Review Article
Lithium–oxygen batteries: At a crossroads?

Tejs Vegge[1,*], Juan Maria Garcia-Lastra[1] and Donald J. Siegel[2]

CrossMark

In this current opinion, we critically review and discuss some of the most important recent findings in the field of rechargeable lithium–oxygen batteries. We discuss recent discoveries like the evolution of reactive singlet oxygen and the use of organic additives to bypass reactive LiO_2 reaction intermediates, and their possible implications on the potential for commercialization of lithium–oxygen batteries. Finally, we perform a critical assessment of lithium–superoxide batteries and the reversibility of lithium–hydroxide batteries.

Addresses
[1] Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark
[2] Mechanical Engineering, Materials Science & Engineering, Applied Physics Program, University of Michigan Energy Institute, and Joint Center for Energy Storage Research (JCESR), University of Michigan, Ann Arbor, MI, USA

*Corresponding author: Vegge, Tejs (teve@dtu.dk)

Introduction

Secondary lithium–oxygen ($Li–O_2$) batteries remain one of the most hotly pursued and hotly contested future technologies for electrochemical energy storage. $Li–O_2$ batteries offer an alluring theoretical-specific energy ($\sim$3.500 Wh/kg) – nearly an order of magnitude greater than state-of-the-art in Li-ion batteries ($\sim$300 Wh/kg) – yet their practically accessible-specific energy remains low.

Two decades after the first report by Abraham and Jiang [1], and roughly a decade after its scientific light-off [2,3], more than 1,700 scientific articles have been published on the $Li–O_2$ system, with more than 57,000 citations [4]. This publication activity appears to have peaked in 2015–2016, raising the question whether this 'peak $Li–O_2$' is a consequence of the fundamental mechanisms being fully understood (perhaps with commercialization imminent)

or instead a sign of wavering interest from the community?

It is our opinion that neither of these viewpoints is entirely correct. Recent publications clearly document that breakthroughs in understanding and novel approaches to improve performance are still emerging at a rapid pace. At the same time, it is equally clear that near-term commercialization remains elusive. Here, we seek to highlight and review some of the most important recent $Li–O_2$ publications and discuss their potential impact on future research and development of secondary $Li–O_2$ batteries.

Fundamental $Li–O_2$ mechanisms

In discussing the current progress in the $Li–O_2$ field, a natural distinction is between aqueous and non-aqueous (aprotic) systems, where the latter has received the most attention due to its higher accessible energy density and greater likelihood for reversibility [5]. Nevertheless, a recent publication from Grey and co-workers sparked renewed interest and debate in the aqueous system [6•], as discussed below.

In the aprotic system, two distinctly different mechanisms for oxygen reduction can lead to the formation of the desired Li_2O_2 (peroxide) discharge product: (i.) a surface-based mechanism, where the LiO_2 (superoxide) reaction intermediate binds to the positive electrode surface or to previously deposited Li_2O_2, and, (ii.) a solution-based mechanism, where the LiO_2 intermediate is dissolved in the electrolyte and disproportionates into insoluble Li_2O_2 particles/toroids and O_2 [7]. Which of these mechanisms dominates depends on the relative stability of surface adsorbed LiO_2^* and LiO_2 in solution, where the latter has been argued to depend on the Gutman acceptor (AN) and donor number (DN) of the electrolyte [8] and the applied ORR potential [9•]. For detailed reviews of the different mechanisms in $Li–O_2$, we refer to Aurbach *et al.* [10] and Kang and co-workers [11].

The limitations of the surface-based mechanism are now well understood. For example, the fundamental overpotential for deposition of Li_2O_2 is very low (as originally predicted from density functional theory (DFT) calculations [12]), while the high charging potentials observed in early studies employing, e.g., carbonate-based electrolytes are due to parasitic chemistry [13,14]. Independent of electrolyte composition, the insulating nature of the formed Li_2O_2 thin-films is the origin of the 'sudden death' during discharge [15–17]. At ambient conditions

Figure 1
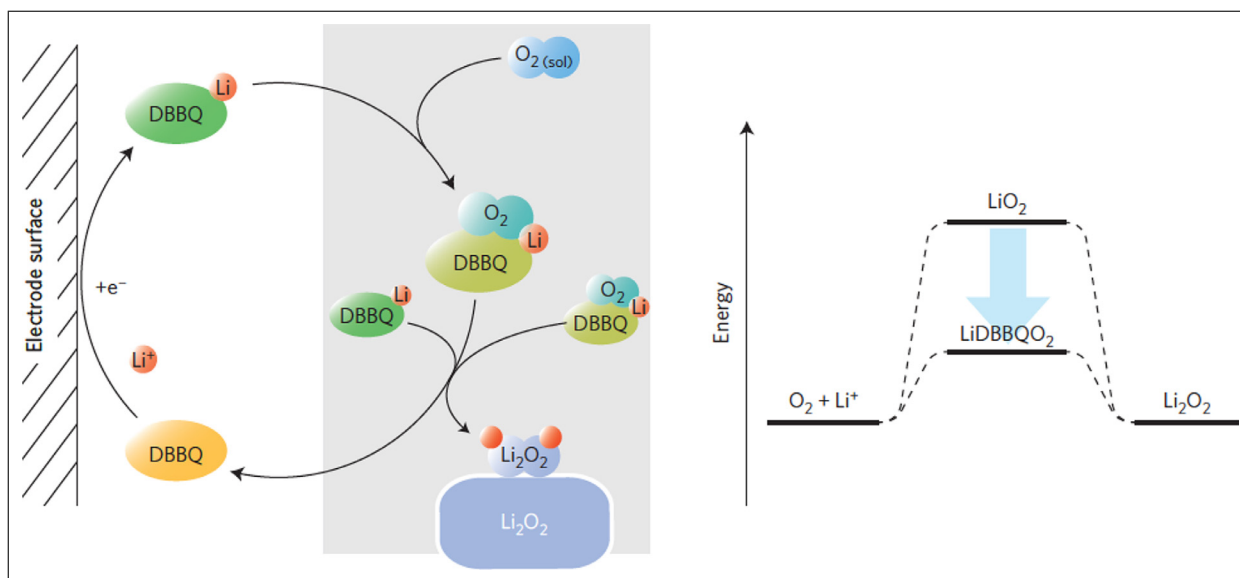
Schematics of reactions on discharge (left) and the effect of DBBQ on the potential determining step (right). DBBQ is reduced at the electrode surface, forming LiDBBQ, and then LiDBBQ reacts with O_2, producing Li_2O_2 and itself being regenerated to DBBQ. The schematic of the free-energy plot is at E° for O_2/Li_2O_2. Reprinted with permission from Ref. [31**]. Copyright 2017 Nature Publishing Group.

and moderate current densities, the electronic conduction is dominated by tunneling of holes in the valence band of Li_2O_2 [18], whereas hole polarons become important at higher temperatures and/or low current densities [19–23]. However, neither mechanism appears capable of providing the electronic conductivity needed to decompose relatively thick Li_2O_2 deposits at moderate current densities and with low overpotentials.

Redox mediators and additives

In terms of maximizing discharge capacity, the solution-based mechanism easily surpasses the surface-based mechanism. This is possible because the solution mechanism allows the formation of large, micron-sized Li_2O_2 particles, typically with toroidal morphologies [7]. However, the electrolytes and impurities that support this mechanism (e.g. water) also increase parasitic side reactions [24]. Also, Li_2O_2 particles formed via this mechanism may be located far from the electrode surface, resulting in very slow recharging, or worse, loss of electrical contact (i.e., Li_2O_2 stranded on the separator).

The use of redox mediators (RM) could circumvent slow charge transfer between 'distant' Li_2O_2 particles and the solid electrode surface. This approach has been investigated intensely since the first reports from Addison et al. [25] and later by Bruce et al. on the use of the tetrathiafulvalene (TTF) RM [26]. Here, the (TTF/TTF$^+$) redox couple facilitates chemical oxidation of Li_2O_2 by acting as a molecular electron-hole transfer agent between Li_2O_2 and the electrode surface [26]. A range of different RMs have now been investigated, including TEMPO

[27], TDPA [28], cobaltocene, and ferrocene [8,29]. Nevertheless, this approach has yet to lead to a major breakthrough, in part due to buildup of Li_2O_2 and other insulating decomposition products on the electrode surface, which block the oxidation of the RM at the electrode. Moreover, RMs often introduce side reactions that may limit performance and can contribute to erroneous conclusions regarding mechanisms. Multiple characterization techniques should therefore be invoked to fully understand their impact [30].

In an interesting recent publication, Bruce et al. showed that using a 2,5-di-*tert*-butyl-1,4-benzoquinone (DBBQ) electrolyte additive can promote solution phase formation of Li_2O_2 in low-polarity and weakly solvating electrolytes; thereby apparently dodging the double-edged sword of high capacity but poor stability of the high AN/DN solvents. Since DBBQ also suppresses the surface reduction to Li_2O_2, this leads to a capacity increase of up to two orders of magnitude [31**]. By utilizing a LiDBBQO$_2$ intermediate, Bruce et al. could bypass the LiO$_2$ intermediate in solution, leading to reduced overpotentials for charge and reduced electrolyte degradation resulting from parasitic side reactions (see Figure 1). Although more work is needed to identify new additive-solvent combinations with improved cyclic performance, the approach shows promise.

Singlet oxygen

The aggressive nature of the strong nucleophiles and bases present in the Li–O_2 battery chemistry, i.e., O_2^-, LiO$_2$, $Li_{2-x}O_2$ and Li_2O_2 species, pose severe challenges

for the stability of electrodes, solvents [32], and salts [33]. It has long been suspected that these reactive species are responsible for the majority of the parasitic reactions that preclude true reversibility, i.e. a perfect 1:1 mapping between the amount of O_2 consumed during discharge with that released during charge (see Figure 2) [34,35•].

A recent discovery by Eichel *et al.*, showing that highly reactive singlet oxygen, $^1O_2$, is evolved upon Li_2O_2 oxidation at potentials above 3.5 V [36••], could change this perception. Eichel *et al.* demonstrated that singlet oxygen plays a crucial role in the electrolyte degradation and carbon corrosion during charging of the Li–O_2 cell. Freunberger *et al.* later documented that singlet oxygen is already produced at the onset of charge and can also be produced via the disproportionation of LiO_2 to Li_2O_2 and $^1O_2$, and that the amount of $^1O_2$ is enhanced in the presence of water impurities [37••]. These interesting findings identify $^1O_2$ as a 'must solve' challenge to achieve reversible cycling by formation/decomposition of Li_2O_2. This discovery opens new research directions in the search for new materials and approaches to improve the stability, e.g. the use of singlet oxygen traps, as discussed by Luntz and McCloskey [35].

Next-generation Li–O_2 electrolytes
Multiple strategies have been proposed to overcome limitations associated with electrolyte stability, including use of alternative electrolyte compositions employing ionic liquids (IL), polymers [38], IL-polymer composites [39], and hybrid solid–liquid electrolytes [40,41]. Following the initial promise of ILs [42,43], subsequent differential electrochemical mass spectrometry (DEMS) studies showed that their stability was ultimately insufficient for practical applications [44,45]. Using a nitrate-based molten salt electrolyte (i.e., an eutectic mixture of $LiNO_3$ and KNO_3), Addison and co-workers, however, recently showed very low charge/discharge overpotentials and enhanced rate capability, due to improved stability and moderate solubility of Li_2O_2 in this electrolyte. Although promising, the observed capacity loss during cycling was still too high for practical applications [46••].

The use of hybrid solid–liquid electrolytes and all-solid-state electrolytes is also being actively pursued [47]. In an interesting recent study, Luo *et al.* used *in situ* environmental transmission electron microscopy to study the Li–O_2 reaction mechanisms in a solid Li_2O electrolyte, yielding valuable insight about the formation and transient disproportionation of metastable LiO_2 in solid electrolytes [48••]. Further progress in the field of solid-state electrolytes is needed, both in terms of increased solubility of the oxygen reduction species and improved electrolyte conductivity [49]. Substantial improvements are being made in the latter area, e.g., through use of garnet ceramic electrolytes like LLZO ($Li_7La_3Zr_2O_{12}$) [50–53] and nano-structured composite electrolytes [54],

Figure 2
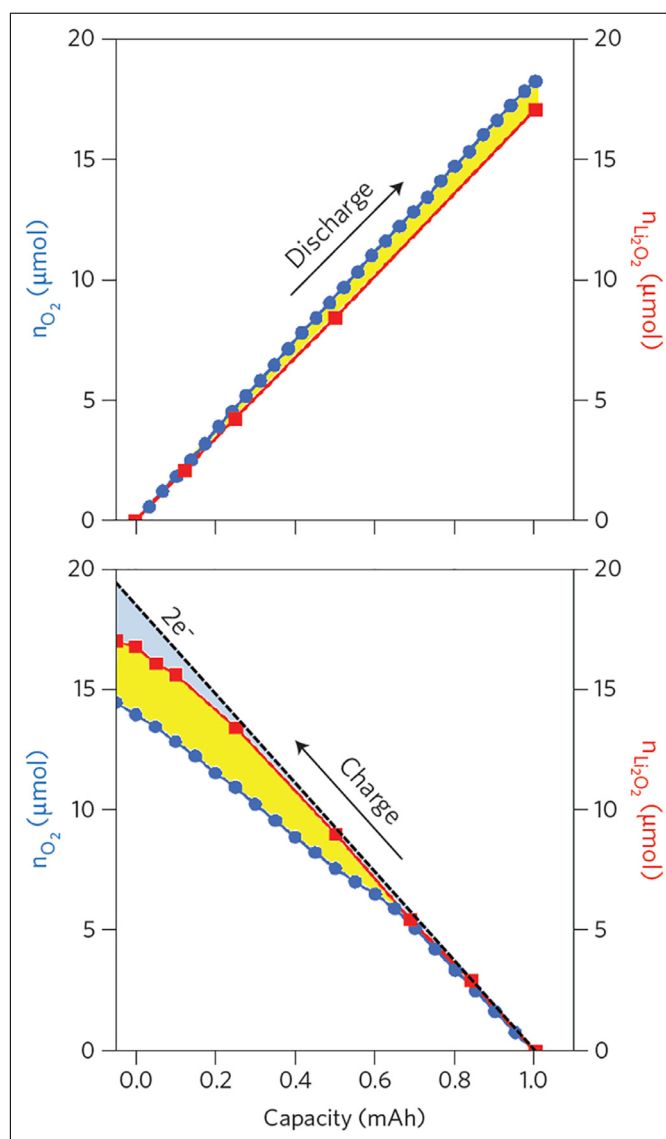
Deviation from a truly reversible Li–O_2 electrochemistry. Top panel: number of moles of O_2 consumed (n_{O_2}, blue) and of Li_2O_2 formed ($n_{Li_2O_2}$, red) during a 1 mAh Li–O_2 discharge. The ideal line for two electrons per O_2 consumed is indistinguishable from the blue points. Bottom panel: number of moles of O_2 evolved (n_{O_2}, blue) and Li_2O_2 consumed ($n_{Li_2O_2}$, red) during recharge of the battery above. The ideal line for $2e^-$ consumption reflects the total charging current. The region in yellow for both discharge and charge reflects the parasitic contribution that could arise from singlet oxygen ($^1\Delta_g$). The region in blue on charge is due to parasitic oxidation of species unrelated to Li_2O_2 and therefore presumably not related to singlet oxygen formation. Reprinted with permission from Ref. [35•]. Copyright 2017 Nature Publishing Group.

but further work is needed to improve performance during battery charging.

Lithium–superoxide batteries
Whereas the related Na–O_2 battery chemistry readily forms sodium superoxide (NaO_2) as the main discharge

product [55,56], stable superoxide products have re-mained elusive in the Li–O$_2$ system. Contrary to the con-ventional behavior of Li–O$_2$ systems, Ammine *et al.* re-cently reported that cathodes based on reduced graphene oxide (rGO) with added iridium (Ir) nanoparticles yield LiO$_2$ as the main discharge product [57$^{\bullet\bullet}$], sparking mas-sive interest. They observed the formation of large rod-like nanoparticles that were identified as LiO$_2$, based on DEMS, high-energy X-ray diffraction (HE-XRD), and electron paramagnetic resonance (EPR) experiments. The DEMS experiments resulted in an e$^-$/O$_2$ ratio of 1.00 (1.02) during discharge (charge), which is the main finger-print of the superoxide formation [57$^{\bullet\bullet}$]. The HE-XRD data is compatible with the DFT-predicted LiO$_2$ crys-talline marcasite structure [58] (no XRD data of LiO$_2$ has previously been reported, as it is an unstable compound). The EPR signal exhibits a peak at g = 2.1019, consistent with the presence of superoxide ions (peroxide ions are silent in EPR).

Ammine and co-workers suggest a complex route for the formation of the LiO$_2$ nanorods: first, the Ir nanoparticles alloy with Li-ions to give rise to Ir$_3$Li nanoparticles; sec-ond, LiO$_2$ nanorods grow epitaxially on top of the Ir$_3$Li substrate. The large size of the nanorods is explained through DFT calculations at the generalized gradient ap-proximation (GGA) level, which showed that LiO$_2$ is a half-metal, allowing the long-range transport of electrons required for the reaction [57$^{\bullet\bullet}$]. The metallic nature of LiO$_2$ is, however, still an open question, since other au-thors have found non-zero bandgaps of 3.6–3.7 [59,60] eV for LiO$_2$ (and 5.3 eV for NaO$_2$ [61]), using higher level theory. Similarly, the measured electrical conductivity of other alkali metal superoxides (KO$_2$, RbO$_2$, and CsO$_2$) is poor [62].

The proposed formation of Ir$_3$Li nanoparticles is not straightforward from a thermodynamic point of view. The enthalpy of alloying per Ir atom in Ir$_3$Li has been calcu-lated as -0.4 eV [63], which is low compared to the exper-imental enthalpy of formation of rutile IrO$_2$, -2.6 eV per Ir atom [64]. Amorphous IrO$_x$ compounds have also been reported to be very stable [65]. Thus, it seems plausible that oxidation of the Ir nanoparticles could occur at the expense of alloying of Ir and Li.

Once IrO$_2$/IrO$_x$ nanoparticles are formed, the subse-quent formation of Li$_2$IrO$_3$ nanostructures is conceiv-able. Indeed, studies by Tarascon *et al.* [66,67] on the electrochemical performance of α-Li$_2$IrO$_3$ and β-Li$_2$IrO$_3$ polymorphs provide an alternative interpretation of the results reported by Ammine *et al.* Early studies showed that α-Li$_2$IrO$_3$ displays some peculiarities with respect to related layered materials. First, α-Li$_2$IrO$_3$ is metallic [68] (rutile IrO$_2$ and amorphous IrO$_x$ are also metallic [65]), which would be compatible with the observation of large nanorods in the experiments from Ammine

Figure 3
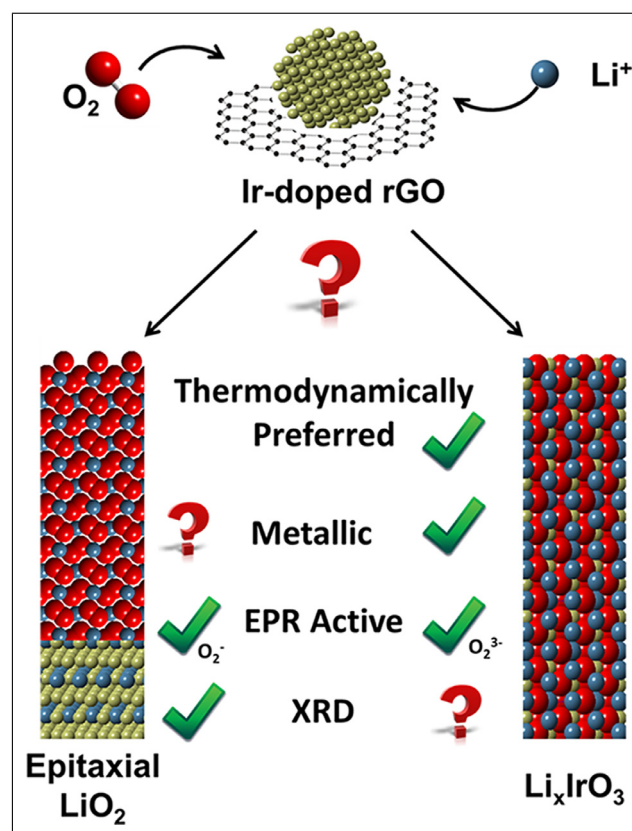
Two possible interpretations of the experiments by Ammine at al. using a reduced Graphene oxide (rGo) doped with iridium nanoparticles as a cathode in Li-O$_2$ batteries. On the left, the original interpretation by Ammine *et al.*, in which epitaxial lithium superoxide nanorods on Ir$_3$Li alloy nanoparticles were hypothesized. On the right, an alternative interpretation based on the formation of lithium iridiate particles. In the middle, the experimental properties which are compatible with each the two interpretations (a question mark means that the compatibility of an experimental property with the corresponding interpretation needs to be investigated).

et al. α-Li$_2$IrO$_3$ decomposes into Li, IrO$_2$ and O$_2$ at a rela-tively low temperature (450 K) [68], which points toward low kinetic barriers for its formation. Furthermore, α-Li$_2$IrO$_3$ can be electrochemically delithiated to Li$_{0.5}$IrO$_3$ [66,69]. Finally, Tarascon *et al.* have shown that the oxidation/reduction of α-Li$_2$IrO$_3$ is very flexible, in the sense that it can happen either at the cations (Ir^{4+} to Ir^{5+}) or at the anions (2$\bullet$O^{2-} to peroxo-like O$_2^{3-}$), which are active in EPR experiments [66]. This last property is shared by the β-Li$_2$IrO$_3$ polymorphs, which can be electrochemically delithiated to give rise to IrO$_3$ [67]. These considerations suggests that a reversible x$\bullet$(Li$^+$+e$^-$+O$_2$) + IrO$_y$ → Li$_x$IrO$_3$ reaction pathway is also compatible with the DEMS, EPR and HE-XRD measurements (see Figure 3).

Aqueous lithium–oxygen batteries

In contrast to the well-studied non-aqueous Li–O_2 cell, where the discharge product is solid Li_2O_2, Liu *et al.* recently demonstrated a system that reversibly cycled LiOH [6•]. Other factors being equal, the formation of LiOH as the discharge product is advantageous, as it is more stable than Li_2O_2, and may therefore suppress parasitic side reactions. The LiOH cell comprised a macroporous rGO positive electrode, and a DME-based electrolyte containing water and LiI. In addition to eliminating reactive Li_2O_2, the LiOH-based cell exhibited extremely high capacities (>20,000 mAh/g_{carbon}) and a discharge-charge voltage hysteresis as low as 0.2 V, corresponding to a round-trip efficiency of 93.2%. The formation of LiOH was claimed to occur via an unusual 4-electron process involving the consumption of water additives in the electrolyte:

$$4Li^+ + 4e^- + O_2 + 2H_2O \rightarrow 4\,LiOH. \tag{a}$$
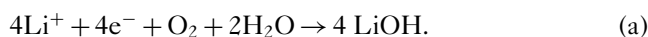
This remarkable performance was attributed to several of factors. First, the LiI additions provide redox mediation through the reaction

$$I_3^- + 2e^- \leftrightarrow 3I^-. \tag{b}$$

Here, I^- is oxidized near the observed charging voltage of 3 V. The resulting I_3^- was proposed to chemically decompose LiOH to water and oxygen gas:

$$4LiOH + 2I_3^- \rightarrow 4Li^+ + 6I^- + 2H_2O + O_2. \tag{c}$$
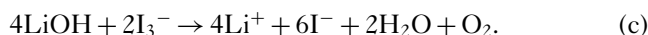
Second, the presence of H_2O and LiI induce the growth of relatively large LiOH particles, contributing to the large observed capacity. Finally, the macroporous rGO support also contributes to the formation of large LiOH particles (tens of microns in diameter), while allowing for rapid diffusion of redox active species.

Liu *et al.*'s report of a reversible LiOH battery has sparked vigorous debate. For example, a pair of technical comments [70•,71•] questioned the possibility of chemical decomposition of LiOH by I_3^-, via reaction (c), which is uphill in free energy and will thus not occur spontaneously, as suggested. This apparent discrepancy is reflected in the more positive equilibrium voltage of reaction (a), 3.4 V under standard conditions, compared to that of reaction (b), 3.0 V. (This voltage trend is the opposite of what is expected for a viable redox mediator, whose redox potential should be slightly more positive than that of reaction (a) being mediated). In their response, Liu *et al.* argued that the non-standard chemical environment of their cell could reduce the voltage of reaction (a) to be closer to the 3.0 V needed for oxidation of I^-. Nevertheless, Liu *et al.* cautioned that "the equilibria that occur in

Figure 4
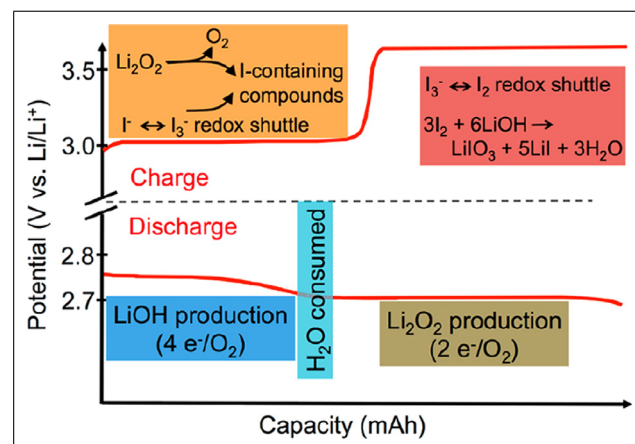
Schematic of the mechanisms associated with discharge and charging of a Li/O_2 cell with LiI and H_2O additives Reprinted with permission from Ref. [74•]. Copyright 2016 American Chemical Society.

the presence of oxygen, water, and iodine are complex..." and "...further mechanistic studies are required to understand the role of these complex equilibria in the redox processes." [72,73].

More recently, Burke *et al.* confirmed the 4-electron process resulting in LiOH formation proposed by Liu *et al.* (reaction (a)) in a cell containing LiI and H_2O [74•]. However, Burke *et al.* were unable to corroborate the charging mechanism proposed by Liu *et al.* Rather, LiOH was observed to decompose at 3.5 V or higher, which is 0.5 V more positive than in Ref. [6•] (see Figure 4). This higher voltage window was observed to coincide with operation of the I_3^-/I_2 couple, and not that of reaction (b). Importantly, LiOH decomposition resulted in the formation of soluble $LiIO_3$, but not O_2 evolution, suggesting that the cell is, unfortunately, not truly reversible. Nevertheless, Burke *et al.* concluded that the electrochemistry in cells with different cathode supports, additives, and electrolyte components should exhibit different, and possibly more promising, behavior. Thus, ample opportunities exist to further explore the composition space of this complex system.

Summary

Although the fundamental mechanisms in the Li–O_2 battery chemistry are becoming increasingly well understood, new insights, interesting concepts, and new challenges continue to emerge. Therefore, we have not yet arrived at the crossroads between commercialization and abandonment.

Several new ideas in the Li–O_2 system have recently emerged, warranting additional research, e.g. the use of additives such as BDDQ, which can help bypass the LiO_2 intermediate and thereby enable more stable electrolytes

like ethers with low DN and combine to yield higher rates, capacity and cycle-life. It is, however, imperative that when new RMs or additives are introduced, careful quantitative analysis and characterization is performed using complementary techniques, as the true origin of a new mechanism may well be hidden under the surface.

An improved understanding of the complexity of the decomposition reactions during charging is still needed. This includes clarifying the exact conditions for generation and suppression of singlet oxygen, and the identification of suitable quenching agents with a sufficiently high electrochemical stability window. These questions appear far more vital than continued investigations of ORR/OER catalysts, which in our opinion have been overemphasized.

Finally, solid or hybrid electrolytes could hold the key to the development of more stable electrolyte strategies, but research for these materials is in its infancy, with many fundamental questions still to be answered.

Acknowledgments

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • Paper of special interest.
- •• Paper of outstanding interest.

1. Abraham K, Jiang Z: **A polymer electrolyte-based rechargeable lithium/oxygen battery**. *J Electrochem Soc* 1996, **143**:1–5.

2. Kuboki T, Okuyama T, Ohsaki T, Takami N: **Lithium-air batteries using hydrophobic room temperature ionic liquid electrolyte**. *J Power Sources* 2005, **146**:766–769.

3. Read J: **Ether-based electrolytes for the lithium/oxygen organic electrolyte battery**. *J Electrochem Soc* 2006, **153**:A96.

4. Web of Science search: Title= "Li-O2 or Lithium-air or Li-oxygen or Lithium-O2 or Li-O-2 or Li-air or Lithium-oxygen or lithium superoxide or lithium peroxide" (Date: 2017-07-05).

5. Lu J, Li L, Park J-B, Sun Y-K, Wu F, Amine K: **Aprotic and aqueous Li−O2 batteries**. *Chem Rev* 2014, **114**:5611–5640.

6. Liu T, Kim G, Carretero-González J, Castillo-Martínez E, Grey CP:
•• **Cycling Li-O2 batteries via LiOH formation and decomposition**. *Science* 2016, **350**:530–533.
Reports on a high reversible cycling capaticycapacity for Li-−O2 by use of LiI additives and H2O.

7. Aetukuri NB, McCloskey BD, Garciá JM, Krupp LE, Viswanathan V, Luntz AC: **Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li–O2 batteries**. *Nat Chem* 2015, **7**:50–56.

8. Knudsen KB, Nichols JE, Vegge T, Luntz AC, McCloskey BD, Hjelm J: **An electrochemical impedance spectroscopy study on the effects of the surface- and solution-based mechanisms in Li–O2 cells**. *J Electrochem Soc* 2016, **9**:A2065–A2071.

9. Kwabi DG, Tułodziecki M, Pour N, Itkis DM, Thompson CV,
• Shao-Horn Y: **Controlling solution-mediated reaction mechanisms of oxygen reduction using potential and solvent for aprotic lithium−oxygen batteries**. *J Phys Chem Lett* 2016, **7**:1204–1212.
Documents the significance of the applied potential on the ratio of the surface to solution-based mechanisms.

10. Aurbach D, McCloskey BD, Nazar LF, Bruce PG: **Advances in understanding mechanisms underpinning lithium–air batteries**. *Nat Energy* 2016, **1**:1–11.

11. Lim H-D, Lee B, Bae Y, Park H, Ko Y, Kim H, Kim J, Kang K: **Reaction chemistry in rechargeable Li-O2 batteries**. *Chem Soc Rev* 2017, **46**:2873–2888.

12. Hummelshøj JS, Blomqvist J, Datta S, Vegge T, Rossmeisl J, Thygesen K, Luntz AC, Jacobsen KW, Nørskov JK: **Communication: elementary oxygen electrode reactions in the aprotic Li-air battery**. *J Chem Phys*, vol 132 2010 071101.

13. Højberg J, Knudsen K, Hjelm J, Vegge T: **Reactions and SEI formation during charging of Li-O2 cells**. *ECS Electrochem Lett* 2015, **4**:A63–A66.

14. Højberg J, McCloskey BD, Hjelm J, Vegge T, Johansen K, Norby P, Luntz AC: **An electrochemical impedance spectroscopy investigation of the overpotentials in Li−O2 batteries**. *ACS Appl Mater Interfaces* 2015, **7**:4039–4047.

15. Viswanathan V, Thygesen KS, Hummelshøj JS, Nørskov JK, Girishkumar G, McCloskey BD, Luntz AC: **Electrical conductivity in Li2O2 and its role in determining capacity limitations in non-aqueous Li-O2 batteries**. *J Phys Chem*, vol 135 2011 214704.

16. Chen J, Hummelshøj JS, Thygesen KS, Myrdal JSG, Nørskov JK, Vegge T: **The role of transition metals interfaces on the electronic transport in lithium-air batteries**. *Catal Today* 2011, **165**:2–9.

17. Radin MD, Monroe CW, Siegel DJ: **Impact of space charge layers on sudden death in Li/O2 batteries**. *J Phys Chem Lett* 2015, **6**:3017.

18. Viswanathan V, Nørskov JK, Speidel A, Scheffler R, Gowda S, Luntz AC: **Li−O2 kinetic overpotentials: tafel plots from experiment and first-principles theory**. *J Phys Chem Lett* 2013, **4**:556–560.

19. Lastra JMG, Myrdal JSG, Christensen R, Thygesen KS, Vegge T: **DFT+U study of polaronic conduction in Li2O2 and Li2CO3: implications for Li-air batteries**. *J Phys Chem C* 2013, **117**:5568–5577.

20. Radin MD, Tian F, Siegel DJ: **Electronic structure of Li2O2 (0001) surfaces**. *J Mater Sci* 2012, **47**:7564.

21. Radin MD, Siegel DJ: **Charge transport in lithium peroxide: relevance for rechargeable metal-air batteries**. *Energy Environ Sci* 2013, **6**:2370.

22. Tian F, Radin MD, Siegel DJ: **Enhanced charge transport in amorphous Li2O2**. *Chem Mater* 2014, **26**:2952.

23. Mekkonen Y, Garcia-Lastra JM, Hummelshøj JS, Chengjun J, Vegge T: **The role of Li2O2@Li2CO3 interfaces on charge transport in non-aqueous Li-air batteries**. *J Phys Chem C* 2015, **119**:18066–18073.

24. Younesi R, Norby P, Vegge T: **A new look at the stability of dimethyl sulfoxide and acetonitrile in Li-O2 batteries**. *ECS Electrochem Lett* 2014, **3**:A15–A18.

25. Chase GV, Zecevic S, Wesley TW, Uddin J, Sasaki KA, Vincent PG, Bryantsev V, Blanco M, Addison DD: **Soluble oxygen evolving catalysts for rechargeable metal-air batteries**. US patent US20120028137 A1 (2012).

26. Chen Y, Freunberger SA, Peng Z, Fontaine O, Bruce PG: **Charging a Li–O$_2$ battery using a redox mediator**. *Nat Chem* 2013, **467**(5):489–494.

27. Bergner BJ, Schürmann A, Peppler K, Garsuch A, Janek J: **TEMPO: a mobile catalyst for rechargeable Li–O$_2$ batteries**. *J Am Chem Soc* 2014, **136**:15054–15064.

28. Kundu D, Black R, Adams B, Nazar LF: **A highly active low voltage redox mediator for enhanced rechargeability of lithium–oxygen batteries**. *ACS Cent Sci* 2015, **1**:510–515.

29. Knudsen KB, Luntz A, Jensen S, Vegge T, Hjelm J: **A redox probing study of the potential dependence of charge transport through Li$_2$O$_2$**. *J Phys Chem C* 2015, **119**:28292–28299.

30. McCloskey BD, Addison D: **A viewpoint on heterogeneous electrocatalysis and redox mediation in nonaqueous Li–O$_2$ batteries**. *ACS Catal* 2017, **7**:772–778.

31. Gao X, Chen Y, Johnson L, Bruce PG: **Promoting solution phase •• discharge in Li–O$_2$ batteries containing weakly solvating electrolyte solutions**. *Nat Mater* 2016, **15**:882–888.
Demonstrates how the use of a homogeneous catalyst for O$_2$ reduction can result in a new solution based mechanism, which may improve capacity and cycle life

32. Yao X, Dong Q, Cheng Q, Wang D: **Why do lithium–oxygen batteries fail: parasitic chemical reactions and their synergistic effect**. *Angew Chem Int Ed* 2016, **55**:11344–11353.

33. Younesi R, Veith GM, Johansson P, Edström K, Vegge T: **Lithium salts for advanced lithium batteries: Li-metal, Li-O$_2$, and Li-S**. *Energy Environ Sci* 2015, **8**:1905–1922.

34. McCloskey BD, Valery A, Luntz AC, Gowda SR, Wallraff GM, Garcia JM, Mori T, Krupp LE: **Combining accurate O$_2$ and Li$_2$O$_2$ assays to separate discharge and charge stability limitations in nonaqueous Li–O$_2$ batteries**. *J Phys Chem Lett* 2012, **4**:2989–2993.

35. Luntz AC, McCloskey BD: **Importance of singlet oxygen**. *Nat • Energy* 2017, **2**:17056.
Outlines the implications of singlet oxygen on the electrolyte and electrode degradation.

36. Wandt J, Jakes P, Granwehr J, Gasteiger HA, Eichel R-A: **Singlet •• oxygen formation during the charging process of an aprotic lithium–oxygen battery**. *Angew Chem Int Ed* 2016, **128**:7006–7009.
Provides the first evidence for the formation of reactive singlet oxygen during charge.

37. Mahne N, Schafzahl B, Leypold C, Leypold M, Grumm S, •• Leitgeb A, Strohmeier GA, Wilkening M, Fontaine O, Kramer D: **Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium–oxygen batteries**. *Nat Energy* 2017, **2**:17036.
Shows that singlet oxygen is formed already at the onset of charge and via disproportionation of LiO$_2$

38. Yi J, Guo S, Heb P, Zhou H: **Status and prospects of polymer electrolytes for solid-state Li–O$_2$ (air) batteries**. *Energy Environ Sci* 2017, **10**:860–884.

39. Amanchukwu CV, Chang H-H, Gauthier M, Feng S, Batcho TP, Hammond PT: **One-electron mechanism in a gel–polymer electrolyte Li–O$_2$ battery**. *Chem Mater* 2016, **28**:7167–7177.

40. He P, Zhang T, Jiang J, Zhou H: **Lithium–air batteries with hybrid electrolytes**. *J Phys Chem Lett* 2016, **7**:1267–1280.

41. Li Y, Wang X, Dong S, Chen X, Cui G: **Recent advances in non-aqueous electrolyte for rechargeable Li–O$_2$ batteries**. *Adv Energy Mater*, vol 6 2016 1600751.

42. Allen CJ, Mukerjee S, Plichta EJ, Hendrickson MA, Abraham K: **Oxygen electrode rechargeability in an ionic liquid for the Li–air battery**. *J Phys Chem Lett* 2011, **2**:2420.

43. Elia GA, Hassoun J, Kwak W-J, Sun Y-K, Scrosati B, Mueller F, Bresser D, Passerini S, Oberhumer P, Tsiouvaras N: **An advanced lithium–air battery exploiting an ionic liquid-based electrolyte**. *Nano Lett* 2014, **14**:6572.

44. McCloskey BD, Bethune DS, Shelby RM, Mori T, Scheffler R,

45. Das S, Højberg J, Knudsen KB, Younesi R, Johansson P, Norby P, Vegge T: **InstaInstability of ionic liquid based electrolytes in Li–O$_2$ batteries**. *J Phys Chem C* 2015, **119**:18084–18090.

46. Giordani V, Tozier D, Tan H, Burke CM, Gallant BM, Uddin J, •• Greer JR, McCloskey BD, Chase GV, Addison D: **A molten salt lithium–oxygen battery**. *J Am Chem Soc* 2016, **138**:2656–2663.
Demonstrates the high potential for use of stable molten-salt electrolytes in Li–O$_2$ batteries

47. He P, Zhang T, Jiang J, Zhou H: **Lithium-air batteries with hybrid electrolytes**. *J Phys Chem Lett* 2016, **7**:1267–1280.

48. Luo L, Liu B, Song S, Xu W, Zhang J-G, Wang C: **Revealing the •• reaction mechanisms of Li–O$_2$ batteries using environmental transmission electron microscopy**. *Nat Nanotech* 2017, **12**:535–539.
Uses *in situ* TEM to reveal the Li–O$_2$ reaction mechanism in a solid electrolyte (in real time)

49. Li Y, Wang X, Dong S, Chen X, Cui G: **Recent advances in non-aqueous electrolyte for rechargeable Li–O$_2$ batteries**. *Adv Energy Mater*, vol 6 2016 1600751.

50. Fu K, Gong Y, Boyang L, Zhu Y, Xu S, Yao Y, Luo W, Wang C, Lacey SD, Dai J: **Toward garnet electrolyte–based Li metal batteries: an ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface**. *Sci Adv*, vol 3 2017 e1601659.

51. Sharafi A, Yu S, Naguib M, Lee M, Ma C, Meyer HM, Nanda J, Chi M, Siegel DJ, Sakamoto J: **Impact of air exposure and surface chemistry on Li-Li$_7$La$_3$Zr$_2$O$_{12}$ interfacial resistance**. *J Mater Chem A* 2017, **5**:13475–13487.

52. Thompson T, Yu S, Williams L, Schmidt RD, Garcia-Mendez R, Wolfenstine J, Allen JL, Kioupakis E, Siegel DJ, Sakamoto J: **Electrochemical window of the Li-ion solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$**. *ACS Energy Lett* 2017, **2**:462–468.

53. Yu S, Schmidt RD, Garcia-Mendez R, Herbert E, Dudney NJ, Wolfenstine JB, Sakamoto J, Siegel DJ: **Elastic properties of the solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)**. *Chem Mater* 2015, **28**:197–206.

54. Blanchard D, Nale A, Sveinbjörnsson D, Eggenhuisen TM, Verkuijlen MHW, Suwarno, Vegge T, Kentgens APM, de Jongh PE: **Nanoconfined LiBH$_4$ as a fast lithium ion conductor**. *Adv Funct Mater* 2015, **25**:184–192.

55. Hartmann P, Bender CL, Vračar M, Duřr AK, Garsuch A, Janek J, Adelhelm P: **A rechargeable room-temperature sodium superoxide (NaO$_2$) battery**. *Nat Mater* 2013, **12**:228–232.

56. Knudsen KB, Nichols JE, Vegge T, Luntz AC, McCloskey BD, Hjelm J: **An electrochemical impedance study of the capacity limitations in Na-O$_2$ cells**. *J Phys Chem C* 2016, **120**:10799–10805.

57. Lu J, Lee YJ, Luo X, Lau KC, Asadi M, Wang H-H, Brombosz S, •• Wen J, Zhai D, Chen Z: **A lithium–oxygen battery based on lithium superoxide**. *Nature* 2016, **529**:377–383.
Reports that formation of a solid LiO$_2$ discharge product can be promoted by use of Ir-nanoparticles on reduced graphene oxide (rGO)

58. Lau KC, Curtiss LA, Greeley J: **Density functional investigation of the thermodynamic stability of lithium oxide bulk crystalline structures as a function of oxygen pressure**. *J Phys Chem C* 2011, **115**:23625–23633.

59. Li S, Liu J, Liu B: **First-principles study of the charge transport mechanisms in lithium superoxide**. *Chem Mater* 2017, **29**:2202–2210.

60. Lee B, Kim J, Yoon G, Lim H-D, Choi I-S, Kang K: **Theoretical evidence for low charging overpotentials of superoxide discharge products in metal–oxygen batteries**. *Chem Mater* 2015, **27**:8406–8413.

61. Yang S, Siegel DJ: **Intrinsic conductivity in sodium-air battery discharge phases: sodium superoxide vs. sodium peroxide**. *Chem Mater* 2015, **27**:3852.

62. Gerbig O, Merkle R, Maier J: **Electrical transport and oxygen exchange in the superoxides of potassium, rubidium, and cesium**. *Adv Funct Mater* 2015, **25**:2552–2563.

63. Fischer CC: *A Machine Learning Approach to Crystal Structure Prediction*. Massachusetts Institute of Technology; 2007.

64. O'Neill HSC, Nell J: **Gibbs free energies of formation of RuO_2, IrO_2, and OsO_2: a high-temperature electrochemical and calorimetric study**. *Geochim Cosmochim Acta* 1997, **61**:5279–5293.

65. Pfeifer V, Jones TE, Velasco Vélez JJ, Massué C, Arrigo R, Teschner D, Girgsdies F, Scherzer M, Greiner MT, Allan J: **The electronic structure of iridium and its oxides**. *Surface Interface Anal* 2016, **48**:261–273.

66. McCalla E, Abakumov AM, Saubanère M, Foix D, Berg EJ, Rousse G, Doublet M-L, Gonbeau D, Novák P, Tendeloo GV: **Visualization of O-O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries**. *Science* 2015, **350**:1516–1521.

67. Pearce PE, Perez AJ, Rousse G, Saubanere M, Batuk D, Foix D, McCalla E, Abakumov AM, Van Tendeloo G, Doublet M-L: **Evidence for anionic redox activity in a tridimensional-ordered Li-rich positive electrode b-Li_2IrO_3**. *Nat Mater* 2017, **16**:580–586.

68. O'Malley MJ, Verweij H, Woodward PM: **Structure and properties of ordered Li_2IrO_3 and Li_2PtO_3**. *J Solid State Chem* 2008, **181**:1803–1809.

69. Kobayashi H, Tabuchi M, Shikano M, Kageyama H, Kanno R: **Structure, and magnetic and electrochemical properties of layered oxides, Li_2IrO_3**. *J Mater Chem* 2003, **13**:957–962.

70. Shen Y, Zhang W, Chou S-L, Dou S-X: **Comment on "Cycling Li-O_2 batteries via LiOH formation and decomposition"**. *Science* 2016, **352**:667-a.
• Proposes an alternative reaction mechanism to account for the observations made by Liu et al. in Ref. [6]

71. Viswanathan V, Pande V, Abraham KM, Luntz AC, McCloskey BD, Addison D: **Comment on "Cycling Li-O_2 batteries via LiOH formation and decomposition"**. *Science* 2016, **352**:667-c.
• Argues that limited-capacity cycling can conceal important parasitic side reactions

72. Liu T, Kim G, Carretero-González J, Castillo-Martínez E, Grey CP: **Response to comment on "Cycling Li-O_2 batteries via LiOH formation and decomposition"**. *Science* 2016, **352**:667-b.

73. Liu T, Kim G, Carretero-González J, Castillo-Martínez E, Grey CP: **Response to comment on "Cycling Li-O_2 batteries via LiOH formation and decomposition"**. *Science* 2016, **352**:667-d.

74. Burke CM, Black R, Kochetkov IR, Giordani V, Addison D, Nazar LF, McCloskey BD: **Implications of 4e$^-$ oxygen reduction via iodide redox mediation in Li$-O_2$ batteries**. *ACS Energy Lett* 2016, **1**:747–756.
• Shows that the presence of LiI and H_2O can promote a 4-electron oxygen reduction to LiOH, but the LiOH is not reversibly oxidized to O_2 on charge