-O_2 cells. Kim et al. reported on the use of a polyurethane based modified separator for stable and reversible Li-O_2 batteries.[253] From the viewpoint of the cell's energy density, using modified separators in Li-O_2 cells is more advantageous than using bi-compartment cells separated by ceramic membranes.

In addition to the above described problems and solutions (related to the reactivity of Li metal anodes), there is a great need to accommodate the massive volume expansion observed on stripping/plating of lithium. In the past few years, material scientists have explored the problem of volume expansion and dendritic growth via 3D architecture hosts (such as reduced graphene oxide, and silicon nanostructures) to accommodate Li deposition.[240,251,254,255] Due to the availability of free spaces and voids, such structures can control volume expansion and suppress dendritic growth - with an additional advantage of restricted contact between Li and the electrolyte, leading to fewer side reactions and high cycling efficiency. However, these 3D architectures help in accomplishing safe operation of LOB's at the expense of decreasing energy density.

The growing attention and the increasing number of papers focussing on the lithium electrode gives a good measure of the importance of the metallic negative electrode in LOBs. Despite some progress, the achieved cyclability and CE is still far away from the set milestones. A better understanding of the surface phenomena on Li metal anodes (surface reactions, the structure of the surface films) seems to be critical for enabling high-efficiency deposition of metallic Li in the corrosive environment developed in Li-O_2 cells.
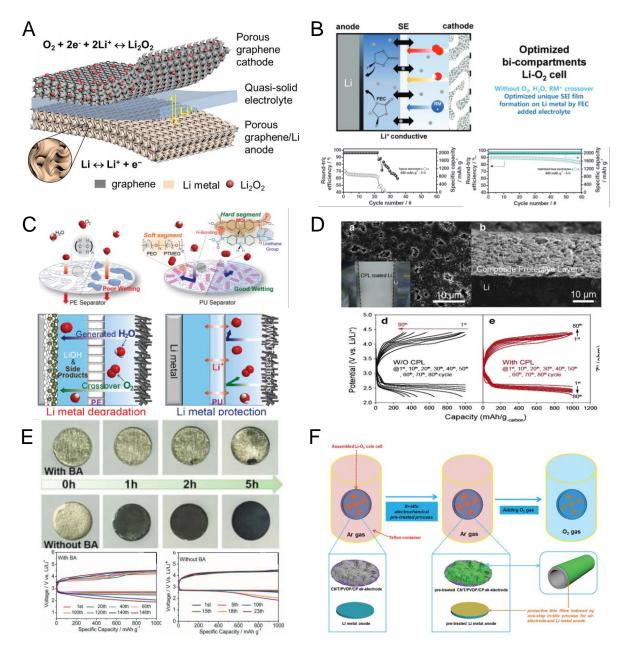
Figure 28. Representative methods for protecting Li metal in Li-O$_2$ batteries. (A) Gel or solid electrolyte. Reproduced with permission from ref.[256]. Copyright 2018 Springer. (B) Separation of electrolytes by lithium conductive membrane. Reproduced with permission from ref.[252]. Copyright 2017 John Wiley & Sons, Inc. (C) Separator. Reproduced with permission from ref.[253]. Copyright 2016 John Wiley & Sons, Inc. (D) Coating composite materials on Li metal. Reproduced with permission from ref.[257]. Copyright 2014 Elsevier. (E) Pre-electrochemical treat. Reproduced with permission from ref.[258]. Copyright 2018 John Wiley & Sons, Inc. (F) Additive for protection of Li. Reproduced with permission from ref.[244]. Copyright 2018 John Wiley & Sons, Inc.

While Li anodes are the first choice, nevertheless, several studies have focused on alternative anodes including lithiated Si, Sn, Al, and carbons. Lithiated Si anodes were

predominantly used to satisfy the required anode capacity. These alternative anodes are electrochemically or chemically lithiated before they are used in the Li-O$_2$ cells (Figure 29A). It was generally realized that Li-O$_2$ cells using alternative anodes behave less reversibly than typical Li-O$_2$ cells containing Li metal anodes (Figure 29B). This is because these lithiated alternative anodes contain a much lower amount of Li (Figure 29C), which quickly deteriorates and becomes inactive due to side reactions not only at the anode side but also at the cathode side (Figure 29D).[259] Hence, the use of alternative lithiated anodes (like Li-Si) may also require their surface protection.
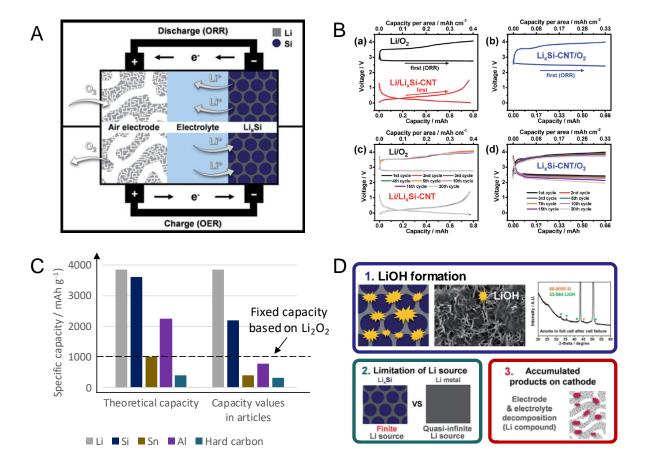
Figure 29. Alternative electrodes for Li metal in Li-O$_2$ batteries: (A) Schematic images for the discussion of the Li-O$_2$ full-cell with lithiated silicon as the negative electrode. (B) Galvanostatic cycling test results of half-cells and full-cells. (C) Theoretical and practical capacities of Li and alternative electrodes. Capacity for formation and decomposition Li$_2$O$_2$ is fixed as 1168 mAh g^{-1} based on the reaction (2Li$^+$ + O$_2$ + 2e$^-$ ↔ Li$_2$O$_2$). The values in the chart come from ref. [254,260–263]. (D) Major issues for the Li-O$_2$ full-cell related to Li loss. Panels A, C and D were reproduced with permission from ref. [259]. Copyright 2016 Royal Society of Chemistry.

From an experimental/didactic perspective, alternative anodes can be useful in experiments concentrating on the evaluation of the reversibility of cathodes.[264] However, for practical purposes, the use of protected Li-metal as the anode is inevitable. If well-protected alternative lithiated anodes and highly reversible cathode to maintain Li source during cycling test without parasitic reactions are achieved, replacement of Li metal will be possible.

3.5. Catalysis

3.5.1. Heterogeneous catalysis for the ORR and OER

Heterogeneous catalysis (or electrocatalysis) is a contentious topic in the lithium-air battery field. Firstly, there is a reasonable argument that any solid catalyst should be of a limited use because it should be quickly passivated by insulating lithium peroxide, or only catalyze oxidation of lithium peroxide in direct contract. The use of redox mediators designed to avoid contact between the cathode surface and the bulk of the lithium peroxide only exacerbates this problem. Secondly, there is a strong evidence that the introduction of a heterogenous catalyst induces decomposition. For example, during the early development of the Li-O_2 battery, MnO_2 catalysts were thought to offer improved performance,[227] but have since been shown to induce significant decomposition of the electrolyte.[85] It should be noted that these earlier studies generally used carbonate-based electrolytes, which are now known to be unstable. McCloskey et al. studied the impact of a series of heterogeneous catalysts including Pt, MnO_2, Au and showed, through analysis of gas evolution, that both Pt and MnO_2 induced considerable decomposition and an increase in CO_2 evolution (Figures 30A-C).[85] Neither Au nor MnO_2 appeared to demonstrate any catalytic activity, although we highlight that the primary purpose of Au cathodes is stability. Studies by Ma et al. have similarly demonstrated that both Pd and Ru based catalysts increase the degree of irreversibility in Li-O_2 cells.[265] Genorio et al. studied

oxygen reduction in dimethoxyethane at well-defined single crystal electrodes (Figure 30).[143]

A decrease in the electrochemical reversibility of the redox couple is observed in the order Au

> Pt > Ir and chemical analysis of the electrode surface showed formation of a solid electrolyte

interphase in the case of Pt and Ir. This is shown schematically in Figure 30E. These data

suggest that the only transition metal suitable for use in lithium-air cathodes is Au and makes

any use of a metal catalyst questionable.
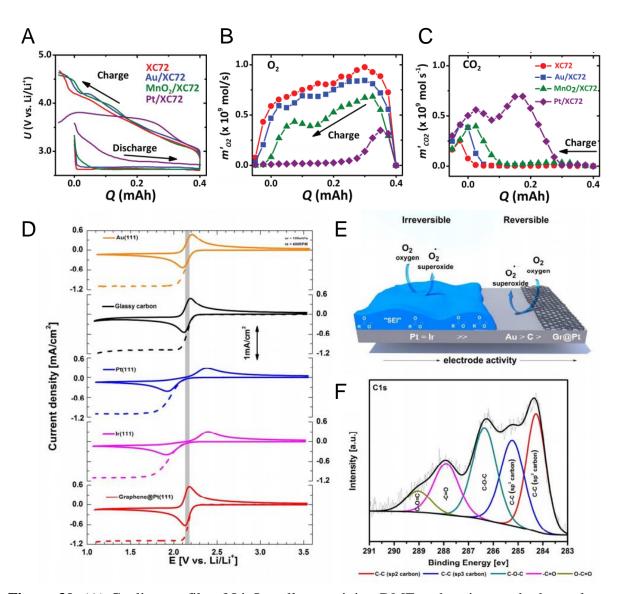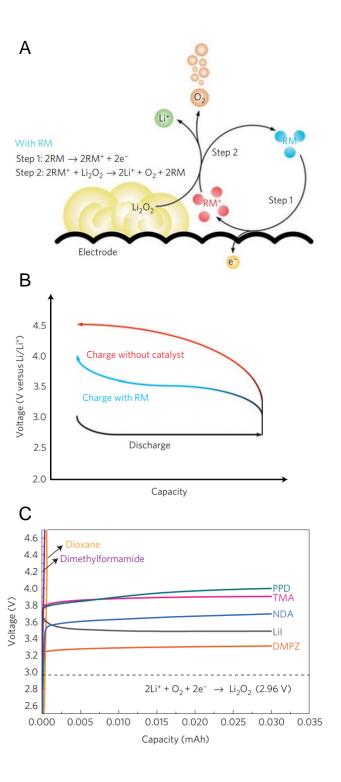
Figure 30. (A) Cycling profile of Li-O_2 cells containing DME and various cathode catalysts and the corresponding (B) O_2 and (C) CO_2 evolution during charging. Reproduced with permission from ref.[85]. Copyright 2011 American Chemical Society. (D) Cyclic voltammetry (sweep rate; 100 mV s^{-1}) and polarization curves by rotating disk electrode voltammetry (rotation rate; 400 rpm) of O_2 electrochemistry in dry 0.15 M TBAPF6/DME saturated with 10% O_2 in Ar at various single crystal metal electrodes and carbons. (E) Schematics of solid electrolyte interface (SEI) formation with corresponding electrode activity increase. (F) X-ray

photoelectron C 1s spectra of the SEI formed during O_2 electrochemistry in DME on Pt(111). Reproduced with permission from ref.[143]. Copyright 2016 American Chemical Society.

3.5.2. Homogenous catalysis with redox mediators

Due to the problems associated with the use of heterogeneous catalysts, mobile homogenous catalysts - dubbed "Redox Mediators" (RM) – were developed for rechargeable aprotic Li-O_2 batteries. RMs act as mobile charge carriers in the electrolyte solution, which facilitate electron transfer between the electrode surface and O2 on discharge and Li_2O_2 on charge (Figure 31A) . During charging, the RM is oxidized to RM^+ at the electrode surface and is then able to diffuse in the electrolyte where it oxidizes the solid Li_2O_2, resulting in oxygen evolution and regeneration of the RM. This greatly lowers the charging potential during the cycling (Figure 31B, C). The decreased charging potential not only increases the energy efficiency, but also promotes cell durability.[208]

The first generation of mediators were reported by Giordani et al.[266] and Chen et al. who demonstrated the concept with LiI and tetrathiafulvalene (TTF), respectively.[267] Li-O_2 cells using TTF in the electrolyte solution exhibited suppressed charge potential, improved rate capability and cyclic stability. Since these earlier studies, several other charge mediators have been proposed.[268,269] Bergner et al. demonstrated the use of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO),[270] and achieved enhanced cycle life compared to LiI or TTF. This work was extended to include other structurally similar mediators based on the nitroxyl group.[271] 10-methylphenothiazine (MPT)[272], tris[4-(diethylamino)phenyl]amine (TDPA)[273], 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO)[274], transition metal complexes (metal porphyrins and metal phthalocyanines)[275–277], and various other organic materials have also been proposed as potential redox mediators for oxidation of Li_2O_2. While LiI has largely been abandoned as a mediator for Li_2O_2 oxidation, it has found use in lithium-oxygen cells where LiOH is the discharge product.[100]

A

With RM

Step 1: $2RM \rightarrow 2RM^+ + 2e^-$

Step 2: $2RM^+ + Li_2O_2 \rightarrow 2Li^+ + O_2 + 2RM$

Li^+

O_2

RM

Step 2

Step 1

Li_2O_2

RM^+

e^-

Electrode

B

Voltage (V versus Li/Li^+)

Charge without catalyst

Charge with RM

Discharge

Capacity

4.5
4.0
3.5
3.0
2.5
2.0

C

Voltage (V)

Dioxane

Dimethylformamide

PPD
TMA
NDA
LiI
DMPZ

$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$ (2.96 V)

4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6

0.000 0.005 0.010 0.015 0.020 0.025 0.030 0.035

Capacity (mAh)
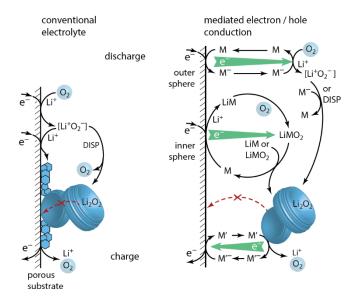
Figure 31. Redox mediators as soluble electron transfer agents. (A) Schematic of the reactions in a conventional Li-O_2 cathode The insoluble and insulating discharge product Li_2O_2 passivates the surface of the conducting porous substrate. Charging is hampered by poor electron transport (left). Mediated electron/hole transport by mediators M and M'. The reduction mediator M may transfer electrons to O_2 either in an outer sphere process or via an O_2-binding transition state in an inner sphere process (right). (B) Schematic discharge (black line) and charge profiles of Li-O_2 batteries with (blue line) and without RM (red line). (C) Charge curves with some examples of RMs. Molecular orbital energies of redox mediators and TEGDME. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of original RMs (black bar) and first oxidized RMs (red bar) in TEGDME electrolyte based on DFT calculations. (A) from Ref [Ref. 135] - Published by The Royal Society of Chemistry. (B,C) adapted with permission from ref. [278]. Copyright 2016 Springer.

OER RMs were mostly evaluated for their charging potential and partly for the electron-to-O_2 ratio. The kinetics of mediated Li_2O_2 oxidation has only recently received attention.[279–281] Chen et al. studied a variety of organic RMs for the kinetics of Li_2O_2 decomposition using scanning electrochemical microscopy (SECM) and demonstrated that the rate is highly dependent the RM used (Figure 32).[279] Among the studied RMs, nitroxides including TEMPO were found to be the fastest. Notably, no clear ratio between heterogeneous rate constant of the RM at Au and C electrodes and the apparent rate constant (k_{app}) for Li_2O_2 oxidation was found. Equally, no simple proportionality between RM potential and k_{app} was found. Both were attributed to dominating steric effects on k_{app}. An important conclusion was that even the

slowest mediators allow for charging rates in porous electrodes that by far exceed practically required values. Importantly however, the detailed mechanism of mediated oxidation and particularly pathways therein that cause electron-to-O_2 ratios to differ from the ideal of two are unknown.

Just as RMs for OER help the decomposition of Li_2O_2 during charging, there are compounds that can serve as mediators for ORR, assisting in the formation of Li_2O_2 deposits during discharging.[282–287] The first generation of discharge mediators was reported by Lacey et al.[269] They used ethyl viologen ditriflate as a redox shuttle to transfer electrons from the electrode surface to oxygen, which then forms O_2^- followed by disproportionation to Li_2O_2. While these results were promising, due to the simple shuttle mechanism, this mediator operates at the same potential as the ORR reaction, did not eliminate parallel O_2 reduction at the cathode and hence the intrinsic problem of electrode passivation on discharge persisted.
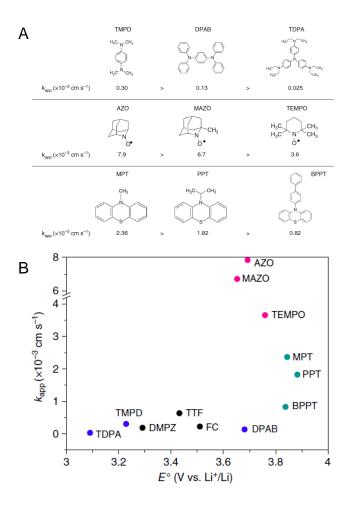
Figure 32. Li_2O_2 oxidation kinetics of redox mediators. (A) Structures of a selection of oxidation mediators and their kinetics of Li_2O_2 oxidation. (B) Comparison of the apparent rate constants (k_{app}) for the reaction between the redox mediators and Li_2O_2 grouped by structure. Reproduced with permission from ref.[279]. Copyright 2018 Springer.

In contrast, the mediator 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) as reported by Gao et al.[286] raises the voltage of mediated above direct O_2 reduction at the cathode. Unlike previous ORR mediators, DBBQ operates as a catalyst, altering the discharge route, Figure 33(A). Following reduction, DBBQ formed Li^+–DBBQ–O_2 in solution instead of the reactive intermediate LiO_2. This process occurs at voltages positive of those needed for direct ORR and thus the problematic oxygen redox chemistry that limits lithium-air capacity is removed. As a result, the cell capacity increased 80- to 100-fold with a higher discharge voltage, in comparison to the case without DBBQ (Figure 33A). Vitamin K2[283], a biological quinone, has

been reported to work in a fashion similar to DBBQ. As discussed previously, protic additives

such as H_2O can improve the discharge performance. Inspired by this, Gao et al demonstrated

that phenol is able to improve ORR in Li-O$_2$ batteries by solvating Li_2O_2 and promoting growth

of large Li_2O_2 particles, while avoiding surface passivation.[287] The result is a greatly enhanced

capacity (35-fold increase) as shown in Figure 33B.
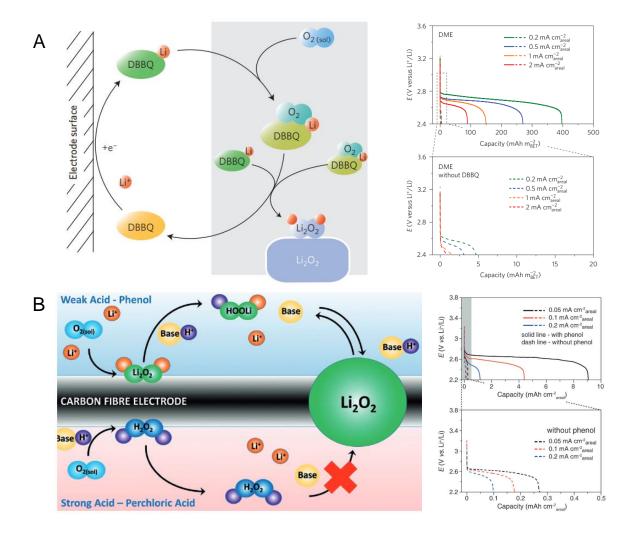
Figure 33. Li_2O_2 formation mediators in Li-O$_2$ batteries. (A) DBBQ. Reproduced with permission from ref. [286]. Copyright 2016 Springer. (B) Phenol. Reproduced with permission from ref. [287]. Copyright 2017 John Wiley & Sons, Inc.

In order to facilitate Li_2O_2 formation and decomposition during both discharge and

recharge processes in Li-O$_2$ cells, several bifunctional red-ox mediators were suggested and

tested.[273,274,288,289]

The combined use of ORR mediator and OER mediator at the same time has shown synergistic effects.[208,290,291] Gao et al demonstrated a cell containing DBBQ and TEMPO as discharge and charge mediators respectively, as shown in Figure 34.[208] This dual redox mediator cell operates without any direct oxygen redox chemistry at the electrode surface and thus was able to significantly suppress parasitic chemistry and enhanced cycling stability.
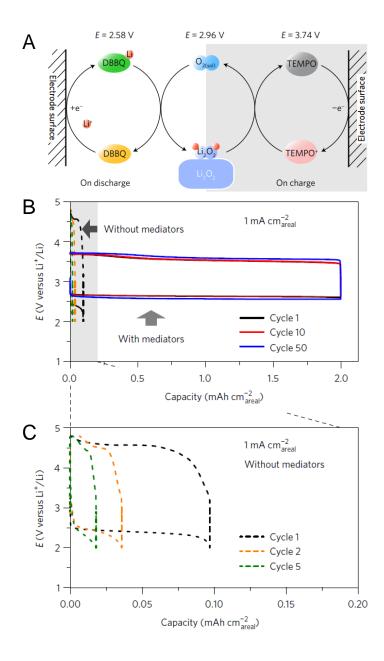
Figure 34. Dual mediators for ORR and OER in Li-O_2 batteries. (A) Schematics of positive electrode reactions on discharge and charge in the presence of DBBQ and TEMPO. (B) Discharge–charge curves of Li-O_2 batteries with (solid lines) and without mediators (dashed lines). (C) Enlarged section of the discharge–charge curves recorded without DBBQ-TEMPO in (B). Reproduced with permission from ref.[208]. Copyright 2017 Springer.

Building on this concept, Liang et al. exploited the mobile nature of the discharge redox mediator to promote growth of lithium peroxide away from the cathode, thus avoiding degradation and cell failure (Figure 35).[291] This is achieved by inserting an electrolyte soaked inert storage layer between the electrochemically active carbon cathode and the electrolyte-O_2 interface. The electrolyte contains both ORR and OER RMs, DBBQ and TEMPO in the present example. At the stationary state, on discharge, a retarded O_2 supply through the storage layer causes O_2 to be fully reduced within the storage layer by the outward-diffusing reduced form of the ORR RM. This way the carbon cathode only serves to reduce (oxidize) the ORR (OER) RM but does not perform O_2 electrochemistry.
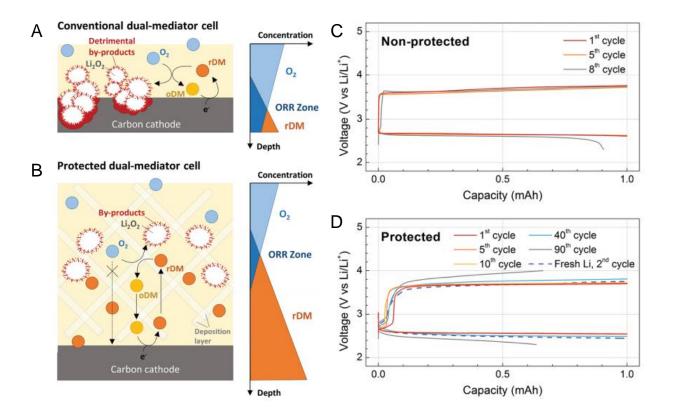
Figure 35. Strategy to protect the carbon electrode from Li_2O_2 using dual mediators in Li-O_2 batteries. During discharge in (A) a conventional dual-mediator cell, the carbon cathode is corroded by reactive oxygen species and passivated by the by-products. By contrast, the cathode in (B) a protected dual-mediator cell is isolated from both the Li-O_2 reaction intermediates and products by a dynamic O_2 shield consisting of reduced dual mediator (rDM) . Comparison of cycling stability of the (C) non-protected cell and (D) protected cell. Reproduced with permission from ref.[291]. Copyright 2018 Royal Society of Chemistry.

3.5.3. Instability issues with mediators

Despite their advantages, RMs introduce further complexity to the cell and not least potential instability. First, they may themselves not be stable with Li metal or may introduce a redox shuttle that curbs coulombic efficiency. Second, as the RMs are in many cases organic molecules, they may be subject to similar decomposition as the electrolyte or carbon.

Redox mediators can cross over to the reactive lithium metal anode due to their mobile nature. Such a phenomenon is referred to as a "redox shuttle"[272,292,293] and could be detrimental to lithium metal, the redox mediator itself, and cycling stability. Similarly, oxidized redox mediators formed during the $Li-O_2$ cell charging step can diffuse to the anode site and be reduced by reaction with the lithium metal – which constitutes self-discharge (Figure 36). Ha et al.[294] also investigated the failure mechanism of the $Li-O_2$ cell containing o-methyl-phenothiazine (MPT). They showed that the redox mediator decomposes the lithium oxide layer within the Li metal SEI through the same catalytic reaction mechanism. This exposed Li metal then directly reacts with the redox mediator resulting in irreversible decomposition, and loss of Li metal. Due to these problems, it is accepted that the lithium metal surface will need to be protected with an artificial SEI or solid electrolyte.
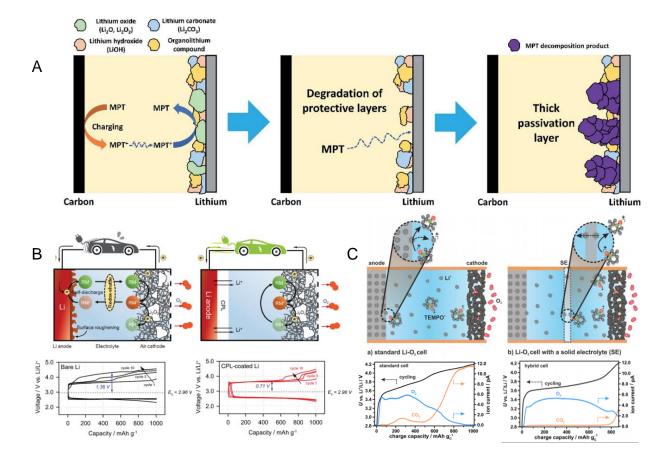
Figure 36. Issue and solution for side reaction of RM with Li metal. (A) Schematic of the failure mechanism of the Li-O$_2$ cell with redox mediator. Reproduced with permission from ref.[294]. Copyright 2017 Royal Society of Chemistry. (B) Coating protective layer on Li metal to prohibit parasitic reaction between RM and Li metal. Reproduced with permission from ref.[295]. Copyright 2016 John Wiley & Sons, Inc. (C) Solid electrolyte as Li$^+$ conductive membrane to prohibit crossover of RM to Li metal. Reproduced with permission from ref.[296]. Copyright 2016 American Chemical Society.

Lim et al. investigated representative organic RMs to find key factors that determine the catalytic activity and electrochemical stability with solvents.[278] They demonstrated that the ionization energy (IE) is a suitable proxy to predict the energy level (redox potential) of a candidate RM, helping to indicate to what extent it can interact with oxygen species in Li-O$_2$ cells, without promoting electrolyte solution degradation. They have shown that RMs with their singly occupied orbitals (SOMO) of the oxidized form close to the HOMO of the solvent are prone to extract electrons from the solvent and decompose it (Figure 37). This is seen in irreversible electrochemistry of these RMs. Based on experimental data and DFT calculations,

they suggested dimethylphenazine (DMPZ) as a low-voltage RM which is not attacking the solvent.
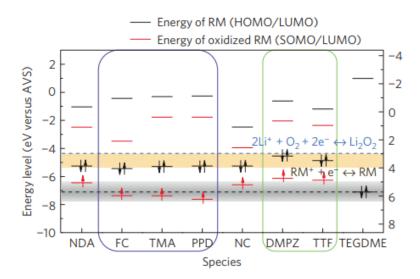
Figure 37. Molecular orbital energies of redox mediators and TEGDME. HOMO and LUMO energies of original RMs (black bar), singly occupied orbital (SOMO) energies of oxidized RMs (red bars with arrows) and HOMO energies of TEGDME electrolyte based on DFT calculations. Adapted with permission from ref. [278]. Copyright 2016 Springer Nature.

In addition to the problem of the RM being degraded by reaction with Li metal, and considering the potential instability of RMs at the cathode, Kwak et al.[297] have shown that several commonly used RMs already decompose in an O_2-free environment upon prolonged cycling. Figure 38A shows, for example, that TTF readily decomposes when cycled over both of its oxidation steps, while it proved more stable when only the first step was accessed. Such instabilities could arise from the oxidized mediator oxidizing the electrolyte as shown by Kang et al.[278] as discussed above. Since most mediators are organic molecules, they are susceptible to the same decomposition as organic electrolytes or carbon by reactive O_2 species. This was tentatively ascribed to instability with superoxide or peroxide.[270] Recently, Kwak et al.[156] investigated the reactivity of TTF and DMPZ towards various O_2 species to clarify possible degeneration routes in typical ethereal electrolyte solutions (Figure 38B). Analogous to the predominant decomposition of solvents by $^1O_2$ (see above), it was confirmed that singlet

oxygen ($^1O_2$) predominantly causes RM decomposition. The electrophilic nature of $^1O_2$ addition reactions render reduced RMs particularly susceptible to attack. While the negative, detrimental effect of $^1O_2$ formation in Li-O_2 cells on the stability of electrolyte solutions and RMs is evident, understanding the exact mechanisms requires further work.
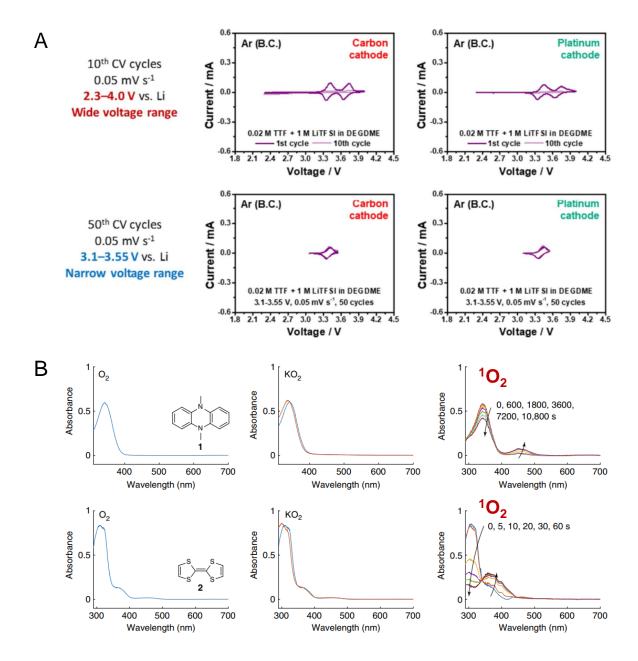
Figure 38. RM instability at the cathode. (A) Instability of doubly oxidized RMs while the singly oxidized form may cycle reversibly. Date were collected under Ar at C cathodes. Reproduced with permission from ref. [297]. Copyright 2018 The Electrochemical Society. (B) Decomposition by singlet oxygen. Reproduced with permission from ref. [156]. Copyright 2019 Springer.

3.6. The important analogous systems

3.6.1. Sodium-oxygen batteries

As the higher analogue of Li-O_2, non-aqueous sodium-air batteries (also known as Na-O_2 cells) open up interesting possibilities. Hartman et al. first demonstrated that sodium superoxide (NaO_2) can be produced as the main discharge product by using a diglyme-based electrolyte.[119] Although Na-O_2 cells offer a lower formal specific energy (1105 Wh kg^{-1} based on NaO_2) than Li-O_2 cells, they feature a much more abundant, sustainable element, sodium, a lower charge overpotential (typically below 0.2 V), and higher reversibility (Figures 39A and B). These merits suggest that Na-O_2 batteries may have practical advantages, and they have attracted great research interest.
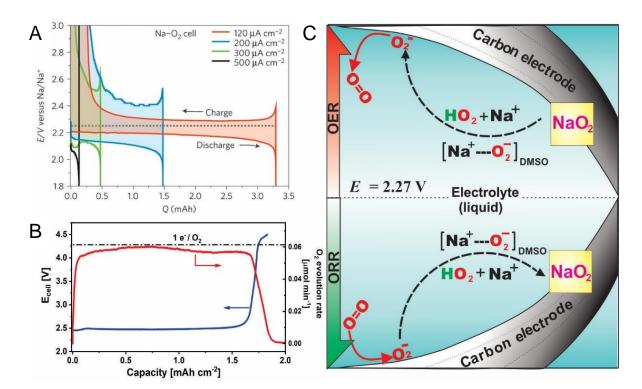
Figure 39. A rechargeable Na-O_2 battery based on NaO_2. (A) Discharge–charge cycles of Na-O_2 cells at various current densities. Cut-off potentials were set to 1.8V for discharge and 3.6V for charge. Dotted line: $E^0(NaO_2)$=2:27 V. Reproduced with permission from ref [119]. Copyright 2012 Springer Nature. (B) Online mass spectrometry analysis of oxygen evolution rate (red curve) upon charge (blue curve is the charge profile). The dashed line indicates an oxygen evolution rate corresponding to a 1 e$^-$/O_2 process. (C) Schematic illustration of the solution-mediated superoxide transfer mechanism during discharge (bottom) and charge (upper). Superoxide anion is solvated as ion pairs in DMSO –a--O_2] or by generating HO_2 intermediate upon reaction with proton-based phase transfer catalysts. Once supersaturation is achieved,

NaO$_2$ precipitates forming cubic-shaped crystals. The charge process follows the reverse pathway of discharge process. B and C Reproduced with permission from ref [95]. Copyright 2015 Springer Nature.

Superoxide versus peroxide stability is a function of the alkali cations. On the basis of the Hard−Soft Acid−Base (HSAB) theory, the Na$^+$ ion with a larger radius possesses lower charge density as compared to Li$^+$ and is therefore more effective in stabilizing O$_2^-$.[71] It suppresses the spontaneous disproportionation of NaO$_2$ to sodium peroxide (Na$_2$O$_2$). On the basis of rotating ring-disk electrode (RRDE) and *in-situ* X-ray diffraction (XRD) studies, it was found that solution-mediated superoxide transfers accounts for the growth and oxidation of cube-shaped NaO$_2$ products.[95,298] As shown in Figure 39C, superoxide species are exclusively formed at the cathode surface upon discharge and then transferred to the electrolyte. Once supersaturation is achieved, NaO$_2$ precipitates and forms cube-shaped crystals. During charge, superoxide species are re-solubilized in electrolyte and diffuse to the cathode for oxidation. This reversible solution-mediated pathway with a lower energy barrier leads to a large discharge capacity and a low charge overpotential. It is reported that the Gutmann DNs of organic solvents and the addition of phase transfer catalysts significantly influence this solution process, albeit through different mechanisms. Based on surface enhanced Raman spectroscopy (SERS) results, Aldous et al. suggested that dimethyl sulfoxide (DMSO) with a large DN facilitates the solution-mediated growth of NaO$_2$ by forming soluble DMSO-solvated [Na$^+$-O$_2^-$] ion pairs.[288] Xia et al. demonstrated that trace amount of weak acids (*e.g.,* H$_2$O, benzoic acid) function as proton-based phase transfer catalysts, enabling the solubilizing of superoxide via the formation of an hydroperoxyl (HO$_2$) intermediate.[95,299] They further provided direct evidence of HO$_2$ species existing in a diglyme-based electrolyte by using *in-situ* electron spin resonance (ESR).[300] Clearly, such reversible solution processes play a critical role in Na-O$_2$ chemistry with a lower overpotential and higher rechargeability. By

contrast, the spontaneous disproportionation of LiO_2 leads to irreversible discharge/charge pathways and the poor rechargeability and high overpotential of Li-O_2 cells.

In addition to NaO_2, sodium peroxide (Na_2O_2) and its dihydrate form ($Na_2O_2 \cdot H_2O$) were also reported as discharge products of Na-O_2 cells, although which of these is preferred is not fully understood.[301] Thermodynamically, the formation of Na_2O_2 is more favourable than NaO_2 (-449.7 KJ mol (Na_2O_2)$^{-1}$ vs. -437.5 kJ mol (2 NaO_2)$^{-1}$).[128] On the other hand, NaO_2 may be the kinetically preferred product due to the requirement of only a 1 e^- transfer (compared to two electrons for Na_2O_2). Thus, generally disproportionation in presence of Na^+ or H^+ will trigger the conversion of superoxide into peroxide (see Figure. 10A). Solvent dependent NaO_2 disproportionation has been shown by Sheng et al. to be accelerated with high DN solvents.[160] Although Na-O_2 cells based on NaO_2 products exhibit the desired electrochemical behaviour, their long-term stabilities are still a topic of concern, due to the associated parasitic chemistry. A number of studies have shown instability of NaO_2 upon prolonged rest.[118,130,132,162,180] Although details vary, they generally report gradual conversion of NaO_2 into $Na_2O_2 \cdot H_2O$ accompanied by electrolyte degradation to form NaOH, Na_2CO_3 and organic compounds including Na formate and acetate. Explanations included nucleophilic attack, H^+ and H-atom abstraction by superoxide. Black et al. reported that 10 mol% of discharge products are such side products as quantified by H-NMR and acid-titration measurements.[130] By using an isotopically labelled ^{13}C model cathode, they also demonstrated that the carbon cathode is oxidized by NaO_2, irreversibly forming carbonate.

Singlet oxygen ($^1O_2$) is now recognized an essential trigger for parasitic reactions as is formed at all stages of cycling.[107] Recently, poor Na_2O_2 yield and pronounced degradation upon NaO_2 disproportionation has been explained within a unified $^1O_2$ formation mechanism that shows growing $^1O_2$ yields as superoxide disproportionates in presence of increasingly weakly Lewis acidic cations (Lewis acidity: $H^+ > Li^+ > Na^+$; $^1O_2$ yield $H^+ < Li^+ < Na^+$).[134] A major

conclusion from this mechanism in conjunction with all papers showing instability of NaO_2-based Na-O_2 cells is that NaO_2 as a thermodynamically metastable discharge product must be avoided as it lacks the required tolerance to slow discharge and rest periods; it will gradually convert to Na_2O_2 and side products. Cycling the Na-O_2 cell highly reversible requires therefore controlled formation/decomposition of Na_2O_2 without superoxide disproportionation steps.

In addition, similar to a Li metal anode, sodium deposits easily grow into a dendritic pattern, resulting in safety concerns.[302] Oxygen species (including oxygen and superoxide) diffuse through electrolyte solution and contaminate the surface of Na anode. Thus, a variety of protective membranes (e.g., polymer, ceramic, etc.) have been used to restrict growth of sodium dendrites and prevent the diffusion of oxygen species.[303,304] Alternatively, Bender et al. replaced sodium metal with a sodiated carbon anode to improve the reversibility of the anode and avoid dendritic growth.[305] However, the long-term reliability of these approaches needs to be further examined.

3.6.2. The potassium-oxygen battery

In seeking alternative metal-oxygen chemistry to overcome the challenges in Li-O_2 batteries, the potassium-oxygen battery based on potassium superoxide (KO_2) as the product was first established by Ren et al.[306] The net battery reaction is $K + O_2 \leftrightarrow KO_2$ ($\Delta G^0 = -239.4$ kJ mol^{-1}, $E^0 = 2.48$ V), which gives a formal specific energy of 935 Wh kg^{-1} (based on KO_2). Differing from LiO_2 and NaO_2, KO_2 is a thermodynamically favourable product (see Figure. 10A). This allows K-O_2 cells to operate exclusively via the O_2/O_2^- redox couple, presenting a high superoxide yield above 98 % (vs. 95 % for Na-O_2 cells), and a low overpotential of 50 mV (vs. 200 mV for Na-O_2 cells).[126] After aging in a glyme-based electrolyte for 30 days, electrochemically formed KO_2 remains stable in the cell and demonstrates 94% coulombic efficiency. By contrast, NaO_2 quickly undergoes irreversible decomposition upon aging in the

electrolyte. Thus, the higher stability and reversibility of KO_2, as compared with LiO_2 and NaO_2, offers $K-O_2$ chemistry significant advantages.

Although ether-based electrolytes are considered to be relatively stable against O_2^- attack, their decomposition in the $K-O_2$ cell is still problematic. By using ion chromatography, Xiao et al. reported that 0.3 % of the KO_2 product is consumed with the decomposition of dimethoxyethane (DME) solvent after the first discharge.[126] More seriously, potassium metal presents much higher reactivity with ether-based electrolytes than lithium and sodium.[307] This owes to the formation of highly reactive solvated electrons and/or potasside (negatively charged potassium ions) by dissolution of K metal in ether solvents. These dissolved species cleave the C−O bonds in ether molecules leading to a very thick passivating layer (~500 μm) precipitated on the potassium surface. Moreover, the crossover O_2 is continuously reduced to superoxide species by potassium, which also accelerates the decomposition of electrolyte. Thus, forming a stable solid electrolyte interface (SEI) is highly desired for achieving reversible potassium stripping/plating. By using appropriate electrolyte salts, applying an artificial SEI, and employing a Nafion-K^+ membrane, the cyclability of $K-O_2$ cells has been significantly improved from a few cycles to hundreds of cycles.[307–309] In addition, potassium-based alloys (*e.g.,* K−Sb alloy and liquid Na−K alloy) as a new class of anode materials demonstrate advantages over K metal in terms of SEI stabilization and elimination of dendrites.[310,311] Very recently, Lu et al. reported on an organic-oxygen cell using a potassium biphenyl complex (BpK)/DME anode and a DMSO-mediated potassium superoxide cathode (Figure 40A). Based on cyclic voltammetry studies, Lu et al. found that Bp^-/Bp redox is stable and reversible. The cell exhibits an unprecedented cycle life (3,000 cycles) with a superior average Coulombic efficiency of more than 99.84% at a high current density of 4.0 mA cm^{-2} (Figures 40B and C).[120] Clearly, developing alternative anode materials with higher stability

and reversibility is a promising approach to increase the cycle life of K-O$_2$ cells; more importantly, it is likely applicable to other metal-oxygen battery systems.

$$\text{Anode:} \left[\langle\rangle\!-\!\langle\rangle\right]^{-} K^{+} \rightleftharpoons \left[\langle\rangle\!-\!\langle\rangle\right] + e^{-} + K^{+} \quad (1)$$

$$\text{Cathode}: O_2 + e^{-} \rightleftharpoons O_2^{-} \quad (2)$$

$$O_2^{-} + K^{+} \rightleftharpoons KO_2 \quad (3)$$

$$KO_2 + e^{-} + K^{+} \rightleftharpoons K_2O_2 \quad (4)$$
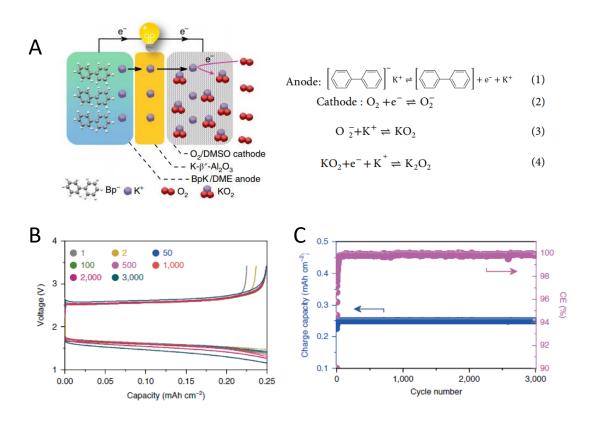
Figure 40. A long-life potassium biphenyl complex-oxygen (BpK-O$_2$) cell. (A) Cell configuration and working principle of BpK-O$_2$ chemistry. (B) Galvanostatic voltage profiles of the BpK-O$_2$ cell at a current density of 4.0 mA cm^{-2} during cycling (C) The corresponding charge capacities (dark blue) and CEs (purple) of the BpK-O$_2$ cell in B. Reproduced with permission from ref [120]. Copyright 2019 Springer Nature.

3.6.3. The magnesium-oxygen battery

Metallic magnesium is an attractive negative-electrode material for battery applications due to its high abundance in the earth's crust, low cost, and better safety in comparison to alkali metals (Li and Na).[312] A magnesium-oxygen battery based on magnesium oxide (MgO) products theoretically delivers a volumetric and a gravimetric energy density of 14 kW h L^{-1} and 3.9 kW h kg^{-1}, respectively. These values are even higher than those of Li-O$_2$ cells (8.0 kW h L^{-1} and 3.4 kW h kg^{-1}). This makes Mg-O$_2$ batteries compelling candidates for large scale and sustainable energy storage devices required for grid integration.

In the past decade, aqueous Mg-O_2 cells were mainly studied as primary batteries owing to the non-rechargeability of the magnesium hydroxide (Mg(OH)$_2$) product.[313] Shiga et al. first reported a secondary Mg-O_2 cell using a DMSO-based electrolyte that operates at elevated temperature (60 °C).[314] The discharge product was assumed to be MgO that is rechargeable in the presence of redox mediators, *e.g.,* iodine (I$_2$) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[314,315] Based on XRD and Raman analysis, Vardar et al. identified that the discharge products were composed of a mixture of crystalline MgO and amorphous magnesium peroxide (MgO$_2$), when a Grignard reagent-based electrolyte was used in a Mg-O_2 cell.[316] They speculated that O_2^- is formed first upon discharge followed by its disproportionation to MgO$_2$ and MgO. After charge, MgO$_2$ is fully oxidized, whereas some MgO remains. The incomplete oxidation of MgO causes low Columbic efficiency and rapid capacity fading. Thus, exploring more effective OER catalysts and redox mediators to oxidize MgO is necessary. Meanwhile, more studies are required to examine the reversibility of Mg-O_2 cells and reveal the underlying chemistry.

3.7. Novel electrolytes and electrodes

3.7.1. The possibilities and development of active metal (Li, Na) protection

As discussed above, various approaches and results have been reported for Li metal stabilization in Li-O_2 batteries. Metal stabilization is required in order to control overall battery performance including stability, lifetime and efficiency of the battery. In contrast to Li-metal and Li-S batteries, the Li-O_2 battery involves reactive oxygen, and more attention needs to be paid to the details. In this chapter, we will discuss the important aspects of Li-metal protection in Li-O_2 batteries and directions for the future.

Li metal deterioration, rather than dendrite formation, is a primary issue in Li-O_2 cells. It results from side reactions with oxygen species, moisture, reaction byproducts, and soluble additives which can crossover from the cathode side. However, most studies have been focused

on the advantage of protective layers to protect the Li metal without consideration of their stability to reactive oxygen species. To verify the importance of the stability of protective layers against parasitic reactions of reactive oxygen species (ROS), Kwak et al. evaluated the chemical stability of different layers and oxygen concentration during recharge in Li-O_2 batteries. It was previously reported that a protective layer containing PVDF or PEO exhibited chemical change and continuous decrease of oxygen. Nevertheless, a composite layer (NCL) based on Nafion - which is known to be stable against oxygen attack – gave effective metal protection without any parasitic reactions by reactive oxygen (O_2^-, $^1O_2$) as shown in Figure 41A. Future studies need to confirm these important results.
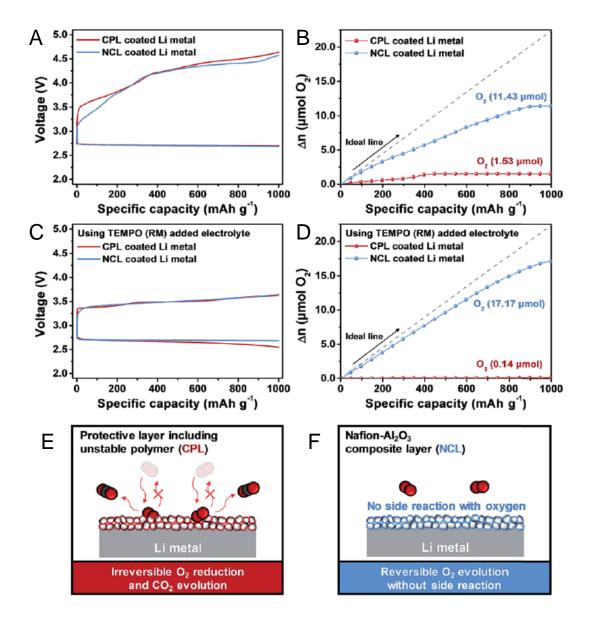
Figure 41. Chemical stability of protective layer on Li metal in Li-O_2 batteries: (A) Galvanostatic voltage profiles and (B) integration of O_2 gas amount for the corresponding charge process. (C) Galvanostatic voltage profiles with redox mediator in the same electrolyte solution and at the same current rate, and (D) integration of the amount of O_2 gas for the corresponding charge process. The red and blue graphs indicate PVdF-based CPL and Nafion-based NCL, respectively. The dashed line in (B), (D) indicates the ideal total amount of O_2 gas. (E, F) schematic illustrations of side reactions on the CPL and the negligible parasitic reaction on the inert NCL, respectively. Reproduced with permission from ref. [317]. Copyright 2019 Royal Society of Chemistry.

Another problem sometimes overlooked in the protection of lithium metal in Li-O_2

batteries is the formation of dendrites. Currently, this problem is not so serious because the

actual capacity value (mAh) and current (mA) are relatively low compared to practical Li-ion batteries, although the specific capacity based on the mass of cathode is high.

In a scale up study[317–319] using large area electrodes and pouch cells (Figure 42A), it was found that the dendritic growth of Li metal was much more pronounced than that of a small sized system based on either coin cells or Swagelok® cells (Figures 42B-E). As the area of the electrode increases, uniform distribution of current is difficult, and dendrite problems become aggravated due to uneven local reactions. This problem leads to an imbalance in Li_2O_2 formation, which greatly reduces the reversibility of the system (Figure 42F).
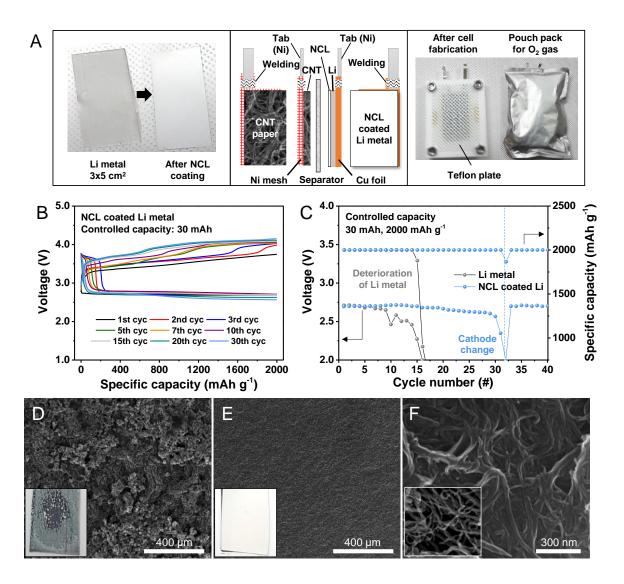
Figure 42. Protective layer for Li metal in large sized Li-O$_2$ cell. (A) Photograph of a Li electrode before and after NCL coating for pouch-type cell fabrication (left), schematic image of the cell configuration of the Li-O$_2$ pouch cell (middle), and a photograph of a Li-O$_2$ pouch cell before and after pouch packing with O$_2$ gas (right). (B) Voltage profiles during the galvanostatic cycling test of a Li-O$_2$ pouch cell using NCL-coated Li metal. (C) Cycling performance (i.e., end voltage of discharge and specific capacity) of Li-O$_2$ pouch cells using Li metal and NCL-coated Li metal as a function of the cycle number. (D–F) SEM images and photographs of (D) Li metal (E) NCL-coated Li metal after the cycling test of Li-O$_2$ pouch cells. (F) SEM image of a CNT paper electrode in a Li-O$_2$ pouch cell using NCL-coated Li metal after the cycling test until cell failure. Reproduced with permission from ref. [317]. Copyright 2019 Royal Society of Chemistry.

As a result, not only must the side reactions of the Li metal surface be considered, but also dendrite growth and volume changes. To make the battery more practical, along with the chemical and physical stability of the protective film, a study of the effect of local current is also required. Future research directions must include scale up through controlling the local current density[320] or using pouch type cells.[317–319]

3.7.2. Solid state Li-air and Na-air batteries

Studies on solid state Li-O$_2$ batteries using solid electrolytes (SE) have been conducted in order to overcome many problems (see below) in Li-O$_2$ batteries which contain electrolytes in organic solvents. In SEs, Li-O$_2$ cells, comprised of ceramic and/or polymeric materials which conduct Li ions, convey Li ions between the carbonaceous oxygen cathode and the lithium metal anode. Dozens of papers have been published in this area over the last decade and several characteristic examples are mentioned below. The use of SEs in these systems have the aim of solving chemical and electrochemical problems of instability, flammability, toxicity and volatility of organic electrolyte solutions. The SE can protect the Li or Na metal anodes and prevent crossover of reactive oxygen reduction products from the cathode to the anode. Using polymeric electrolytes also enables fabrication of flexible batteries[321,322]

The first demonstration of solid-state Li-O$_2$ cells was presented by Kumar et al.[323] Their design was comprised of a ceramic-glass electrolyte (LAGP) placed between polymeric membranes based on polyethylene oxide (PEO) blended with lithium salt. The cells demonstrated stable performance for 40 cycles and excellent thermal stability up to 105 °C.

Research on solid state Li-O$_2$ batteries can be divided into two categories: one direction promotes the use of pure solid state electrolytes and does do not contain any liquid component; in the other, quasi-solid state systems are developed, including mixtures comprised of polymeric matrices (sometimes including ceramic particles) and liquid electrolyte solutions based on organic solvents or ionic liquids. An example of the first category is the work of Wang et al., in which pure solid electrolyte Li-O$_2$ cells utilizing the Li$^+$ conducting materials Li$_{2+2x}$Zn$_{1-x}$GeO$_4$ (LiSICON),[324] Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP), Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) were used. This cell also emphasized the problem of the generally low ionic conductivity of the solid electrolytes, which results in low rate capability. In addition, there are severe interfacial contact failure problems between the electrodes and the solid electrolytes during the cycling of these cells.[325] A possible solution to problems of contact between solid electrolytes and cathodes could be their integration into a single solid mixture, as suggested by Zhu et al.[326]

An important use of solid electrolytes in Li-O$_2$ cells is in developing protected Li anodes. Once the Li metal anodes are protected by artificial pre-designed solid electrolyte interphases, the reactivity problems related to the negative electrodes can be fully alleviated.[327,328]

Another approach in design and elaboration of solid state Li-O$_2$ or Na-O$_2$ cells is the use of polymeric electrolyte membranes that separate the anode and cathode in the cells. [329,330]These systems may be fully polymeric or quasi-solid, gel-type, comprising polymeric matrices and electrolyte solution included therein. [330–332]

It is worth mentioning the pioneering work of Peled et al. which was a first step in developing solid Na-O$_2$ battery systems; namely polymeric matrices containing NaClO$_4$, and a carbonaceous oxygen cathode.[333] Peled's preliminary Na-O$_2$ cells were operated at 105 °C which is above the sodium melting point of 97.8 °C. The liquid sodium metal cells demonstrated 100 cycles with limited normalized capacity. That work was a first attempt in the direction of using sodium anodes in a solid state configuration.

Using quasi-solid polymeric matrices as the electrolytes in Li-O$_2$ or Na-O$_2$ cells reflects a compromise. These matrices are less reactive with the electrodes and the oxygen reduction products than the liquid electrolytes. Using such cells at elevated temperatures enable achievement of reasonable rate capabilities. Hence, one may be able to obtain longer cycle-life compared to Li-O$_2$ cells with liquid electrolytes solutions. However, their use does not fully mitigate side reactions and there are obviously contact problems that impede fully uniform current distribution in these cells.

An interesting use of polymeric membranes as in Li-O$_2$ cells was demonstrated by Wu et al. who fabricated and tested Li-O$_2$ cells containing a super-hydrophobic quasi-solid electrolyte incorporating poly-isobutylene, silicon dioxide treated with di-methyl-dichlorosilane, and ionic liquids.[334] The main advantages of these cells included a flexible configuration, good protection of the Li metal anodes and blockage of detrimental flux of oxygen reduction products from the cathode to the anode. An important advantage in the use of such combinations is the possibility of solving the contact problems, from which most types of SE based Li(Na)-O$_2$ cells suffer. At first glance, while solving some instability problems, the complexity of solid state Li/Na-O$_2$ batteries may set aside many possible advantages of such systems, regarding energy density and rate. A great advantage of this system may be the ability to use ambient air as the feed gas, instead of pure oxygen. Since a solid electrolyte at elevated temperatures is used in this case, the presence of water and CO$_2$ contaminations in air

may be much less detrimental for basic Li-O$_2$ cell operation as compared to Li-O$_2$ cells based on liquid electrolyte solutions. Work in this direction continues.

3.7.3. On the use of ionic liquids and molten salts

Ionic liquids (ILs), also known as room temperature molten salts, possess negligible volatility, a wider electrochemical window, and lower flammability than conventional organic solvents.[335] Kuboki et al. first used imidazolium-based electrolytes for primary Li-air cells.[336] The hydrophobic ILs with zero vapor pressure avoid the evaporation of electrolyte and the hydrolysis of lithium anode in moist air. These make ILs excellent solvents for the lithium-air batteries operated under ambient conditions. Subsequently, a variety of IL-based electrolytes (*e.g.,* pyrrolidium and ammonium-based electrolytes) were developed for secondary Li-O$_2$ cells.[337] Nevertheless, the chemical stability of ILs is still under debate. Based on rotating ring-disk electrode (RRDE) studies, Herranz et al. found that the pseudo-first-order reaction constant of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr$_{14}$TFSI) with O$_2^-$ is at least three orders of magnitude lower than that of propylene carbonate (PC).[338] By contrast, Piana et al., through DEMS and NMR studies, concluded that Pyr$_{14}$TFSI does not have sufficient long-term stability against superoxide attack.[339] Katayama et al. also reported the instability of imidazolium-based IL electrolytes based on cyclic voltammetry measurements.[340] In addition, the viscosities of ILs are usually one magnitude higher than those of conventional organic solvents. They lower the ionic conductivity of electrolyte and decrease the diffusion coefficient of oxygen/superoxide, which results in a low discharge capacity and poor rate capability.[341] Therefore, more efforts are needed to explore novel ILs with higher stability and lower viscosity.

Inorganic molten salts (*e.g.,* molten nitrate eutectic) typically melt above 100 °C and thereby allow Li-O$_2$ cells to operate at higher temperatures. The first molten salt Li-O$_2$ cell was reported by Giordani et al. using the LiNO$_3$-KNO$_3$ eutectic.[343] The cell shows a very low

overpotential of 50 mV and an improved rate capacity at 150 °C due to the reversible transfer of the Li_2O_2 product in the molten nitrate electrolyte. Based on *in situ* pressure and gas analyses, they found that $Li-O_2$ chemistry is reversible in this medium, which reflects on the high stability of the inorganic electrolyte. Recently, Xia et al. reported on a $Li-O_2$ cell using a molten nitrate electrolyte and solid ceramic membrane that reversibly forms and oxidizes Li_2O in a stepwise four-electron redox process (Figures 43A-C).[342] As shown in Figure 43D, the cell exhibits stable cycling performance for 150 cycles with a very low polarization of 0.2 V and a high Coulombic efficiency close to 100%. By tuning the operating temperature and using a bifunctional lithiated nickel oxide catalyst, this $Li-O_2$ battery overcomes the barriers of thermodynamics and kinetics, leading to the electrochemically reversible formation of octahedral lithium oxide (Li_2O) crystals instead of hexagonally-shaped Li_2O_2 crystals that are formed on carbon cathodes (Figures 43E and F). The use of chemically stable inorganic electrolytes, and a non-carbonaceous cathode circumvents the degradation of organic electrolyte and carbon corrosion, which are the main failure mechanisms for nonaqueous $Li-O_2$ cells. It demonstrates that $Li-O_2$ electrochemistry is not intrinsically limited, once problems of electrolyte, superoxide, and cathode host are overcome. However, since this system must be driven at very high temperatures about 150~180 °C, suitable materials and components that can withstand high temperature are needed, which makes the experiment and research difficult. Furthermore, since this is an early stage of research, the number of documents is relatively small low compared to conventional room temperature $Li-O_2$ batteries. Therefore, future study to verify the reliability and improve previous work is required.
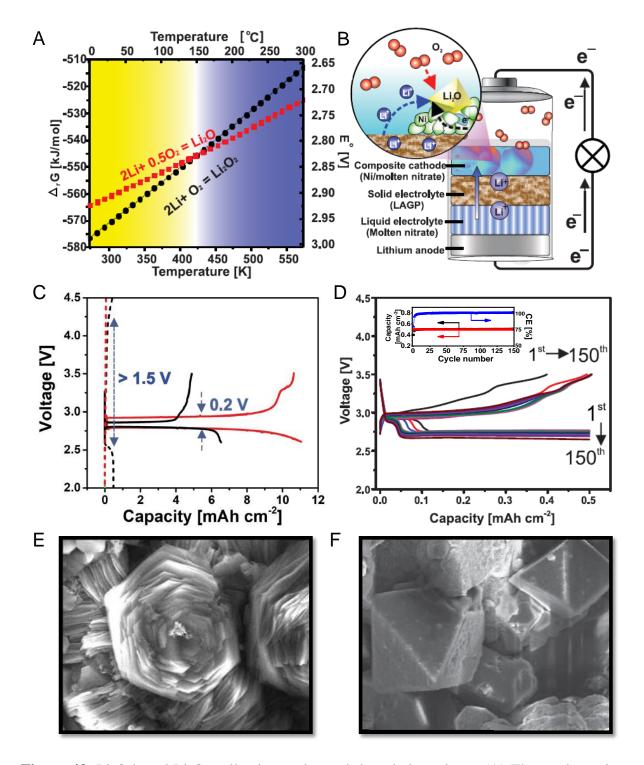
Figure 43. Li$_2$O based Li-O$_2$ cell using molten salt-based electrolytes. (A) Thermodynamics and configuration of the Li-O$_2$ cell. (A) Gibbs reaction energy for formation of Li$_2$O and Li$_2$O$_2$ as a function of temperature. (B) Configuration of the inorganic electrolyte Li-O$_2$ cell and schematic illustration of Li$_2$O formation during discharge. (C) Voltage profiles of Li-O$_2$ cells with a carbon cathode (black) and a Ni-based cathode (red) using aprotic electrolyte, 0.5 M LiTFSI in TEGDME, were examined at 25°C (dashed lines), whereas the cells using the molten nitrate electrolyte were measured at 150°C (solid lines). (D) Cycling performance of a molten nitrate Li-O$_2$ cell with a lithiated-nickel oxide catalyst at 150°C. SEM images of the discharged cathodes using molten nitrate electrolyte and carbon cathode(E), and molten nitrate electrolyte

and lithiated-nickel oxide catalyst(F), respectively. Reproduced with permission from ref. [342]. Copyright 2018 The American Association for the Advancement of Science.

3.7.4. On the possible use of solid Li-oxide cathodes and the connection to lithiated transition metals

Intensive studies have been carried out on high capacity cathodes for Li ion batteries with the formulae $Li_{1+x}Mn_yCo_zNi_{1-x-y-z}O_2$ (x>0, y > 0.5), known as Li and Mn rich NMC cathodes. These studies revealed that their redox mechanisms, leading to a very high specific capacity (approaching 300 mAh g^{-1}), involve electrochemical activity of oxygen species. The synthesis of these materials that includes high temperature calcination stages, naturally forms a mixture of integrated phases: an electrochemically inactive monoclinic phase, Li_2MnO_3, and an active rhombohedral phase with the general stoichiometry $LiMn_xCo_yNi_zO_2$. When electrodes comprising, these materials are polarized to high enough potentials (e.g. 4.8 V vs. Li), a complex activation process takes place which affects the structure of the monoclinic phase, de-lithiates the entire cathode material, and makes it fully electrochemically reversible (Figure 44). Traditional thinking attributed the activation process and the subsequent further behavior of these systems to changes in the oxidation state of the transition metal cations and related structural re-arrangements. However, recent studies, starting with the pioneering work of Sathiya et al.,[344] discovered that the activation process of these materials involves oxidation of the oxide anions to oxygen moieties with a higher oxidation state at a potential > 4.6V vs. Li. Upon repeated cycling, the process is reversible and the oxidized oxygen moieties are reduced back to oxides at around 3 V. This involvement of oxygen electrochemistry, in fact enables the high specific capacity of these cathode materials, that may reach the highest limit relevant for Li insertion cathodes with the general formula $Li_{1+x}M_{1-x}O_2$ (300 mAh g^{-1}). Thackeray et al. reported similar study for an approach to exploiting Li-O_2 electrochemistry using particularly iron oxides (Li–F–O) which can react with lithium and oxygen to produce compounds that contain a Li_2O component for hybrid Li-ion/O_2 batteries.[345]

However, the process of activation and reversible operation, capacity fading mechanisms and average voltage fading mechanisms - are not fully clear yet. It appears that oxidation of the oxide moieties may lead to irreversible evolution of molecular singlet oxygen which is detrimental. Also, due to their partial oxidation, upon charging, the resulting nucleophilic oxygen moieties are highly reactive with the electrophilic alkyl carbonate solvents. Thereby, effective surface protection of these materials by coatings (to avoid oxygen release and detrimental contact with solution species) is mandatory for their stable reversible cycling. Figure 44 summarizes several important experimental aspects related to these cathodes. Intensive work is being currently carried out on these materials (references 355–364 are typical examples out of hundreds of publications that have appeared in recent years).
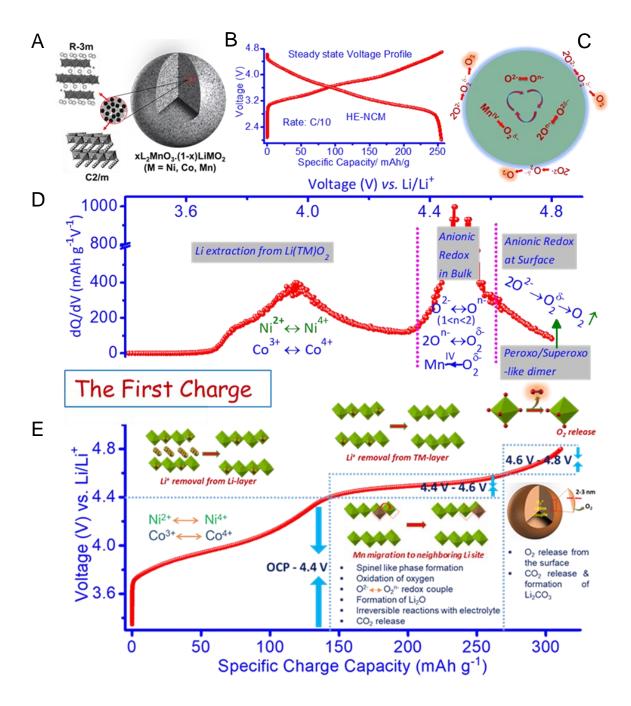
Figure 44. Li and Mn-rich cathode materials: schematically describing (A) structure, (B) steady state voltage profiles, (C) anionic oxygen redox activity in the bulk and on the surface and (D, E) the first charge dQ/dV vs. V and voltage profile demonstrating Li extraction, cationic & anionic redox activity.[346–364]

3.8. Studies with consideration of practical metal-air batteries

3.8.1. Li Batteries with lithium oxygen compound cathodes (and closed systems)

One of the ways to overcome the challenge of operating in air (which requires reduction in CO_2 and H_2O levels from the incoming gas stream) is to have a closed $Li-O_2$ system, where the oxygen is already stored in the battery. One approach is to store O_2 in a tank, while this adds weight and volume, it is offset, to a greater or lesser extent, by obviating the need for gas scrubbers. An alternative approach is to incorporate the oxygen in the solid state, e.g to make the cell in the discharged state incorporating Li_2O_2 powder in a conductive carbon matrix to form a composite cathode. Early studies used this cathode preparation method to investigate the OER mechanism in a more controlled manner. The first composite cathode was described by Ogasawara et al. where ball-milling was used to mix commercial Li_2O_2 with high surface carbon and PTFE binder[83]. It was demonstrated that the Li_2O_2 can be completely oxidized at high enough potentials. In a later study, Meini et al. reported that commercial Li_2O_2 contains 5% of impurities such as LiOH and Li_2CO_3.[365] They explained that these impurities can influence the OER process and can introduce undesirable side-products. As mentioned above, several studies have described the chemical and electrochemical differences between crystalline and amorphous Li_2O_2 phases.[102,103] We note that these studies did not investigate the cyclability of these types of preloaded Li_2O_2 cathodes.

Bhargav et al. attempted to cycle a closed $Li-O_2$ battery comprised of a composite cathode prepared from commercial Li_2O_2 and nano-graphite to form a composite cathode.[366] The first discharge process showed a high specific capacity of more than 1000 mAh g^{-1}. However, after four cycles, the discharge capacity dropped by more than 50%. The capacity fading was attributed to the purity and size of the Li_2O_2 particles and their dispersion in the carbon matrix. The same group observed improvement in the battery cycle life when the cathode was made from highly pure synthesized nanocrystalline Li_2O_2 particles that were

embedded in carbon nanofibers.[367] The influence of the Li_2O_2 loading in the carbon cathode

can also be a limiting factor in maximizing the energy density of the cathode. Luo et al. showed

that the impedance of the preloaded cathodes increased with more insulating Li_2O_2. They

concluded that 20 wt. % Li_2O_2 in the carbon black matrix delivered the highest energy

efficiency. The crossover of oxygen evolved from Li_2O_2 particles to the lithium anode can

result in different decomposition reactions which can degrade the Li-O_2 performance.[64,368]

In a recent study, Zhu et al. proposed a new alternative closed Li-O_2 system where a

cathode made of Co_3O_4 nanoporous matrix is filled with nanolithia (Li_2O).[369] In this type of

cell, the cathode cycles between the discharged Li_2O and the Li_2O_2/LiO_2 formed during the

charge process. The authors proposed that the large OER overpotential observed in standard

Li-O_2 cells is due to the phase transition between the solid products (Li_2O_2) and the evolving

O_2 gas which lead to a severe kinetic bottleneck. Unlike a standard Li-O_2 cell, the proposed

lithia based system is based on redox chemistry in the condensed state. As can be seen from

the cyclic voltammogram in Figure 45, the difference in voltage between the reduction and

oxidation peaks is only 0.24 V. As seen from Figure 45, a cell comprised of a lthia cathode and

lithium metal anode exhibited 200 cycles at around 600 Ah kg^{-1} capacity with low capacity

loss.
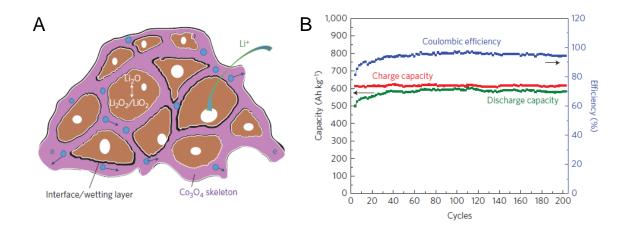
Figure 45. Cyclic voltammogram of nanolithia cathode between 2.35 and 3.0 V with a scan rate of 0.05 mV (b) Cycling performance and coulombic efficiency of nanolithia cathode vs. Li metal anode. Reproduced with permission from ref.[369]. Copyright 2016 Springer Nature.

3.8.2. Challenges of capacity and kinetics

The use of redox mediators has overcome many of the challenges introduced by the intrinsic oxygen electrochemistry, especially the otherwise limited rate and capacity of Li-O_2 cells when operated in low DN solvents such as ethers, as described above in section 3.5b. However, oxygen redox limitations are only one aspect of the problem. Lithium peroxide preferentially forms at the air interface of the cathode and blocks the electrode pores (Figure 46A).[208] The bulk of the cathode volume remains relatively free of discharge product which is detrimental to capacity. Simulated discharge curves by Liu shows that oxygen depletion and pore clogging is mainly responsible for limited capacity and cell death.[370] Figure 46 presents this schematically, showing the O_2 concentration through the cathode at high and low rates. It indicates that the O_2 availability is limited to the air interface and much of the cathode is starved and inactive. Gittleson et al. explored the effect of O_2 and Li^+ transport in different solvents and concluded that low oxygen solubility and pore blocking at the air interface were now the major factors limiting capacity and inducing cell death.[371]
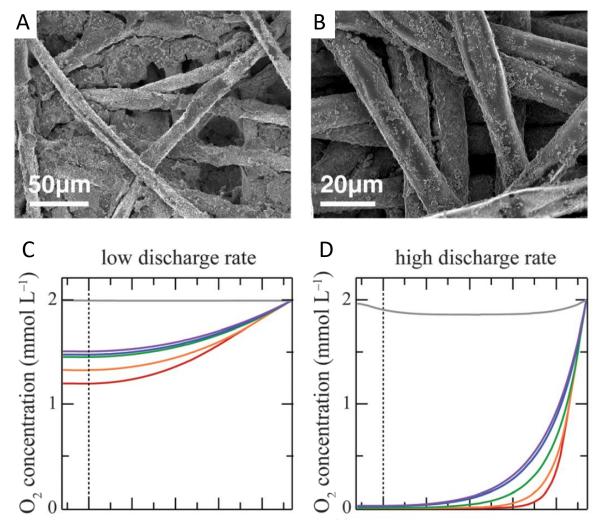
Figure 46. SEM images of a dual mediator cathode at (A) the O_2 interface and (B) the separator interface. Reproduced with permission from ref.[208]. Copyright 2017 Springer Nature. (C,D) Plots of O_2 concentration distribution in the electrolyte of the cathode at six depths of discharge. Reproduced with permission from ref. [370]. Copyright 2016 Royal Society of Chemistry.

These results highlight the need for methods to enhance O_2 mass transport in the lithium-air battery. It is unlikely that strategies can be directly translated from the aqueous fuel cell as the solvents share little common chemistry. In addition, operation of the two systems differ considerably. The product of the aqueous fuel cell is the solvent, while the Li-air battery forms a new solid phase (lithium peroxide). New engineering and chemical methods for oxygen delivery are required for the lithium-air battery. One such example of a chemical solution to this problem is the use of the perfluorocarbons (PFC), which increase oxygen solubility and mass-transport. PFC additives can be classified as miscible[372,373,374] and immiscible.[375,376]

Nishikami et al. showed that BrC_6F_{13} forms a miscible solution with TEGDME up to 60 wt% improving the discharge capacity by 50%,[374] although at the expense of electrolyte conductivity. Contentiously, Wijaya et al. suggested that the enhancement observed with miscible PFCs is due to parasitic currents from PFC attack by superoxide.[377] Immiscible PFCs have been proposed to avoid this problem and introduce three phase regions into the cathode where the PFC acts as oxygen channels.[377] This method doubled the discharge capacity at low current densities but had a negative impact on capacity at higher rates. The authors proposed that this was due to greater pore blocking. Enhancement is also seen when immiscible PFCs are introduced to a dual mediator cell.[376]

3.8.3. On the validity of energy density calculation of Li (Na)-oxygen batteries

The exceptional theoretical specific energy of the Li-air cell led many people to rush to the conclusion that this would translate into practical specific energies and energy densities many times that of Li-ion. Such confusion is often compounded by reports that use only the carbon mass to normalize the capacity. By analysing current reported protocols for $Li-O_2$ cells evaluation in the literature, Noked et al. demonstrated that many of the reports fall short in specifying the exact cell composition and cycling conditions.[61] When trying to clarify the practical potential of the Li-air battery system, we need to keep two major aspects in mind: (1) careful examination of reported values in the literature, (2) what can we expect as performance from a Li-air battery - even if we solve all the stability and kinetic limitation issues of these systems. Of course, Li-ion batteries are not immune from this problem, for example the often quoted capacity of Si, 3579 $mAhg_{Si}^{-1}$ (8334 mAh cm_{Si}^{-3}), is misleading as it ignores the Li in Li3.75Si, and the need for volume expansion is also often ignored. The true figures are 1857 $mAhg^{-1}$ and 2290 $mAhcm^{-3}$ with respect to the lithiated phase. The Li-air battery is very different from Li-ion, most notably the former requires a balance of plant associated with gas

handling, and the need to reduce the CO_2 and H_2O content in the gas stream. These uncertainties led some researchers to question whether even if the problems of Li-air can be solved, it would outperform Li-ion and Li-S. The first rigorous attempt to truly compare Li-ion, Li-S and Li-air batteries (as opposed to cells), was made by Gallagher et al in 2014.[53] They modified the Argonne Batpac modelling software to permit prediction of the specific energy and energy density of a practical Li-air battery, including the air handling/balance of plant. They concluded that while Li-air was shown to have a higher specific energy compared with Li-ion and Li-S, this would not be the case volumetrically compared with a cell containing a Li metal anode and a Li rich NMC cathode. However, as detailed in this review, our understanding of the Li –air battery has been transformed over the last 6 years and the introduction of redox mediators and recognition that significant quantities of H_2O can be tolerate, alleviating the need to complex, heavy and bulky air handling, changes the assumptions required to model performance. Taking account of recent advances including the use of redox mediators, reduced balance of plant overhead, and a protected Li anode, which reduces the need for a large excess of Li, we predict the specific energy and the energy density of a full Li-air battery, including the balance of plant, to be 610 $Whkg^{-1}$ and 680 WhL^{-1} respectively, compared with 450 for each in the case of Li-S and 300 Wh kg^{-1} and 500 Wh L^{-1} for a Li anode and Li rich NMC. Larger energy batteries increase this difference as the mass fraction associated with the balance of plant diminishes relative to the pack and conversely, Li-air is not competitive for small batteries such as consumer electronics. The major advantage of Li-air is in specific energy. As a result, it might prove particularly useful for challenges such as aviation where, mass and specific energies beyond what Li-ion can deliver are essential.

In summary, the gap between the very high theoretical energy density of Li-air batteries - and practical expectations is very wide, reducing the advantage of Li-air over other Li batteries, however Li-air is still predicted to offer performance beyond the other battery

technologies, especially in terms of mass, and this is based on full cell analysis and operation in air. As a result, while Li-air is still some way from a technology, the advances indicate that work on these systems should be further promoted as discussed in the conclusion section.

3.8.4. From oxygen to air

The lithium-air battery must operate in air if it is to reach its maximum performance. Most lab scale cells operate using pure oxygen, but a scaled practical battery pack using pure O_2 would offer significantly lower specific energy compared to an open battery.[53] Moving to an atmospheric gas introduces a number of challenges, but surprisingly also brings some benefits. Lowering the O_2 partial pressure has been shown to impact capacity.[378] As discussed above, as yet unimagined strategies are needed for oxygen delivery which may help to eliminate this problem. Atmospheric nitrogen will not be compatible with the lithium metal anode, but it is generally accepted that lithium will have to be protected with an artificial SEI or ceramic interphase in any case.

Contrary to established thinking, a series of papers from Meini, Schwenke and Aetukuri showed that H_2O can be an advantageous additive in lithium-air electrolytes, by increasing capacity and lowering the charge overpotential.[94,96,97] Later this was convincingly shown in work by Qiao et al. (Figure 47) where increasing the H_2O content from 0 to 30% results in increasing discharge capacity, and lowers the charge potential to below 3.5 V.[379] SEM analyses shows that the lithium peroxide particle size increases with increasing H_2O content and X-ray diffraction confirms formation of lithium peroxide. We note however that LiOH has been observed at higher H_2O concentrations.[96] The large particles and enhanced capacity confirm discharge by a solution route and two theories have been proposed to explain this. Aetukuri et al. suggest that the acceptor number of the H_2O additive results in enhanced solvation of superoxide.[94] Schwenke et al. proposed that protonation of lithium peroxide by water results in soluble peroxide.[96] Both mechanisms effectively enable formation of a soluble product able to

nucleate large particles and avoid electrode surface passivation. H_2O is also beneficial for performance when using Quinone based discharge mediators and more than doubles the discharge capacity.[380] It is proposed that this is due to stabilization of the reduced Quinone and quinone-O_2 complex by H_2O, which effectively increases diffusion lengths and supports peroxide filling of the cathode structure. Finally, in the presence of an LiI catalyst, H_2O can promote formation of LiOH in a 4e⁻ reduction step.[100,381] Decomposition due to H_2O is an area that needs further consideration.
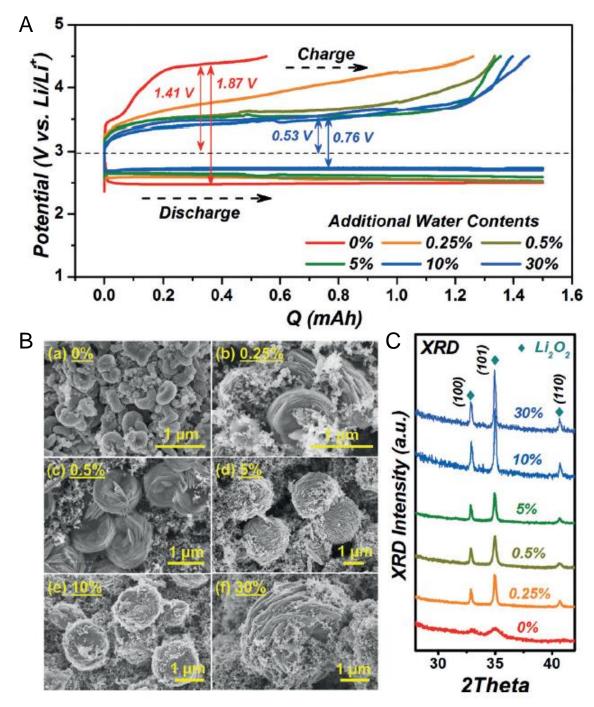
Figure 47. Discharge profiles of lithium-O_2 cells with varying H_2O content and SEM images and XRD patterns of the discharge cathodes. Reproduced with permission from ref [379]. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

In contrast to H_2O, CO_2 may be detrimental to the performance of the lithium-air battery. Thermodynamically the reaction between lithium peroxide and carbon dioxide to form lithium carbonate is favourable.[63] Early work in this area by Takechi et al. showed that

introduction of CO_2 into the lithium-air battery results in the formation of lithium carbonate, and proposed that this occurred via formation of a peroxydicarbonate ion ($C_2O_6^{2-}$).[382]
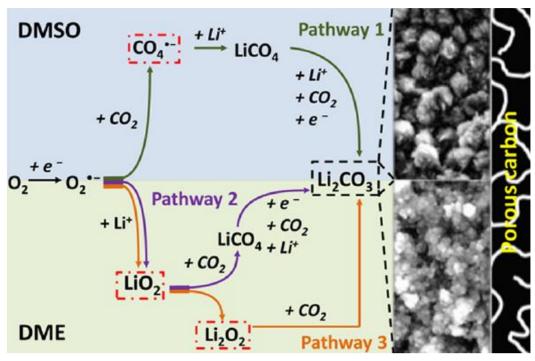
Figure 48. Reaction routes for the most likely paths in Li-O_2/CO_2 battery. Reproduced with permission from ref [383]. Copyright 2016 American Chemical Society.

Unfortunately, these studies used carbonate-based electrolytes which are now known to be unstable and decompose to Li_2CO_3 and CO_2.[63] Gowda et al. performed similar studies but using a more stable DME-based electrolyte, which also clearly demonstrated the formation of Li_2CO_3.[384] Yin et al. proposed a holistic reactions mechanism for Li-O_2/CO_2 in these Li-active gas batteries, Figure 48.[383] Three possible pathways are described that can be summarized as reaction of CO_2 with either O_2^-, LiO_2 or Li_2O_2. Theoretical and experimental studies by Lim et al. imply that the solvent can influence the reaction of superoxide with CO_2. The reaction of CO_2 with Li_2O_2 suggests that the formation of Li_2CO_3 in lithium-air batteries is inevitable and that CO_2 must be removed from the oxygen feed gas. However, Liu et al. has demonstrated the use of redox mediators to remove accumulated Li_2CO_3 in the lithium-air battery.[385] Recently

there has also been interest in harnessing the Li-O_2/CO_2 reaction, either as a higher performance battery or as a means of CO_2 capture.[386,387,388,382]
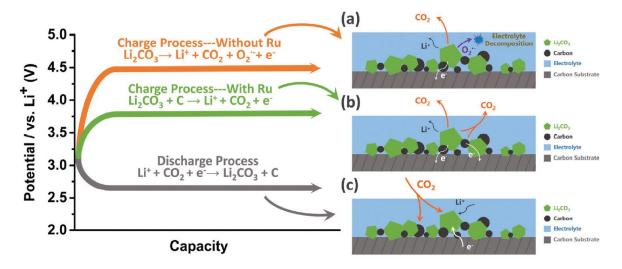
Figure 49. Proposed reaction routes for Li-CO_2 batteries without O_2. Reproduced with permission from ref[389]. Copyright 2017 Royal Society of Chemistry.

These studies have enabled the expansion of this research field to the study of new batteries using pure CO_2 gas as the cathode's active material, having Li_2CO_3 as the main discharge product. This new system can be denoted as a Li-CO_2 battery (Figure 49). However, several research groups have cast doubts on their technological viability because batteries which use pure CO_2 gas exhibit low discharge capacity as compared to batteries that use a mixture of O_2/CO_2 as the cathode active mass. Therefore, there is a serious debate about possible mechanisms that can enable effective electrochemical reduction of CO_2 in Li-CO_2 batteries without the presence/involvement of O_2.[173]

It is important to note that the study of Li-O_2/CO_2 batteries and Li-CO_2 batteries is rather new. As a result, there are no established mechanisms that explain how these systems can work reversibly. There are controversial opinions whether the reduction of pure CO_2 is possible during discharge and which mechanism is reliable for this system. It seems that possible reaction mechanisms for such systems can be determined only by the use of *in-situ* spectro-electrochemical techniques.

3.8.5. Configuration of Li-air cells and the balance of plant

The lithium-air field has rightly focused on advancing the basic science and understanding of battery chemistry. Impractical coin and Swagelok cells account for the bulk of the studies. Thus, an established cell, pack and system design has yet to emerge. Due to the pace of advancement in the field over the past 5 years, this is perhaps not unfortunate as designs would quickly become obsolete. For example, a lithium-air system designed today would benefit from the development of redox mediators and an increased tolerance to H_2O. The excellent system model by Gallagher et al. provides the most robust design of a full lithium-air battery, which considers the complete system including the pack design and the balance of plant.[53] Figure 50 shows the proposed layer structure for a practical lithium-air cell.[53] The layer consists of a lithium anode on copper foil protected from the cathode by a ceramic electrolyte. Excess lithium must be minimized to achieve the highest performance. The cathode consists of a porous carbon and would house 60 vol% of lithium peroxide. Use of a thick cathode is essential to minimizing excessive current collector mass. An aluminum foil flow field is used for oxygen delivery.
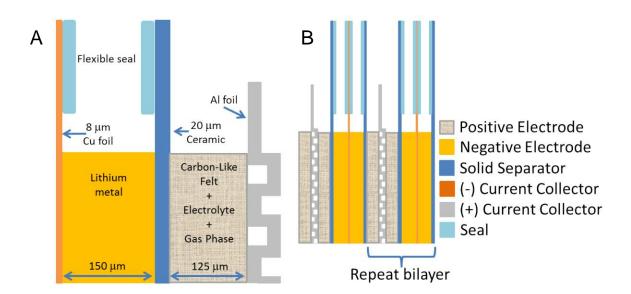
Figure 50. A schematic of a (A) single layer and (B) multiple layers of a lithium-air cell. Reproduced with permission from ref[53]. Copyright 2014 Royal Society of Chemistry.

An alternative cell design (Figure 51) has been proposed by Samsung, which employed a folded cell architecture that minimizes inactive component volume and mass.[319] Here the carbon cathode fulfils the additional roles of oxygen flow field and current collector. Performance of 1214 Wh kg$^{-1}_{cell}$ and 896 Wh L$^{-1}_{cell}$ at the cell level is demonstrated, which exceeds that of Gallagher's cell model (Figure 51), although like-for-like comparisons between cell designs are not trivial.[53]
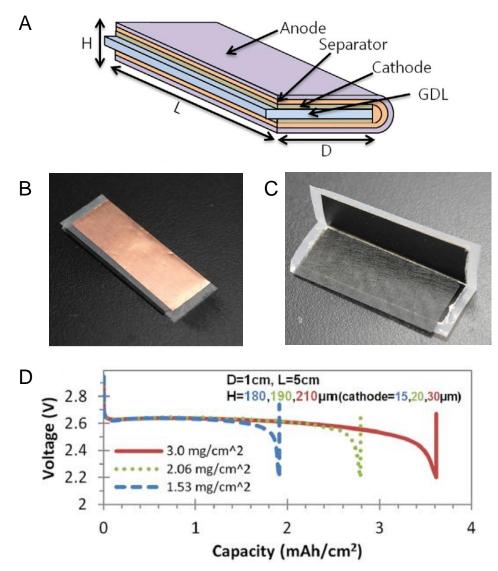
Figure 51. (A) A schematic, (B,C) images and (D) discharge curves of a single folded cell. Reproduced with permission from ref[319]. Copyright 2019 Elsevier.

Repeated bilayers would form a module, typically based on a bipolar plate design similar to those used in a fuel cell,[390] The system model by Gallagher proposes a doubling of the mass and volume from cell to pack (Figure 52). This includes consideration of thermal management and oxygen delivery. If the battery is to operate in air, then a balance of plant (BoP) will be needed to deliver a suitable oxygen and manage solvent volatility. The system prosed by Gallagher consists of a compressor, pressure swing adsorption unit and a solvent addition and capture unit.[53] The BoP adds an additional 70 kg to the overall system mass and has a significant impact on overall performance. Based on this overall design, and included resent advances, a favorable lithium-air system level performance of 610 Wh kg^{-1}_{system} is predicted versus 300 Wh kg^{-1}_{system} for a lithium metal/Li-rich NMC system. For example, the model assumes electrochemical performance based on a lithium-air cell without mediators.[391] The balance of plant is designed to achieve ppm levels of H_2O in the gas stream, but it is likely that this is not necessary and H_2O may improve performance. Of course, H_2O is detrimental to Li anode and the origin of parasitic formation of LiOH, which may shorten the cycle life Li-O_2 batteries. Therefore, H_2O content should be considered carefully during system design and cell fabrication.
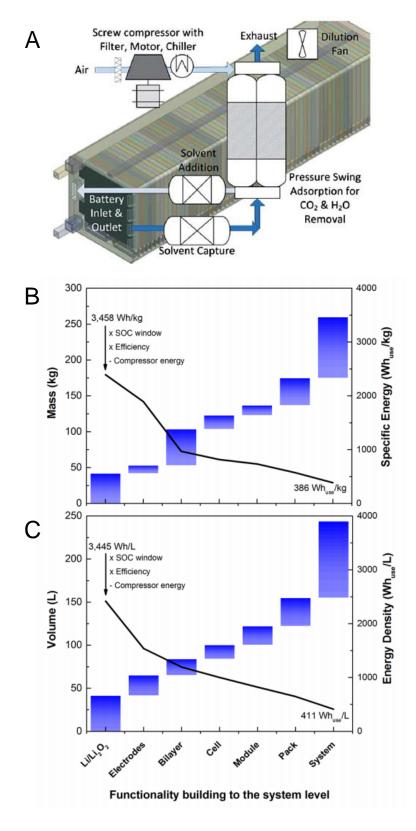
Figure 52. A proposed lithium-air system showing: (A) the components required to the balance of plant needed to operate under atmospheric gas and plots showing the (B) mass and (C) volume breakdown of the open lithium-air system (100 kWh and 80 kW) together with the specific and volumetric energies. Reproduced with permission from ref[53]. Copyright 2014 Royal Society of Chemistry.

Further improvements may be achieved in the pressure swing adoption units by development of efficient selective gas scrubbers that are able to remove only CO_2 or fractional amounts of H_2O, e.g. metal-organic frameworks and amine based compounds.[392,393,394] In addition, selective membranes have been proposed as methods of eliminating atmospheric impurities.[395] Lower vapor pressure solvents such as TEGDME will help minimize the mass penalty imposed by solvent capture units, which is based on DMSO in current models.[396,397] Perhaps most importantly, current models are designed for automotive applications, but varying the energy versus power needs can significantly lower the relative contribution of the parasitic BoP overhead and increase performance. System models must be continuously developed and updated to help direct research, identify challenges and opportunities, track progress and evaluate advancement.

4. FUTURE PERSPECTIVE

A number of the significant advances made in the last five years in understanding the science of the rechargeable aprotic lithium-air battery have been reviewed here. It is important to understand that O_2 reduction to Li_2O_2 on discharge, and the reverse on charge, does not have to occur on the electrode surface, as previously thought, leading to low rates and capacities. Rather, it can occur in solution - avoiding electrode passivation and yielding significantly higher rates and capacities. This realization can begin to change the prospect for the lithium-air battery. Redox mediators can enable solution mediated O_2/Li_2O_2 to occur in more stable, low polarity solvents such as ethers. The rates and capacities in these solvents are several mA cm^{-2} and mAh cm^{-2}, while also significantly reducing the overpotential on discharge and charge will further advance the prospects of a lithium-air technology.

Although cells may be cycled 100 times with minimal capacity loss, this does not mean that all the challenges of lithium-air have been met. Stability of the electrolyte solution is one of the main problems that must be addressed, as discussed above. However, the recent

recognition that singlet oxygen ($^1O_2$) is formed during oxidation of Li_2O_2 during charge as well as during its formation on discharge, and that this reactive species appears to be the main culprit in electrolyte degradation provides the new understanding necessary to mitigate instability. Oxidation mediators offer the opportunity to change mechanisms that form $^1O_2$, which would suppress electrolyte degradation.

In addition, it has been shown that mediators enhance the stability of carbon electrodes making them viable despite critical instability with O_2 electrochemistry directly taking place on their surface. Focus on oxidation mediators is therefore a key challenge for future research. The use of redox mediators to facilitate the O_2/Li_2O_2 reaction has largely addressed the limitations of the intrinsic electrochemistry at the cathode. The rate and capacity are now limited by the mass transport of O_2 and the pore space. In the flooded porous electrode this relies on the dissolution of O_2 at the gas interface, and then its diffusion throughout the electrode. As for fuel cells, a true gas diffusion electrode is required. This is because O_2 transport occurs in the gas phase entering the electrolyte solution such that it only has to defuse short distances to the reduction mediator in order to be converted to Li_2O_2. We cannot utilize the approach of aqueous fuel cells, which relies on hydrophobic gas channels and hydrophilic pores for the electrolyte.

New approaches and designs of electrode architecture are needed that will facilitate mass transport in aprotic Li-air cells. The design of porous gas diffusion cathodes would enable a further step change towards the realization of our Li-O_2 cell; however, alone these do not address the problem of operating in air. As discussed in the review, it is now understood that significant quantities of H_2O can be tolerated in ether-based solvents, while preserving the two-electron reduction of O_2 to Li_2O_2; indeed, some water can be advantageous. The ability to operate with a gas stream which does not have to be rigorously dried, potentially operating up tO2 g_{H2O}/m^3, makes operation in air much more viable than was thought previously. The

extensive work on CO_2 removal by, for example, porous metal organic framework solids (MOFs), driven by interest in other fields, provides potential routes to the removal of sufficient CO_2 from the gas stream.

It is important to develop further approaches to the balance of plant especially related to air handling. Much of the focus has been on the challenges associated with the reaction at the cathode. To realize the full potential of the Li-air battery it is necessary to develop a protected lithium metal anode, which avoids reactivity with O_2 and with redox mediators. While specific attention will be critical to understand the solid electrolyte/liquid electrolyte interface of a protected anode in the lithium-air battery, the anode itself is being pursued intensively because of its potential application in other lithium battery technologies. Therefore, this challenge is not specific to Li-air.

There is a well-established path to disruptive technologies. It starts with recognition that the technology would, if realized, provide a step change in performance or cost reduction or both. This drives a "gold rush" to commercialization that almost inevitably fails as the underpinning science is unknown. The attempts to commercialize do uncover the barriers facing the technology. Concentrated effort follows on the basic science, which provides the knowledge that is essential to either overcome the barriers or demonstrate that the barriers are insurmountable. Lithium-air is on this journey.

5. CONCLUSION

Research and development of Li-air batteries is one of the most exciting and interesting fields of modern electrochemistry, with its emphasis on power sources, energy and materials science. These systems possess the highest theoretical energy density, promising cost effectiveness and the chance to rival internal combustion engines by clean and elegant electrochemical power sources. Over the last decade, intensive work has been invested into these systems by many of the most prominent research groups worldwide. Despite these

impressive efforts, more work is required even to reach various go/no-go decisions. This is due to the highly complex nature of Li-O_2 cells (even before dealing with ambient air as the cathode feed).

While the intensive R&D efforts related to these systems have yet to reach practical goals, the electrochemistry, energy and materials science communities have gained a lot from the prolific research work carried out during recent years. The benefits and spinoffs from these studies include highly innovative contributions to electro-catalysis, active metals electrochemistry, oxygen chemistry, non-aqueous electrochemistry and solution chemistry - as we describe in this review article. The scope of this paper has included several important related analogous systems: various active metal anodes (sodium, potassium); assorted active gas cathode materials like CO_2; and recently discovered reversible oxygen redox activity in high capacity lithium transition metal oxide cathodes.

In this review, we described in detail important aspects of this field: heterogeneous electro-catalysis; homogeneous electro-catalysis by redox mediators; and possible side reactions of the relevant electrolyte solutions with the highly reactive oxygen moieties which are formed in Li-O_2 cells. Special attention was paid to the recently discovered role of the reactive singlet oxygen which forms during disproportionation of Li superoxide to Li peroxide.

The article covers all aspects of major components: anodes (including search for alternative, less reactive ones), cathodes, and electrolyte systems – including organic or ionic liquid-based solutions, and solid state electrolytes (ceramic and polymeric). We described also innovative efforts to develop new solvents that can be more stable towards the reactive oxygen moieties in these cells. In addition, we have covered a detailed description of basic science aspects. The article analyzes all facets of the gap between the state-of-the-art Li-O_2 cells and practical Li-air battery technology.

We have covered past, present and future perspectives of this challenging field. After great initial enthusiasm that also included some unsupported promises, the large research community working on active metals and air battery technologies, has reached an appropriate maturity and realistic approaches to the R&D efforts of these systems. Work is in progress and further work and investments of innovative efforts and means is required. It should also be noted that the field can further expand to include Li-Li_2O closed systems, high temperature solid state Li and Na air batteries and Li (Na) -CO_2 batteries.

The risk of failure is obvious, but the benefits of success are enormous. Developing practical rechargeable active metal–air batteries will revolutionize the field of electrochemical power sources and will further promote the electro-mobility revolution.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: peter.bruce@materials.ox.ac.uk

*E-mail: lfnazar@uwaterloo.ca

*E-mail: yksun@hanyang.ac.kr

*E-mail: Doron.Aurbach@biu.ac.il

ORCID

Won-Jin Kwak: 0000-0002-9807-1434

Rosy: 0000-0001-5985-8587

Daniel Sharon: 0000-0002-3385-1536

Hun Kim: 0000-0002-3789-914X

Lee R. Johnson: 0000-0002-1789-814X

Peter G. Bruce: 0000-0001-6748-3084

Linda F. Nazar: 0000-0002-3314-8197

Yang-Kook Sun: 0000-0002-0117-0170

Malachi Noked: 0000-0001-8995-0632

Stefan A. Freunberger: 0000-0003-2902-5319

Doron Aurbach: 0000-0002-1151-546X

Author Contributions

ψWon-Jin Kwak and Rosy have contributed equally.

Notes

The authors declare no competing financial interest.

Biographies

Won-Jin Kwak is currently a Postdoctorate Research Associate in the Energy and Environment Directorate, PNNL. He has expertise and extensive experience in next-generation lithium batteries, especially lithium-oxygen batteries. His research interests are focused on the development of functional materials and the design of novel cell configuration, for stable and efficient battery systems. He has published more than 20 papers as a first author in peer-reviewed professional journals and holds 5 patents. He obtained his Ph.D. from Hanyang University in 2018 under the supervision of Prof. Yang-Kook Sun. His main research topic was to find efficient redox mediators and improve their stability in lithium-oxygen batteries based on degradation mechanisms associated with lithium metal and singlet oxygen.

Rosy is a Post-Doctoral researcher in the Noked group under the PBC fellowship program for outstanding postdoctoral researchers from India and China. She received her Ph.D. in electrochemistry in 2017 from Indian Institute of Technology, Roorkee. Her research includes alkali metal batteries, electrode protection, and online electrochemical mass spectrometry studies.

Daniel Sharon is currently a postdoctoral fellow in the Institute for Molecular Engineering at the University of Chicago. He earned his Ph.D in Physical Chemistry from the Bar-Ilan University in Israel under the supervision of Professor Doron Aurbach. Daniel has been

working on the development of new electrolyte solutions, including polymer electrolytes, for next generation non-aqueous lithium ion batteries. His research focuses on understanding the electrochemical processes occurring at the electrodes-electrolyte systems.interfaces.

Chun Xia obtained his Bachelor of Science degree from Yanghzou University (China) in 2006 and Ph.D. degree from Tianjin University (China) in 2011. He was a postdoctoral researcher at Justus Liebig University Giessen (Germany) between 2012 and 2014. Since April 2014, he has worked as a postdoctor in the group of prof. Linda Nazar at the University of Waterloo (Canada). His research focus on the fundamental chemistry and electrocatalysis in lithium-oxygen and sodium-oxygen batteries.

Hun Kim is a Ph.D. candidate under the supervision of Prof. Yang-Kook Sun at Hanyang University. He received a Bachelor of Science degree in the department of Energy Engineering at Hanyang University. He has been interested in lithium metal protections and redox mediators in lithium-oxygen batteries. His researches are focused on material chemistry and materials development of next generation metal-oxygen batteries.

Lee R. Johnson received his Ph.D from the University of Nottingham in 2011 and was a postdoctoral fellow at the University of Oxford working under the supervision of Prof P. G. Bruce. He is an Associate Professor at the University of Nottingham and the recipient of a Nottingham Research Fellowship and an EPSRC-UKRI Innovation Fellowship. He is the author of 24 original research articles. His research interests include organic electrochemistry and the study of electrochemical phenomena of electrolytes and interfaces in batteries. He established theory that underpins aprotic oxygen reduction with alkali ions within the lithium-air battery and identified leading redox mediators for catalysis of the discharge reaction.

Peter G. Bruce is Wolfson Professor of Materials at the University of Oxford. His research interests embrace materials chemistry and electrochemistry, with a particular emphasis on energy storage, especially lithium and sodium batteries. Recent efforts have focused on the synthesis and understanding of new materials for lithium and sodium-ion batteries, on understanding anomalous oxygen redox processes in transition metal oxides used as high capacity Li-ion cathodes, the challenges of the lithium-air battery and the influence of order on the ionic conductivity of polymer electrolytes. His pioneering work has provided many advances. Peter received the Tilden Prize of the Royal Society of Chemistry in 2008, the Carl Wagner Award of the Electrochemical Society in 2011, the Liversidge Award of the Royal Society of Chemistry in 2016 and the Hughes Medal of the Royal Society in 2017. He has also been selected as Highly Cited Researcher by Thomson Reuters/Clarivate Analytics in 2015, 2016, 2017 and 2018. As well as directing the UK Energy Storage Hub (SuperStore), a consortium on solid-state batteries and a consortium on lithium batteries, Peter is a founder and Chief Scientist of the Faraday Institution, the UK centre for research on electrochemical energy storage. Peter also took up the position of Physical Secretary and Vice President of the Royal Society (UK's national academy) in November 2018.

Linda F. Nazar, FRS(C) received her Ph.D. in Chemistry from the University of Toronto in 1986 with Prof. Geoff Ozin in inorganic materials chemistry, and was an Exxon postdoctoral fellow at the Exxon Research Labs in Annandale, N.J with Dr. Allan Jacobson where she started to work on electrochemistry. She then joined the faculty at the University of Waterloo, Ontario, Canada where she is now a Senior Canada Research Chair in Solid State Energy Materials and Distinguished Research (full) Professor. Nazar is known for her research on

electrochemical energy storage with topics that span Li-ion batteries and "beyond Li-ion" (including Li-O$_2$, and Li-S), solid state ionics, and the role that nanotechnology plays in energy materials. She has co-authored over 235 publications garnering over 35,000 citations on the WoS. She is on the Web of Science's 2014, 2016, 2017 and 2018 Highly Cited Research Lists, and an Officer of the Order of Canada.

Yang-Kook Sun received his Ph.D. degree from the Seoul National University, Korea. He has worked at the Hanyang University in Korea as a professor since 2000. His research focuses on Electrode materials for Li-ion secondary battery for electric vehicle, Lithium Sulfur and Lithium Air Batteries, Electrode materials for Na, K-ion battery, Lithium-metal batteries. He published more than 580 papers and his papers were cited more than 46,000. And he filed more than 450 patents and patent applications. As recognized for research, he selected as the Highly Cited Researcher at the field of material science from Clarivate Analytics and received Research Award, Technology Awards from The Electrochemical Society. He continues his active research works to contribute to the popularization of science and to the world society.

Aryeh A. Frimer received his Ph.D. at Harvard University with Prof. Paul D. Bartlett in 1974 elucidating the mechanism of Singlet Oxygen with vinyl ethers. He then crossed the ocean to become a Senior Weizmann Fellow with Prof. Dov Elad. In 1975, Dr. Frimer joined the faculty of Bar Ilan University, where he is now the Ethel and David Resnick Professor Emeritus of Active Oxygen Chemistry. In addition to active oxygen species, his group has been exploring chemistry within biomembranes, the preparation and neutralization of green energetic materials, and most recently the formation and chemistry of active species in Li-O$_2$ batteries.

Malachi Noked is currently senior lecturer (Assistant Professor) Alon Fellow in the department of chemistry at Bar Ilan University in Israel. He earned his Ph.D. in chemistry in 2013 and was a Fulbright Ilan- Ramon postdoctoral fellow and research associate at the University of Maryland from 2013 to 2016. His research interest focuses on electrochemistry, energy storage, and functional thin films.

Stefan Freunberger obtained his PhD in Chemistry from ETH Zürich and was post doc with Peter Bruce at the University of St Andrews, working on many aspects of Li-O$_2$ chemistry. He has been PI at Graz University of Technology, Austria, and since 2020 Assistant Professor at the Institute of Science and Technology Austria (IST Austria) with research interests embracing energy-storage materials, including alkaline-ion and metal-O$_2$ batteries, electrolytes, and in situ techniques. Key contributions to metal-O$_2$ chemistry concern elucidation of reaction mechanisms, parasitic chemistry and most recently the involvement of singlet oxygen. His research has been recognized by the Srinivasan Young Investigator Award of The Electrochemical Society, the invited visiting professorship La Chaire Total de la Fondation Balard, elected membership of the Austrian Academy of Sciences, the Tajima Prize of the International Society of Electrochemistry and an ERC Starting Grant.

Doron Aurbach is a full professor, department of chemistry, chemical engineer, leading the electrochemistry group (40 people) at Bar-Ilan university (BIU) Israel, He leads INREP: Israel national research center for electrochemical propulsion (since 2012, 25 research groups, 7 Israeli institutions), which develops power sources for electric vehicles. His teams study the electrochemistry of active metals, non-aqueous electrochemical systems, develop spectroscopic methods (in situ and ex situ) for sensitive electrochemical systems, study electrochemical intercalation processes, electrochemical water desalination, electronically conducting red-ox polymers and develop rechargeable high energy density batteries and

supercapacitors. He serves as a senior editor in the journal of the electrochemical Society (JES), ECS, ISE, MRS fellow, recipient of the Alan Bard Award of the Electrochemical Society (ECS, 2017) , the Alexander Frumkin Medal of the International Society of Electrochemistry (ISE, 2018) and the Eric and Sheila Samson Prime Minister prize for innovation in alternative fuels for transportation (2018).

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NOMENCLATURE AND ABBREVIATIONS

$^1O_2$: singlet oxygen

AN: acceptor number

AFM: atomic force microscopy

CE: coulombic efficiency

CPL: composite protective layer

CT: charge transfer

DABCO: 1,4-diazabicyclo[2.2.2]octane

DABCOnium: onium salt form of 1,4-diazabicyclo[2.2.2]octane

DBBQ: 2,5-di-tert-butyl-1,4-benzoquinone

DFT: density functional theory

DMA: 9,10-dimethylanthracene

DMDMB: 2,3-dimethyl-2,3-dimethyoxybutane

DMDMP: 2,4-dimethoxy-2,4-dimethylpentan-3-one

DME: 1,2-dimethoxyethane

DMF: dimethylformamide

DMPZ: dimethylphenazine

DMSO: dimethyl sulfoxide

DN: donor number

DOL: 1,3-dioxolane

E^{act}: activation energy

E^0: equilibrium potential

EDDI: energy dispersive diffraction

EPR: electron paramagnetic resonance

ESR: electron spin resonance

EVs: electric vehicles

HGVs: heavy goods vehicles

HMD: 2,2,4,4,5,5-hexamethyl-1,3-dioxolane

HOMO: highest occupied molecular orbital

HPLC: high-performance liquid chromatography

IE: ionization energy

IL: Ionic liquid

k_{app}: apparent rate constant

LIB: lithium-ion battery

LiTf: Lithium trifluoromethanesulfonate

LiTFSI: Lithium bis(trifluoromethanesulfonyl)imide

LOB: lithium-oxygen battery

LUMO: lowest unoccupied molecular orbital

Me-Im: methyl-imidazole

MPT: 10-methylphenothiazine

MWCNT: multi-walled carbon nanotubes

NCL: nafion based composite protective layer

NIR: near infra-red

NMC: nickel-manganese-cobalt

NMP: N-methyl-2-pyrrolidone

NMR: nuclear magnetic resonance

OCV: open circuit voltage

OEMS: online electrochemical mass spectroscopy

OER: oxygen evolution reaction

ORR: oxygen reduction reaction

PAN: polyacrylonitrile

PC: propylene carbonate

PEO: polyethylene oxide

PFC: perfluorocarbons

PMMA: poly(methyl methacrylate)

PTIO: 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide

PVC: polyvinyl chloride

PVdF: polyvinylidene fluoride

PVdF-HFP: poly(vinylidene fluoride-co-hexafluoropropylene)

PTFE: polytetrafluoroethylene

PVP: polyvinylpyrrolidone

RM: redox mediator

ROS: reactive oxygen species

RRDE: rotating ring-disc electrode

RROS: reduced reactive oxygen species

SE: solid electrolyte

SECM: scanning electrochemical microscopy

SEI: solid electrolyte interphase

SERS: surface enhanced Raman spectroscopy

SFG: sum frequency generation

SOMO: singly occupied orbitals

TBA: tetrabutylammonium

TDPA: tris[4-(diethylamino)phenyl]amine

TEGDME: tetraethylene glycol dimethyl ether

TEMPO: 2,2,6,6-tetramethylpiperidinyloxyl

TTE: 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether

TTF: tetrathiafulvalene

TMO: transition metal oxide

UV: ultraviolet

XANES: X-ray absorption near edge structure

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

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