

Advances in Understanding Mechanisms Underpinning Lithium-Air Batteries

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Abstract

The rechargeable lithium-air battery has the highest theoretical specific energy of any rechargeable battery and could transform energy storage if a practical device could be realised. At the fundamental level, little was known about the reactions and processes that take place in the battery, representing a significant barrier to progress. Here we review recent advances in understanding the chemistry and electrochemistry that govern the operation of the lithium-air battery, especially the reactions at the cathode. The mechanisms of O₂ reduction to Li₂O₂ on discharge and the reverse process on charge are discussed in detail, as are their consequences for the rate and capacity of the battery. The various parasitic reactions involving the cathode and electrolyte during discharge and charge are also considered. We also provide views on understanding the stability of the cathode and electrolyte and examine design principles for better lithium-air batteries.

Introduction

Society will need energy storage that exceeds the limits of current technologies if we are to significantly reduce CO₂ emissions. The lithium-ion battery is a spectacular success and will continue to improve incrementally for years to come. However, it is imperative that we investigate now alternatives that offer the possibility of going beyond the limits of Li-ion technology, if we are to have any hope of meeting the energy storage needs of future generations^{1,2,3,4}.

The Li-air battery, which uses O₂ derived from air, has the highest theoretical specific energy (energy per unit mass) of any battery technology, 3500 Wh/kg^{5,6}. Estimates of practical energy storage are uncertain, as many factors are unknown, but values in the range 500 to 1000 Wh/kg - sufficient to deliver significantly in excess of a 500 km driving range if employed as an electric vehicle battery - have been proposed, **Fig. 1a**⁷. The fuel at the positive electrode, O₂, is freely available. Operation of the aprotic Li-O₂ battery, which uses a non-aqueous based electrolyte, is illustrated in **Fig. 1b**. Although Li-air batteries have the energy storage advantage over many other rechargeable batteries, understanding of the underpinning chemistry and electrochemistry is lacking. Li-air combines two challenging electrodes, Li metal and O₂. Li metal electrodes have been investigated for many years and still do not deliver the necessary cycling efficiency (ratio of discharge/charge capacity) and related suppression of dendrites.⁸ However the prospect of a protected Li anode - in which a solid electrolyte is interposed between the Li metal and the liquid electrolyte - offers an important path of exploration towards a functional high energy Li battery⁹. In contrast, when the aprotic Li-air battery began to be explored there were but a handful of papers on O₂ reduction in relevant electrolyte solutions,

rendering understanding of the O_2/Li_2O_2 redox reaction in aprotic solvents a high priority. Aside from the O_2/Li_2O_2 redox couple, aprotic $Li-O_2$ faces a number of other challenges, not least of which is the stability of the electrolyte solution and the cathode towards reduced oxygen species. All of these processes need to be understood and mastered if we are to achieve progress towards a practical battery. Even then the issue of air handling and filtering would need to be addressed by new chemical engineering solutions. Nonetheless, only through a deeper understanding of the science and engineering underpinning the Li -air battery can we hope to make reliable, evidence based predictions of whether it can be a viable technology.

In this Review we focus on the topics that were least understood and on which there has been the greatest progress over the last few years, including the mechanism of O_2 reduction to Li_2O_2 at the cathode on discharge and the oxidation of Li_2O_2 on charge and the mechanisms of electrolyte and cathode degradation. As with all such potentially game changing ideas, they begin with over-hyped expectation, followed by the inevitable disillusionment, thereafter equilibrium is often established; $Li-O_2$ is now in this third phase¹⁰. There has been real progress in understanding the fundamental science underpinning Li -air, progress that has explained why many previous results led to the belief that $Li-O_2$ would inevitably be a low rate, low capacity, high polarization cell, whereas new work on the fundamentals is revealing this is not necessarily the case. No one yet knows if $Li-O_2$ will ever be a technology, but we owe it to society and our future to explore what might be possible.

1. Mechanisms at the Aprotic O_2 Electrode

Unlike O_2 reduction in fuel cells, which produces H_2O , the product at the positive electrode in the $Li-O_2$ cell is the insulating solid Li_2O_2 , and this has profound implications for the operation of the cell.

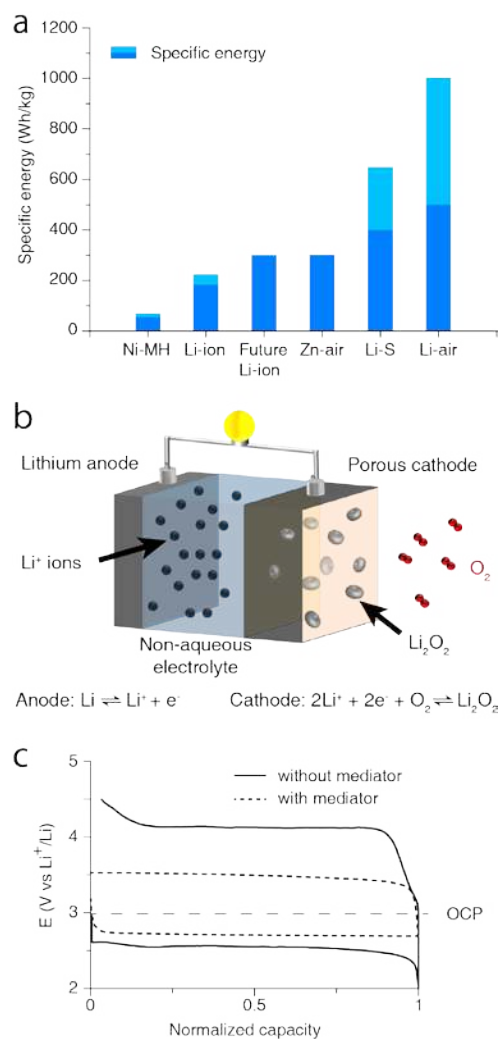


Figure 1 | The basics of lithium-air battery. (a) Practical specific energies for some rechargeable batteries. These are reduced from the theoretical values by e.g. current collectors, cell packaging and system overheads. Light blue indicates range of specific energies; (b) schematic of an aprotic $Li-O_2$ cell and (c) schematic of a typical load curve for discharge and charge of a $Li-O_2$ cell without (solid line) and with (short-dash line) redox mediators (molecules that shuttle electrons between the electrode surface and O_2/Li_2O_2 in solution). OCP = open circuit potential.

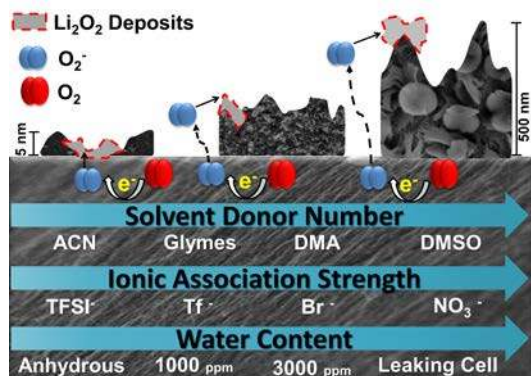


Figure 2 | Surface and solution growth mechanisms of Li_2O_2 in different electrolyte solutions. The final step in the formation of Li_2O_2 can be either chemical (disproportionation) or electrochemical (second reduction). ACN, Glymes, DMA and DMSO are the solvents acetonitrile, polyethers ($\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$), dimethyl-acetamide and dimethyl sulfoxide. TFSI⁻ and Tf⁻ are the anions bis(trifluoromethane)sulfonimide and trifluoromethanesulfonate. Donor numbers provide a scale for nucleophilicity of solvents, as defined in Ref. 17. The ionic association strength of a salt is determined by the negative charge delocalization, size, and steric effects for a given anion as explained in Ref. 18.

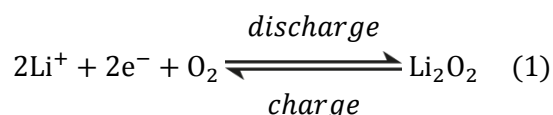
O_2 reduction to Li_2O_2 on discharge

The processes that occur on discharge are highly dependent on competitive factors involving the effective current density /overpotential and whether the LiO_2 intermediate is dissolved in solution or adsorbed on the electrode surface^{11,12,13}. At high overpotentials/high current densities O_2 is reduced to Li_2O_2 , which grows as a film on the electrode surface. However, batteries must operate at low overpotentials and relatively high currents to maximise energy density (and must be designed to do so). At low overpotentials, Li_2O_2 has been observed to grow as surface films or large particles from a solution process, depending on the solvent or salt from which the electrolyte solution is formed or depending on additives in the electrolyte solution (**Fig. 2**)^{11,12,13, 14, 15, 16}. Bulk Li_2O_2 exhibits ionic conductivity via lithium vacancies, and electronic conductivity via electron holes, both being very low¹⁷.

At low overpotentials, whether Li_2O_2 forms as a film on the electrode or particles from solution is controlled by the solubility of the LiO_2 intermediate¹³. The O_2 reduction mechanism is summarized in **Fig. 3** and eqs. 2 to 7. The first step is the 1-electron reduction of O_2 (dissolved in the electrolyte solution at the electrode surface) to form LiO_2 . An equilibrium exists between LiO_2^* adsorbed on the electrode and LiO_2 dissolved in the electrolyte solution,¹¹ the position of which is governed by the competition between LiO_2 solubility and the adsorption free energy of LiO_2^* on the electrode; the former is a significant factor, **Fig. 3**^{13,14,16}. As is generally the case for salts dissolved in aprotic solvents (no hydrogen bonding), the solubility depends primarily on solvation of the cations by the solvent molecules (Gutmann donor number(DN)¹⁸ and the ionic dissociation strength)¹⁹ although interactions between the O_2^- ion and high acceptor number additives were also observed to play a role in LiO_2 solubility^{14,16}. Where a solvent has a sufficiently high donor number to strongly solvate Li^+

A typical plot of voltage as a function of coulombs passed on the discharge and charge cycle of a $\text{Li}-\text{O}_2$ cell is shown in **Fig. 1c**.

The kinetics of the Li anode are relatively facile, so the deviations from the thermodynamic potential (open circuit potential) on discharge and charge (overpotentials) in **Fig. 1c** are dictated primarily by reactions at the cathode. The ideal cathode reaction is shown in equ. 1.



Many factors can influence the overpotentials, such as deposition of side-reaction products from electrolyte and electrode degradation. These factors and how they may be mitigated are discussed in subsequent sections. However, the mechanism of the reversible reaction described by equ. 1 lies at the heart of operation of the $\text{Li}-\text{O}_2$ battery and understanding it is key to addressing the technological challenges, hence we begin with this below.

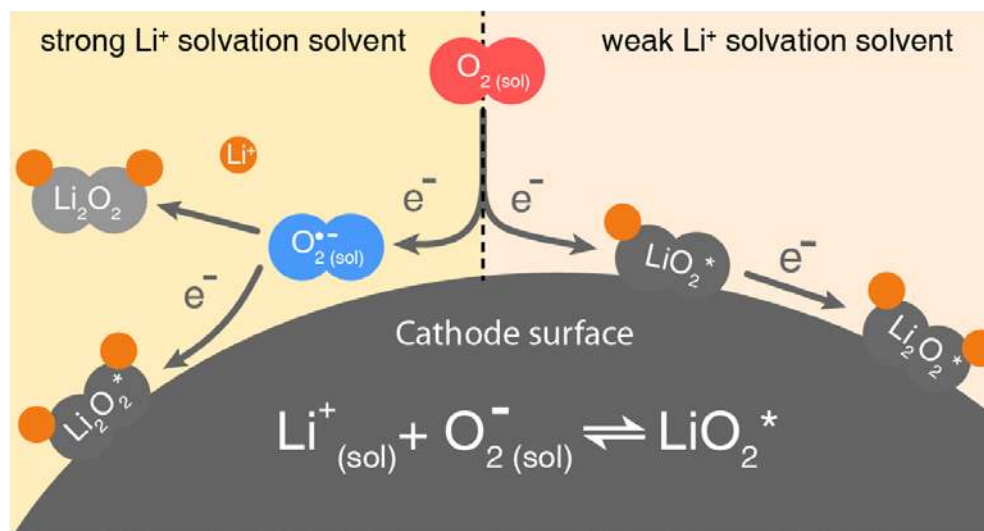
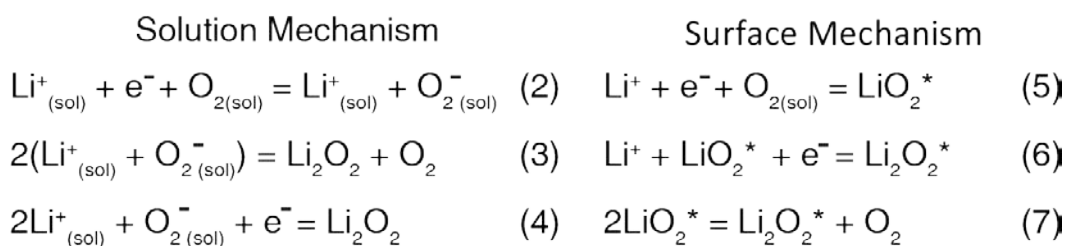


Figure 3 | Reduction mechanisms in a Li-O₂ cell at low overpotentials. Where LiO₂ is soluble (e.g. due to use of a high donor number solvent that strongly solvates Li⁺) Li₂O₂ grows as particles from solution. Where LiO₂ is insoluble (e.g. due to use of a low donor number solvent that weakly solvates Li⁺) Li₂O₂ grows on the electrode surface. Reactions above refer to those occurring during discharge via the solution mechanism and the surface mechanism.

(e.g. dimethyl sulfoxide, DMSO, DN = 30) then LiO₂ is dissolved mainly in the electrolyte solution, where it disproportionates to Li₂O₂ that grows as micron sized particles, **Fig. 3** and eqs. 2 and 3^{13,14}.

If, on the other hand, Li⁺ is weakly solvated (e.g. acetonitrile CH₃CN, DN = 14) then LiO₂ is present primarily on the electrode surface (equ. 5) where it undergoes a 2nd electron reduction or disproportionation (eqs. 6 and 7) to form a Li₂O₂ film on the electrode.

It is interesting that the fate of Li₂O₂ in aprotic solvents (i.e. without protic additives) depends primarily on the solvation of Li⁺ and not the species actually formed on reduction, O₂⁻.¹⁶ Superoxide radicals can be stabilized indirectly by the electrolyte counter anions^{20, 21, 22}. In solutions containing highly associated lithium electrolytes, the counter anions are strongly coordinated to the solvated lithium cations. Somewhat analogous to high donor number solvents strongly solvating the Li⁺ ions, this stabilizes the LiO₂ lowering its free energy and favouring its presence in solution. The LiO₂ species in solution can then go on to disproportionate to Li₂O₂. Hence, superoxide moieties formed by oxygen reduction can be stabilized even in solvents with low DN number such as glymes.²⁰

Additives to the electrolyte solution can also influence the LiO₂ solubility, through solvation of Li⁺ or by direct solvation of superoxide using Lewis acidic (electron accepting) electrolyte compositions. For example, when added at impurity (<1 vol%) levels, water, a strong Lewis acid, along with other protic compounds, can induce solution growth of Li₂O₂ through interactions with reduced oxygen species.^{14,23,24} Water unfortunately also induces other parasitic reactions within the cell, such that a search is needed for other, more stable additives that provide a solution pathway to Li₂O₂ formation

and hence increased cell capacity. Additive design criteria to provide both appropriate stability and oxygen species solvation are still not entirely understood.

Understanding the O_2 reduction mechanism has important implications for practical Li- O_2 batteries. Much work in the literature has employed ether-based electrolyte solutions. The above mechanistic understanding explains why these low donor number solvents (DN \sim 20) result in significant Li_2O_2 film growth on the electrode. Such insulating films can grow only to 6-7 nm, resulting in electrode passivation²⁵ and leading to low capacities, low rates and early cell death. In contrast, electrolyte solutions that dissolve LiO_2 minimize surface film growth, resulting in high rates, high capacities and sustained discharge^{11,12,13}. This changes thinking regarding the design of porous cathodes for Li- O_2 , away from high surface areas and towards electrodes with a high proportion of large pores to store the Li_2O_2 particles growing from solution. Li- O_2 cells with such electrodes can deliver relatively high specific energies (gravimetric) and energy densities (volumetric) compared with those that rely on surface films of Li_2O_2 ¹³.

The LiO_2 intermediate is a disadvantage, especially in its solubilized form. It is reactive, especially towards high donor number solvents that might be used to dissolve LiO_2 , it is reactive towards possible electrode materials, and it pins the discharge potential at a value somewhat lower than the open circuit potential even in the absence of mass transport limitations²⁶. Very recently, an approach has been described that persuades reduction of O_2 to Li_2O_2 along a different pathway, avoiding LiO_2 and its disadvantages²⁷. A molecule such as 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) is added to the electrolyte solution. On discharge, it is first reduced to $DBBQ^-$ at the cathode, then binds Li^+ and reduces O_2 to O_2^- , in the process forming the complex $LiDBBQO_2$ in solution, $LiDBBQO_2$ in turn disproportionates to Li_2O_2 and reforms DBBQ. The cycle repeats to sustain discharge²⁷. By avoiding LiO_2 , relatively stable electrolyte solutions that do not dissolve LiO_2 e.g. LiTFSI in DME, may be used while still forming Li_2O_2 in solution, resulting in significantly high discharge rates and high capacities (typically by 80 fold) than is the case in the absence of DBBQ in the same DME electrolyte, **Fig. 4**. The new intermediate, $LiDBBQO_2$, is more stable (lower free energy) than LiO_2 thus lowering the overpotential on discharge, **Fig. 1c**. Another benefit of avoiding reactive solution-soluble LiO_2 is potentially reduced side-reactions, evidenced by higher yields of Li_2O_2 (95% with DBBQ in DME compared with 87% without). This reduction mechanism may be distinguished from previous studies that used molecular shuttles, which reduce O_2 by outer-sphere electron transfer at potentials lower

than direct reduction, e.g. viologen, or by molecules that bind O_2 before and after reduction, phthalocyanines.^{28,29,30}

Other discharge mechanisms that result in different products have also very recently been reported. Lu *et al.* suggested that it may be possible to stabilize LiO_2 , which is known to be stable only at < 50 K^{31,32}, by adsorption on an iridium-based electrode such that this becomes the product of the reaction rather than an intermediate³³. Such a cell reportedly shows much better reversibility than the O_2/Li_2O_2 reaction. It should be noted that work continues on the aqueous $Li-O_2$ battery and its related $Zn-O_2$ cousin^{34,35}. The fascinating prospect of a $Li-O_2$ aprotic battery in which the reaction at the cathode involves the formation of $LiOH$ has also been raised recently although the mechanism is still not yet clear³⁶.

Li_2O_2 oxidation to O_2 on charge

Electrochemical oxidation of Li_2O_2 does not require a true electrocatalyst – as does oxidation of $LiOH$ in non-aqueous media, for example – because the O-O bond is not cleaved on reduction. Oxidation of thin Li_2O_2 -films on the electrode surface may be relatively facile whereas oxidation of large particles of insulating Li_2O_2 is a challenge (see next sections). Theoretical studies intriguingly suggested that the peroxide surface exhibits a half-metallic state³⁷, but experimental proof of surface conductivity is lacking to date.

Many Li_2O_2 oxidation mechanisms have been invoked to provide a description of galvanostatic charge potential profiles. Elucidating the mechanistic origin of the charge profile is complicated by its dependence on two factors: (1) the discharge Li_2O_2 deposition mechanism, and hence the Li_2O_2 morphology, and (2) formation of products from parasitic reactions involving the cathode and

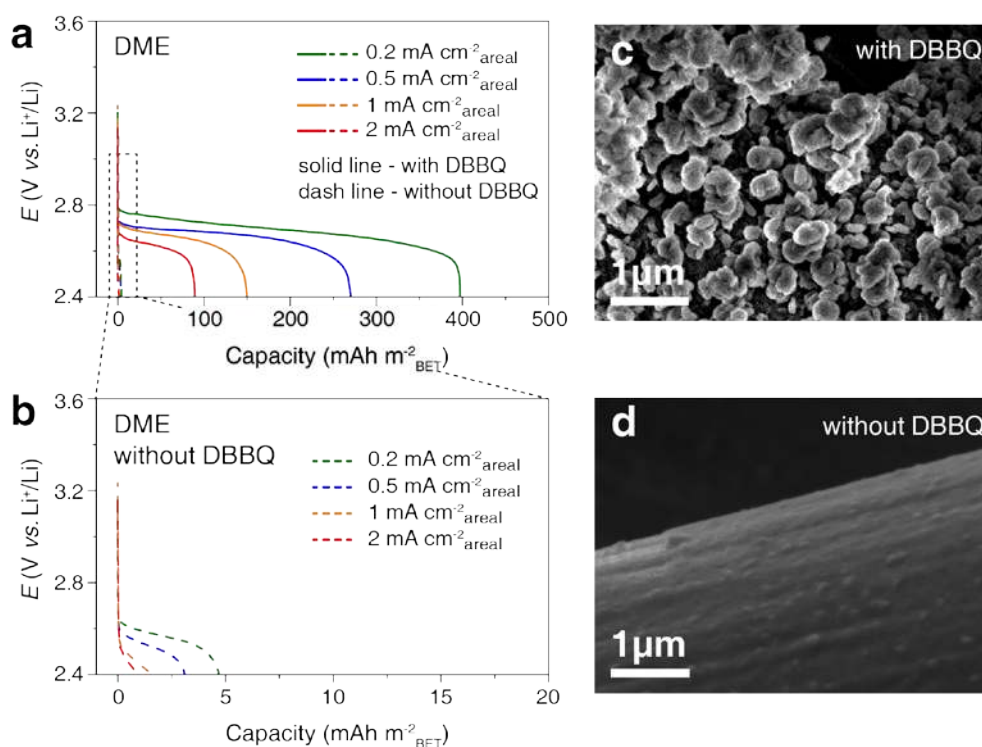


Figure 4 | Significant effect of DBBQ on discharge in ethers. Load curves for discharge of a $Li-O_2$ cell (a,b); electrolyte solution LiTFSI in DME, at a gas diffusion electrode. By adding 10 mM DBBQ to the solution the capacity is increased 80 fold as the discharge mechanism changes from electrode surface (c) to solution growth of Li_2O_2 (d). Figure reproduced from Ref. 27.

electrolyte during discharge and charge. These variables are intrinsically linked to the cell composition (i.e., the cathode and electrolyte employed), and numerous questions about the influence of these complexities on the mechanism and charge overpotential still remain to be answered. In theory, low overpotentials (<0.2 V) exist for O_2 evolution from Li_2O_2 at many Li_2O_2 crystal facets, as calculated using density functional theory³⁸. This is in agreement with observations of O_2 evolution at low (~ 3 V vs. Li^+/Li) potentials at early stages of charge from conformally deposited Li_2O_2 . The ever increasing overpotential observed in these cells was proposed to be related to the deposition of solid carbonates at the Li_2O_2 -electrolyte interface^{39,40} (see below).

Studies on charging electrodes pre-loaded with crystalline lithium peroxide have helped disentangle the oxidation of Li_2O_2 from side-reactions occurring on reduction related to Li_2O_2 -induced decomposition of both the cathode and electrolyte. Such reactions deposit products on the peroxide that exhibit very high oxidation potentials, and thus inhibit Li_2O_2 oxidation to O_2 ^{24,41}. First, the studies demonstrate that the surface chemistry of the cathode support is critical in determining the efficiency of electron transfer to the insulating Li_2O_2 ⁴². Studies using preloaded cathodes have also elucidated the role of passivating films formed on surfaces such as nitrides and carbides which can either shut down or facilitate charging, as further discussed below. Second, micron sized crystalline peroxide particles exhibit a rather low charge overpotential (only ~ 600 mV for passivated metallic TiC cathode surfaces); much lower than one might expect. This is in agreement with the above finding - namely that lithium peroxide can be rather readily oxidized if decomposition products can be avoided to insure facile transport across interfaces.

Various mechanisms have been proposed for oxidation of Li_2O_2 deposited as toroids or incorporated into the cathode as a macroscopic particle-containing powder. Ganapathy *et al.* used *operando* X-ray diffraction (XRD) to show that a Li deficient component (i.e., $Li_{2-x}O_2$) is formed during the charging process, presumably as a result of a one electron Li^+ de-insertion⁴³. In fact, this mechanism was first proposed by theoretical studies which showed that topotactic delithiation based on $Li_{2-x}O_2$ is rendered accessible at relatively small overpotentials of $0.3 - 0.4$ V⁴⁴. Li_2O_2 formed electrochemically via the solution mechanism described above often crystallizes in flat platelets, as determined from X-ray broadening, and as also observed by imaging⁴⁵. In reference 43, these are embedded in an amorphous lithium-bearing component (**Fig. 5a**), which may be comprised of both Li_2O_2 and side products arising from electrolyte degradation, such as formate, that can be oxidized at relatively low potentials without a catalyst⁴¹. Such products, formed on discharge, probably account for the less than 100% yield of peroxide (with respect to electrons passed in the cell) as determined by detailed assay studies⁴⁶. The non-crystalline phase is removed first (**Fig. 5a** \rightarrow **5b**) and at higher potentials, the underlying crystalline peroxide is proposed to charge *via* the Li-deficient solid solution ($Li_{2-x}O_2$) phase. The small actively oxidizing fraction results in a gradual reduction of the Li_2O_2 crystallites until their complete disappearance (**Fig. 5d**). Although the mechanism of oxygen release is not yet clear, it is probable that Li-deficient $Li_{2-x}O_2$ exists at the surface of Li_2O_2 in the cathode and immediately undergoes disproportionation as it forms to evolve O_2 .

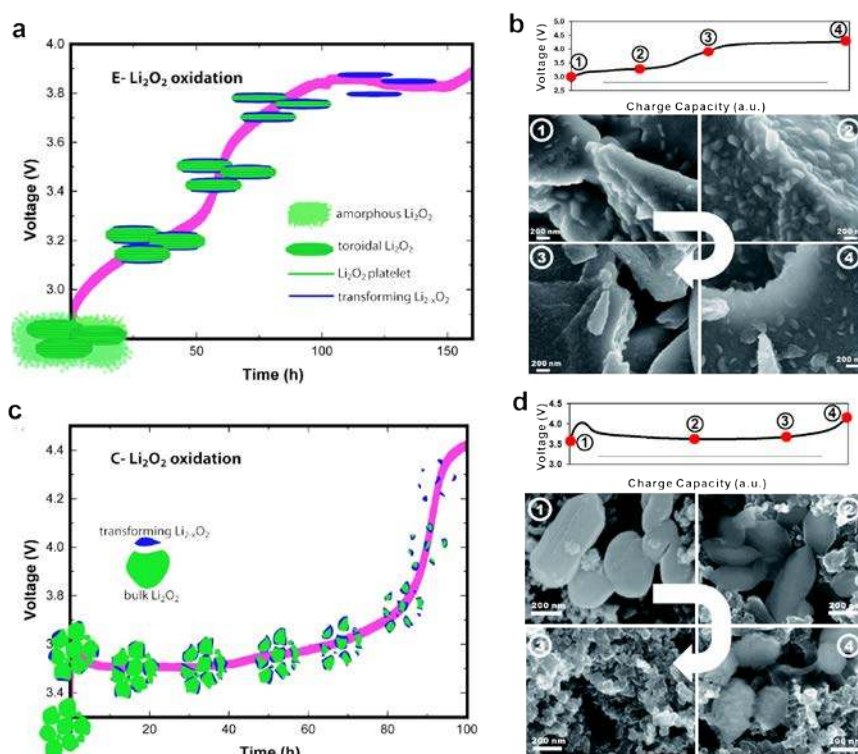


Figure 5 | Schematic showing the mechanism of Li_2O_2 oxidation during the charge. (a) Electrochemical E- Li_2O_2 and (c) crystalline C- Li_2O_2 . Scanning electron microscopy images (SEM) recorded at different stages of oxidation of E- Li_2O_2 and C- Li_2O_2 (1–4) are depicted in panels (b) and (d) respectively which show the electrochemical profiles. The white arrows indicate increasing state of charge. Figure reproduced from Ref. 43 American Chemical Society.

We note that some studies have suggested that the initial charging regime at low potentials is due to oxidation of a $\text{LiO}_2/\text{Li}_2\text{O}_2$ type material formed on discharge based on observation of paramagnetic superoxide domains based on Raman and magnetic measurements⁴⁷. While Li-deficient species are undoubtedly present at the peroxide surface, the Raman signature of the superoxide species is very close to that of the product formed by decomposition of the binder (PVdF)⁴⁸ which has been well established to occur⁴⁹, thus complicating the assignment. In fact, importantly, the signature peak does not appear when using Teflon as a binder in the cathode⁴⁸. Further work is needed to resolve this open question.

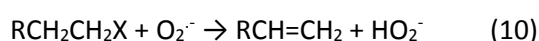
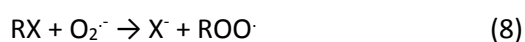
Soluble oxidation mediators for improved charging efficiency

Although solution growth of Li_2O_2 is advantageous on discharge, as described above, it makes the charging of Li-O₂ cells more challenging, because of the need to oxidize relatively large Li_2O_2 particles in the pores of the cathode somewhat remote from the electrode surface. Oxidation mediators can address this problem. They are molecules dissolved in the electrolyte that are oxidized at a potential slightly above the equilibrium potential of Li_2O_2 formation. Once oxidized at the electrode surface they diffuse to and oxidize Li_2O_2 particles. The substantially reduced charging overpotential is evident in the presence of an oxidation mediator is shown in **Fig. 1c**. Important properties include a high diffusion coefficient, fast charge transfer kinetics (particularly the charge transfer associated with Li_2O_2 oxidation) at voltages approaching the Li_2O_2 formation potential, and high stability. Many redox mediators have been proposed and explored⁵⁰. Substantial interest in oxidation mediators was spurred by Chen *et al.*'s report of tetrathiafulvalene as an efficient mediator⁵¹. While the oxidation potential of TTF is higher than desired, recent reports have demonstrated other oxidation mediators with potentials closer to that for Li_2O_2 oxidation, including tris[4-(diethyl amino)phenyl]amine⁵²,

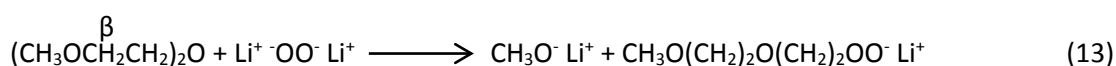
TEMPO^{53,54}, LiI^{55,56,57}, and a variety of quinone analogs and other redox-active molecules^{58,59}, that lower charge overpotentials without severely compromising electrolyte stability. Nevertheless, the search for a perfectly stable mediator with an appropriate operating voltage is still an important challenge. We note that the mediator approach requires the Li anode to be protected by a solid electrolyte membrane to avoid reaction of any mediator that diffuses to the anode.

2. Li-O₂ battery electrolytes

Perhaps the largest scientific challenge facing Li-O₂ batteries is long-term stability of the electrolyte. Li-O₂ cell configurations employ a liquid electrolyte comprised of a Li salt dissolved in an aprotic organic solvent. These electrolytes encounter highly reactive conditions. There are a plethora of critical reactions that the highly reactive reduced oxygen species (RROS) [e.g., O₂^{•-}, O₂²⁻, HOO[•] and HO[•]] can undergo with various polar aprotic solvents. Over the past half-century in-depth studies have been carried out on the reactivity of these reduced oxygen species in general, and superoxide in particular, towards a wide-range of organic substrates^{60,61}. While Li cations are highly electrophilic, in aprotic media, superoxide can function as a supernucleophile (eqs. 8 and 9), as an efficient base (equ. 10), and as a good electron-transfer agent (equ. 11).



Polar aprotic solvents (e.g., propylene carbonate, DMSO, DMA, DMF), all contain heteroatoms and, hence, polarized bonds. These polar solvents can undergo thermodynamically favourable reactions with RROS in the presence of Li ions⁶⁰. A good example are alkyl carbonates which undergo nucleophilic attack that is effected either by the electrochemically formed superoxide anion radicals (O₂^{•-}; equ 9) or by the peroxide dianion [O₂²⁻]^{62,63,64}. Polyethers such as glymes are not highly polar. Hence they are generally more inert solvents, although they too can undergo limited attack on α-H and β-H (different possible locations in the polyether molecules for nucleophilic attack) by superoxide and peroxide species formed by oxygen reduction^{65,66,67,68,49} (equ. 12&13).



Reactivity is attributable to two factors. One is that not only the superoxide, but also the peroxide, is considered a super-nucleophile owing to the adjacent pairs of non-bonding electrons.⁶⁹ The actual nucleophilicity is much higher than would have been expected based on its basicity. The second factor is the omnipresence of the highly electrophilic lithium cations. The latter bond strongly to the lone pairs of the oxygen atoms of the ether molecules which are hard Lewis bases. This promotes conversion of the alkoxy groups of polyethers into much better leaving groups, facilitating their loss upon nucleophilic attack.

Despite their relatively inactive nature, glyme molecules can be also attacked by $O_2^{\cdot-}$ or O_2^{2-} moieties, which act as bases. While peroxide and superoxide species are not necessarily strong bases (e.g. the pK_a of HOO^- is 4.7), the presence of Li^+ ions - which are strong Lewis acids - in solutions may facilitate concerted elimination reactions of glymes. The Li ions interact with the oxygen atoms of the ethers thus enabling formation of Li -alkoxide leaving groups (e.g. CH_3OLi) simultaneous with proton abstraction by superoxide or peroxide moieties.

Another important possible route of reactions may relate to the radical nature of superoxide moieties. While the superoxide anion radical is a “super” nucleophile, and it is not considered a strongly active radical moiety, evidence of its (or the hydroperoxy radical) deleterious effect exists.⁷⁰

Finally, it was also suggested that superoxide can induce the oxidation of various substrates via initial hydrogen atom abstraction⁷¹. However, thermochemical calculations and experimental data may suggest that superoxide is not a strong enough oxidizer. Any oxidation process observed during ORR may result from base-catalysed autoxidation (rather than from oxidation by superoxide). This suggestion certainly warrants further study. Consequently, it can be concluded that the partial instability of polyether solvents during oxygen reduction in the presence of Li ions stems from a combination of nucleophilic substitution and elimination reactions as major possible side reactions³⁸.

In previous work, Li_2O_2 was found to be reactive with glymes as it was electrochemically formed, and prolonged exposure of Li_2O_2 at low currents resulted in lower Li_2O_2 yields during discharge.⁴⁶ Based on extensive work and observation, the side reactions of these solvents in $Li-O_2$ cells are most pronounced and fast when the oxygen reduction products are present in the solution phase, before final precipitation⁷¹. To overcome the instability of the ethereal solutions, Nazar *et al.* protected the ethylene oxide backbone of dimethoxyethane (DME) by methylation.⁷² These analogues demonstrated better cyclability of $Li-O_2$ cells and less accumulation of side products compared to unprotected DME.

DMSO based electrolyte solutions and carbon free electrodes such as Au ⁷³, and TiC ⁷⁴ have demonstrated impressive cycling behaviour. However, as with all solvents studied so far, DMSO reacts with superoxide radicals⁷⁵, and also peroxide^{76,77} to generate the dimethyl sulfone anion and a hydroperoxy radical nucleophile⁷⁸. The latter can attack the sulfur atom of the sulfoxide moiety, yielding the corresponding dimethyl sulfone ($(CH_3)_2SO_2$) and lithium hydroxide. DMSO also reacts with lithium metal, and thus lightly protected anodes and/or a combination of the above-mentioned reactivity may underlie variability in reported results for this electrolyte solvent.

Given the particularly aggressive nature of RROS species towards organic molecules, exploration of purely inorganic electrolytes may be an interesting direction of research. To this end, solid inorganic ceramics have been employed to serve as both a $Li-O_2$ electrolyte and an oxygen and water-impermeable Li metal protective layer^{34,79,80,81,82}. Engineering a low-impedance porous cathode-electrolyte interface with long-term stability will be a critical challenge facing this cell architecture. Recently, an intermediate temperature (~ 150 °C) molten salt electrolyte, based on the $LiNO_3$ - KNO_3 eutectic, was also found to be stable in the presence of the $Li-O_2$ cathode electrochemistry⁸³. Identifying lower temperature inorganic molten salt alternatives and cathodes with improved stability (discussed in a later section) are useful directions to explore when employing these electrolytes.

In summary, it appears that all “commercial” off the shelf electrolytes examined to date exhibit instability to superoxide/peroxide moieties formed during oxygen reduction, in the presence of Li ions. Some modifications, e.g., using fluorinated solvents may enhance stability but severely reduces Li salt solubility. Hence, a compromise must be found, which could arise from designer electrolytes.

3. Designing better cathodes'

Many important properties have to be considered when designing a practical Li-air battery cathode. Li_2O_2 is an electronic insulator, insoluble (or very sparingly soluble) in all known organic liquid-based electrolytes, and a strong oxidizer. As a result, a cathode has to be designed to provide sufficient electronic conductivity and Li^+/O_2 transport, be resilient towards Li_2O_2 -induced oxidation, and not promote parasitic processes associated with the electrolyte and Li_2O_2 (Fig. 6). Typical Li- O_2 battery cathodes usually comprise a mixture of high surface area carbon/catalyst powders bound to a porous current collector using a polymer binder. A large number of materials have now been studied for each of these cathode components, and general guidelines for material development are still emerging. This section will highlight useful cathode material properties and the effect of cathode composition on the performance of a Li-air battery.

Heterogeneous Catalysis at the Cathode. Substantial effort in the Li-air field has been devoted to identifying heterogeneous electrocatalysts to reduce overpotentials of both the oxygen reduction (discharge) and, in particular, oxygen evolution (charge) reactions. However, given the problematic stability issues observed with the electrolyte and cathode carbon, careful quantitative analysis of product formation must always be performed to confirm any claims of true Li_2O_2 formation/oxidation electrocatalytic performance⁸⁴. In fact, when such quantitative measures are taken, parasitic electrolyte decomposition has been observed as the primary reaction being catalysed when using efficient aqueous ORR electrocatalysts⁸⁵. For example, the best known ORR catalyst, Pt, was observed to most efficiently catalyse these parasitic reactions, allowing electrolyte oxidation to occur at potentials (<3.5 V) that, by themselves, would lead to erroneous conclusions about efficient Li_2O_2 oxidation⁸⁵. Additionally, in cases where Li_2O_2 forms as a film on the electrode surface, the presence of a heterogeneous electrocatalyst on the electrode would be of little value beyond the first monolayer. It has been shown by Viswanathan *et al.*, that electrochemical formation and oxidation of Li_2O_2 films is actually quite facile on glassy carbon surfaces, with constructed Tafel plots for this redox reaction being similar to what would be expected of a fast, reversible reaction with an exchange

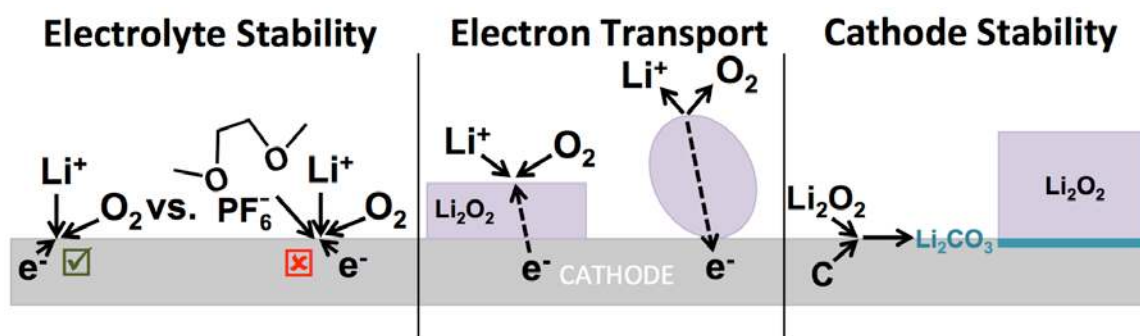


Figure 6 | Challenges facing the Li- O_2 battery cathode. The three largest challenges are the suppression of electrocatalytic activity towards electrolyte degradation, solutions to circumvent Li_2O_2 -induced electrode passivation, and stability of cathode materials at high voltages and in the presence of Li_2O_2 . The electrolyte stability image depicts the ideal case of O_2 reacting solely with Li^+ and e^- at the electrode surface, ultimately forming Li_2O_2 , and the non-ideal, parasitic case of solvent (dimethoxyethane shown as an example) and anion (hexafluorophosphate shown) participation in the electrochemical reaction. The electron transport image depicts the electronic conductivity limitations through a conformal, insulating Li_2O_2 film, as may happen during discharge, and conductivity limitations through large Li_2O_2 toroids during the charging process (Li_2O_2 film or toroid formation is controlled by electrolyte properties discussed previously). The cathode stability image depicts a potential parasitic reaction that can occur between Li_2O_2 and porous carbon, which is typically used as a cathode material.

current density of $\sim 1 \text{ mA/cm}^2$ (Fig. 7a)⁸⁶. In fact, Viswanathan *et al.* make a compelling argument that reducing overall cell impedance is substantially more important to eliminate overpotentials than improved ORR electrocatalysis.

On charge, the apparently large overpotential has been linked to deposition of solid electrolyte decomposition products at the O_2 evolving surface, the Li_2O_2 -electrolyte interface (Fig. 7b), and not to poor Li_2O_2 oxidation kinetics^{39,86}. As they are continuously formed, these carbonaceous products cover an increasingly larger portion of the Li_2O_2 -electrolyte interface, therefore necessarily driving the charging potential to higher values over the course of the charging process. At the end of charge, the decomposition products oxidize at high ($> 4.2 \text{ V vs Li}^+/\text{Li}$) potentials. The identification of stable electrolytes that are not susceptible to oxidation, even with a carbon-only cathode, should result in improved energy efficiency. For example, the molten nitrate eutectic electrolyte mentioned previously exhibits high stability and measurable Li_2O_2 solubility, allowing Li_2O_2 to diffuse back to electronically accessible cathode surfaces⁸³. As a result, extremely low overpotentials ($\sim 50 \text{ mV}$ at 0.25 mA/cm^2) throughout discharge and most of charge, with analytically confirmed $2e^-$ ORR and OER, were observed when employing this electrolyte in a carbon cathode-based cell.

Cathode stability. Although carbon has many desirable characteristics (high electronic conductivity and surface area, cost effective) that make it widely used as a cathode material, it degrades during Li-O_2 battery operation. For example, $^{13}\text{CO}_2$ evolution was observed during charge from a Li-O_2 cell employing a cathode composed of high purity ^{13}C carbon black, indicating that a parasitic reaction between Li_2O_2 and C occurs during cell operation, particularly at oxidative potentials (Fig. 7b)^{39,87}. Thotiyl *et al.* and Itikis *et al.* observed that this $\text{Li}_2\text{O}_2/\text{C}$ reaction is influenced by the carbon surface composition, with a more hydrophilic and defective carbon surface resulting in faster carbon degradation^{87,88}.

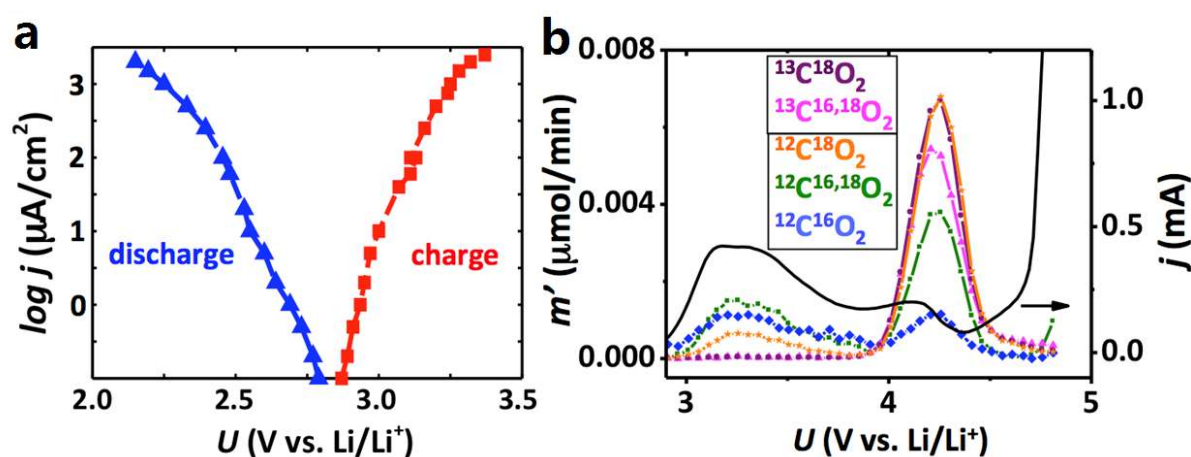


Figure 7 | Kinetics of Li_2O_2 formation and oxidation and origins of CO_2 evolution. (a) Cathodic (discharge) and anodic (charge, after a short discharge) Tafel plots for Li-O_2 electrochemistry at a flat, nonporous glassy carbon working electrode in a well-mixed bulk electrolysis cell (1 M LiTFSI in DME as the electrolyte). j is the current density in mA/cm^2 . (b) Linear sweep voltammogram (0.5 mV/s) and concomitant CO_2 evolution from a Li-O_2 cell discharged ($\sim 1 \text{ mAh/cm}^2$) under $^{18}\text{O}_2$, employing a ^{13}C cathode and normal isotope abundance electrolyte (1 M LiTFSI in DME). m' is the gas evolution rate in $\mu\text{mol/min}$. $^{12}\text{CO}_2$ is evolved at low potentials ($< 4 \text{ V}$), and has been linked to a parasitic reaction that deposits alkyl carbonates at the Li_2O_2 -electrolyte interface. A mix of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ is evolved at high potentials when solid carbonate products from carbon and electrolyte decomposition are oxidized. O_2 evolution was roughly 50x higher than total CO_2 evolution below 4 V and is not shown for clarity. Figures adapted with permission from Ref. 86 (panel a) and 39 (panel b).

Although these latter studies hold hope that a resilient carbon cathode could eventually be engineered, the search for alternative stable materials is also underway. Au and TiC were initially identified to provide more stable cycling than carbon^{73,74}. Theoretical work confirms that growth of Li₂O₂ on TiC occurs via a surface conduction mechanism.⁸⁹ Metallic nitrides are fully oxidized by Li₂O₂ when an anodic current is applied, completely inhibiting further electron transfer⁴². However, thermodynamically more stable metallic carbides, such as TiC, form a thin layer of conductive TiO_{2-x}, which acts to passivate the surface and inhibit further oxidation^{42,74}. Li₂O₂ oxidation is facilitated with a greatly decreased overpotential. Not all carbides are so stable. Mo₂C reacts to form a surface layer of MoO₂ on discharge, which appears to result in a low charge overpotential⁹⁰, but in fact forms soluble Li_xMoO₃ and leads to electrode degradation⁹¹. Thus practical cathode materials must be designed such that their surfaces inhibit excessive oxidation and/or are concealed by conductive oxide layers.^{92,93,94} Deposition of thin metal oxide coatings, such as Al₂O₃, has also been used as a strategy to protect carbon from degradation⁹⁵. Furthermore, electrocatalytic activity towards electrolyte decomposition also has to be taken into consideration when designing a new electrode material (**Fig. 6**).

Also of note, the stability of certain polymer binders has been called into question, with poly(vinylidene fluoride), a typical binder used in Li-ion batteries, being identified by Black *et al.* as unstable during battery operation.⁴⁹ Higher stability alternatives include polyethylene, poly(tetrafluoroethylene), and Nafion, as shown from studies on chemical stability of polymers in the presence of Li₂O₂ by Nasybulin *et al.*⁹⁶.

Cathode passivation limiting cell capacity. The primary advantage that Li-air batteries potentially have over current state-of-the-art Li-ion batteries is their high theoretical specific energy. Of course, to attain high energy densities, the electrochemical capacity of the cell should be very high, with the required minimum Li-O₂ capacity ultimately being a function of the battery pack configuration and composition. The projected required capacities by Gallagher *et al.* and Christensen *et al.* (5-30 mAh/cm²) are relatively large compared to most reported capacity values found in the literature^{7,97}.

Numerous potential causes have been conjectured for the observed poor capacity, all of which are related to processes occurring at the porous cathode (rather than the Li metal anode). These include pore clogging induced by solid Li₂O₂ deposition, O₂ transport limitations, and charge transport limitations⁷. When the surface mechanism for Li₂O₂ formation is dominant, cell death has been clearly linked to a substantial increase in charge transfer resistance related to a growing conformal Li₂O₂ film^{13,14,98,25}. Charge transfer through the growing Li₂O₂ film was probed by Viswanathan *et al.* to show the direct influence of charge transfer resistance and cell death at a flat, nonporous electrode, where pore clogging was not a possible cause for cell death⁹⁸. A clear correlation therefore exists between cell capacity and the total cathode surface area when Li₂O₂ film growth is observed, as was reported by Meini *et al.*⁹⁹. As was discussed earlier, the ideal cathode design in a cell with a dominant solution mechanism of Li₂O₂ is likely different, with low surface area and high porosity possibly required.

Outlook

There has been real progress in understanding the fundamental chemistry and electrochemistry underpinning the aprotic Li-O₂ battery. Work on the mechanism of the reaction at the positive

electrode, $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{Li}_2\text{O}_2$ has shown that electrolyte solutions which

strongly solvate Li⁺ result in O₂ reduction to Li₂O₂ occurring in solution, whereas solutions that weakly solvate Li⁺ result in Li₂O₂ films on the electrode surface. Much recent Li-O₂ work has focused on ether-based electrolytes, because of their superior stability compared with alternatives (especially those with high donor numbers). We can now understand why the use of such low donor number ethers

leads to Li_2O_2 surface films, passivating the electrode and resulting in low rates and early cell death, whereas the use of high donor number electrolyte solutions, dominated by Li_2O_2 growth in solution, can lead to relatively high rates and high capacities. Nevertheless, low donor number solvents are attractive because they are generally more stable, being less susceptible to nucleophilic attack by reduced oxygen species. Recent work has shown that the pathway by which O_2 is reduced to form Li_2O_2 can be altered, such that the intermediate LiO_2 , reactive towards electrolyte solutions, can be avoided and O_2 reduction to Li_2O_2 can take place in solution despite the use of low donor number ethers. As a result, Li- O_2 cells using ether based electrolyte solutions can deliver high rates and high capacities, avoiding early cell death. This is achieved using a solution soluble mediator, which also raises the discharge potential.

Understanding charge overpotentials after Li_2O_2 has been formed via the solution mechanism is an important direction of future research. Charge transport associated with toroids likely contributes to the overpotentials observed on charge, and hence the interest in developing stable oxidation redox mediators. However, other factors could also substantially contribute to the observed overpotential, such as electrolyte and cathode degradation. It is worth comparing the solution mechanism of Li_2O_2 formation to the chemistry of the Na- O_2 battery, where NaO_2 rather than Na_2O_2 is the product, formed as large crystals tens of microns in size¹⁰⁰. NaO_2 is solubilized *via* a phase transfer catalyst that operates both on discharge and charge, leading to little hysteresis and a low overpotential on charging despite the large crystallite size¹⁰¹. Thus, to take advantage of Li_2O_2 growth, it is necessary to utilize soluble oxidation mediators to oxidize the insoluble Li_2O_2 particles on charging. In effect the reaction at the positive electrode becomes one in which Li_2O_2 acts as the energy storage medium, coupled electrochemically to the electrode surface via molecular mediators.

Work on the effect of H_2O has shown that in contrast to earlier expectations, several 100s of ppm H_2O can be tolerated with the overall reaction still being dominantly Li_2O_2 formation and oxidation. However, there is evidence that H_2O changes the reaction pathway. Importantly the proton activity of H_2O in an aprotic organic solvent can be much less than in water, explaining in part why addition of significant quantities of H_2O does not radically change the overall reaction (i.e., Li_2O_2 is still the dominant discharge product even in a water-contaminated cell).

Although advances in understanding the underlying mechanisms has opened up promising directions for Li- O_2 cells exhibiting good rate and capacity with cycleability, challenges remain. In particular, in our opinion, these are the problems of electrode and electrolyte stability. Although there have been important advances in exploring cathode materials including modified carbons, breakthroughs are still required to demonstrate a low-cost, low mass, conductive, and highly stable porous gas diffusion cathode. A deeper understanding of the decomposition reactions occurring in the electrolyte solution is providing sound foundation of fundamental understanding that will define directions for the exploration of more stable electrolytes. It is important to place electrode and electrolyte stability in context. Most batteries are thermodynamically unstable and operate because of kinetic stability. Namely, there are always decomposition reactions, such as in the case of lead-acid batteries. It is not a question of whether the electrode or electrolyte is stable or unstable in Li- O_2 but rather is the degree of instability sufficiently small to not decrease performance over the cycle and calendar life of the battery. The nature of the decomposition products are important. If these are benign and soluble they may not degrade performance, whereas if they are insulating and deposited on the electrode surface, they strongly limit cell lifetime. Comparing Li- O_2 with other so called “beyond Li-ion” batteries, Li-S has been commercialized but not in a form that takes full advantage of its high specific energy. Rechargeable divalent metal batteries, Mg, Ca and Zn, still present formidable challenges. The jury is out on which, if any, beyond Li-ion batteries will make it to the market place.

In conclusion, disruptive technologies do not happen overnight. Generally, years of effort and fundamental understanding and its exploitation in addressing challenges is required. In fields outside batteries this has been well illustrated and well understood. The recent example of the commercialization of organic light emitting diodes, which, some 20 years ago was identified as a potentially promising game changing technology, illustrates this reality. It is not yet known whether the problems that remain a challenge for the aprotic Li-O₂ will ultimately be solved, but the last few years have identified many promising pathways forward to a solution.

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