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Controversial Topics on Lithium Superoxide in Li−O_2 Batteries

For years, nonaqueous Li−O_2 batteries have been considered to be a promising candidate for next-generation Li-ion batteries because of their theoretical energy density, which is extremely high compared to those of conventional Li-ion batteries.[1−4] Although the operation of Li−O_2 batteries is based on the simple formation and decomposition of lithium peroxide during the oxygen reduction reactions (ORRs, during discharging) and oxygen evolution reactions (OERs, during charging), their practical application remains unlikely because of two critical issues: low energy efficiency and a short cycle life. Both of these issues are related to the main discharge product, Li_2O_2 (lithium peroxide), which accumulates because of the nonreversible characteristics of its production, resulting in clogged pores and passivation of the cathode surface.[1−4] To solve such problems, it is necessary to elucidate the reaction mechanism related to the discharge products.[5,6]

Depending on the solubility of the electrolyte toward lithium superoxide (LiO_2), which is a known unstable intermediate at room temperature, the amount and morphology of Li_2O_2 can be changed via the route of formation reaction:[7,8] film-type Li_2O_2 is produced by the surface mechanism, while toroidal-type Li_2O_2 is produced via the solution mechanism.[9,10] These two types of Li_2O_2 impart significant differences in the electrochemical performances of a Li−O_2 battery. Film-type Li_2O_2, which precipitates via the surface mechanism, results in fast surface passivation, causing a capacity drop. In contrast, the solution mechanism produces larger toroidal-type Li_2O_2 particles that contact the cathode without causing surface passivation. As a result, the Li_2O_2 formed by the solution mechanism is less influenced by the structure of the cathode, leading to a higher capacity.[5,6,9,10]

In other words, controlling the formation route and morphology of Li_2O_2 based on LiO_2 chemistry is key for Li−O_2 batteries. Recently, studies on LiO_2 have been performed, and the results of various perspectives on the role of LiO_2 have been published.

However, there remain controversial issues that should be discussed related to LiO_2 as (1) a final discharge product and (2) an intermediate material that promotes a side reaction in Li−O_2 batteries, as shown in Figure 1. Therefore, in this Viewpoint, we present these controversial issues related to LiO_2 to facilitate understanding of the contrasting LiO_2-related opinions and identify the right direction for future studies.

LiO_2 as a Stabilized Final Discharge Product in Li−O_2 Batteries. Typically, with its extremely short lifetime at room temperature, LiO_2 is considered to be an intermediate of the ORR in Li−O_2 batteries. However, Li_2O_2 with remaining stable LiO_2 species has been reported, which resembles the $Li_{2-x}O_2$ intermediate with respect to charge.[11−13] These assignments were mostly based on surface-enhanced Raman spectra, which can distinguish O−O stretch vibrations in Li_2O_2 (1505 cm^{-1}) and LiO_2 (1123 cm^{-1}).[13−15]

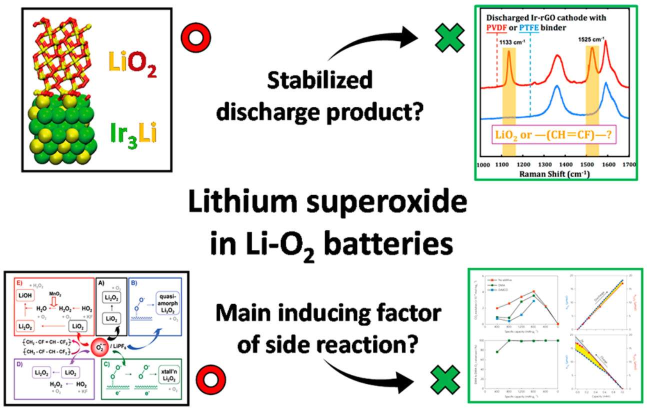

Figure 1. Controversial issues related to lithium superoxide in Li−O_2 batteries. (Reprinted with permission from ref 16, Copyright 2016, Nature; ref 31, Copyright 2017, Nature Energy; ref 32, Copyright 2017, Nature Energy; ref 18, The Journal of Physical Chemistry Letters; and ref 20, Journal of the American Chemical Society.)

Recently, on the basis of reports regarding LiO_2 that have been published to date, a Li−O_2 battery with LiO_2 stabilized by an Ir-rGO cathode as a discharge product was developed by Amine's group, as shown in Figure 2a.[16] They reported that the Ir-rGO cathode can stabilize LiO_2 because the crystallographic lattices of intermetallic Ir_3Li[17] and LiO_2 are similar. Compared to Li_2O_2, LiO_2 decomposes much more readily at a low overpotential during charging; therefore, a Li−O_2 battery based on LiO_2 could be more reversible. However, as shown in Figure 2b, it was recently shown that decomposition of the PVDF binder can lead to peaks that mimic those of LiO_2.[18] Therefore, it is uncertain and problematic to determine that LiO_2 is the final discharge product.

Nevertheless, the concept of controlling LiO_2 as a discharge product is intriguing for the generation of highly efficient and reversible Li−O_2 batteries. Although the discharge capacity of LiO_2 is smaller than that of Li_2O_2, it is possible to increase the energy efficiency and hinder the decomposition of the cathode and electrolyte because LiO_2 decomposes at a lower charge potential.

It is known that uncontrolled, unstable LiO_2 can decompose the cell components;[19,20] however, stabilization of the LiO_2 using a catalyst makes it possible to suppress this side reaction.

Whether LiO_2 can be stabilized as a discharge product has not yet been clarified, and more reliable verification is needed. However, stabilization of LiO_2 by electrode catalysts is a promising method not only to fundamentally solve the irreversibility issue of Li_2O_2 during charging but also to suppress side reactions related to the presence of unstable LiO_2 and

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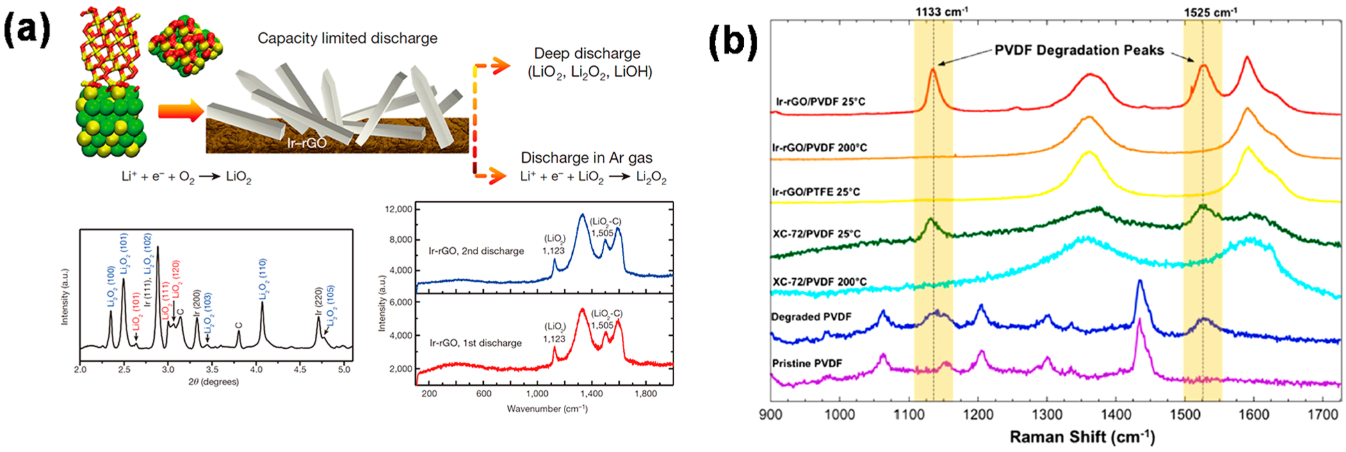

Figure 2. Possibility of LiO_2 as a final discharge product. (a) Schematic showing the lattice match between LiO_2 and Ir_3Li that may be responsible for the LiO_2 discharge product found on the Ir−rGO cathode. HE-XRD pattern and Raman spectra of the discharge product on the Ir−rGO cathode after discharge. (b) Raman spectra of discharged electrodes as well as pristine and alkaline-degraded PVDF pellets. Stable LiO_2 formation via the 1 e^-/O_2 process is not an active discharge reaction in Li−O_2 batteries. (Reprinted with permission from ref 16, Copyright 2016, Nature and reprinted from ref 18, The Journal of Physical Chemistry Letters.)

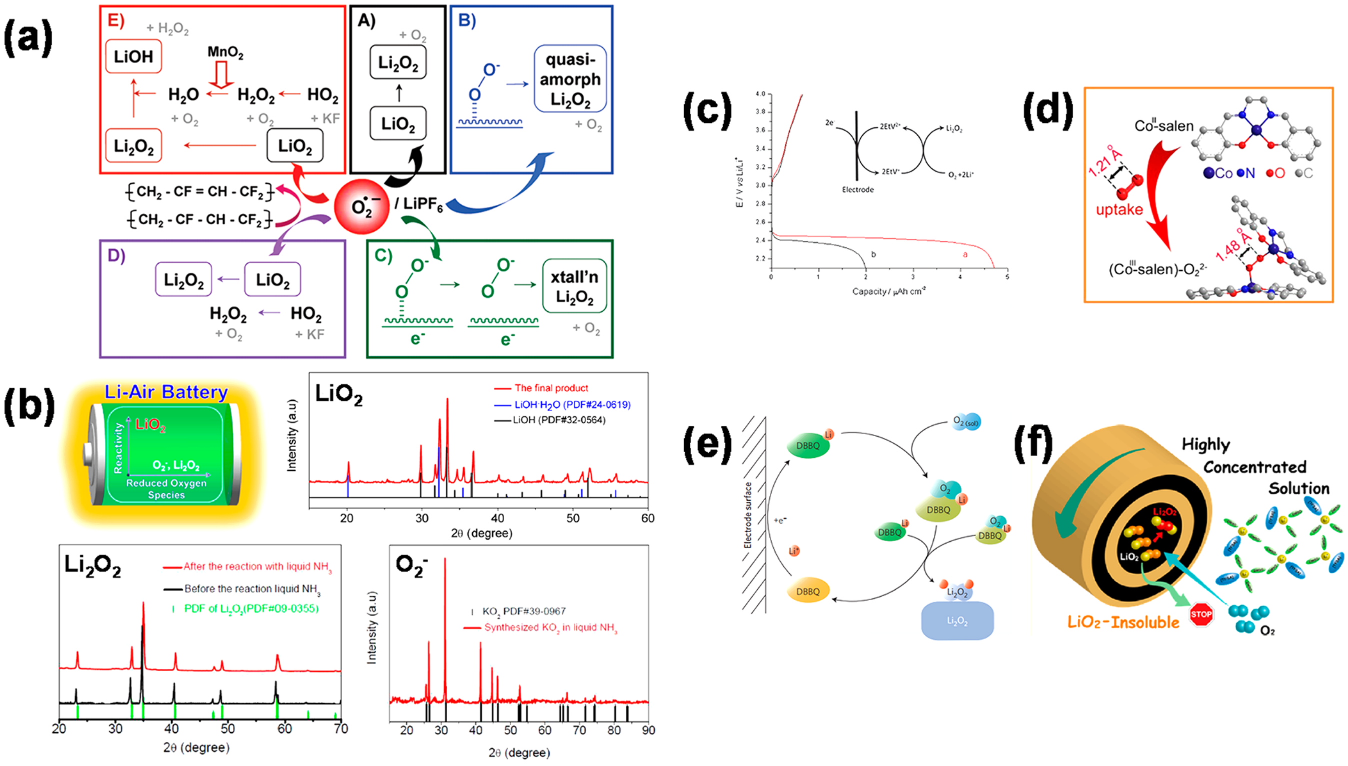

Figure 3. One contributor to the side reactions in Li−O_2 batteries is LiO_2 (O_2^-). (a) Exploratory reactions of superoxide in Li−O_2 batteries. (b) Reactivity of LiO_2 compared to that of Li_2O_2 and O_2^-. (c−f) Strategy for the prevention of LiO_2 formation: (c) redox reaction by ethyl viologen, (d) O_2 transfer by Co^{II}-salen, (e) complex model with Li and O_2 interacting with 2,5-di*tert*-butyl-1,4-benzoquinone, and (f) controlled LiO_2 solubility by a highly concentrated electrolyte. (Reprinted with permission from ref 25, Copyright 2015, Chemical Communications; ref 28, Copyright 2016, Nature Materials; ref 20, Journal of the American Chemical Society; ref 24, The Journal of Physical Chemistry Letters; ref 27, Nano Letters; ref 29, The Journal of Physical Chemistry C.)

high-voltage conditions. Therefore, further research into stabilization of LiO_2 as a discharge product is needed to improve the practicality of Li−O_2 batteries.

LiO_2 as a Main Inducing Factor (Origin) of Side Reactions in Li−O_2 Batteries. Another controversial issue that must be discussed is the reactivity of LiO_2 and the corresponding side reactions. For many years, the poor reversibility of Li−O_2 batteries has been attributed to parasitic side reactions between the cell components (i.e., cathode and electrolyte) and reduced oxygen species (i.e., O_2^-, LiO_2, and Li_2O_2) formed at the cathode during the electrochemical process (Figure 3a).[19−23] To generate stable and reversible Li−O_2 batteries without these side reactions, it is crucial to have a fundamental understanding of the reactivity of the reduced oxygen species formed in Li−O_2 batteries.

Although the reactivity of reduced oxygen species has been studied in depth both experimentally and theoretically, those

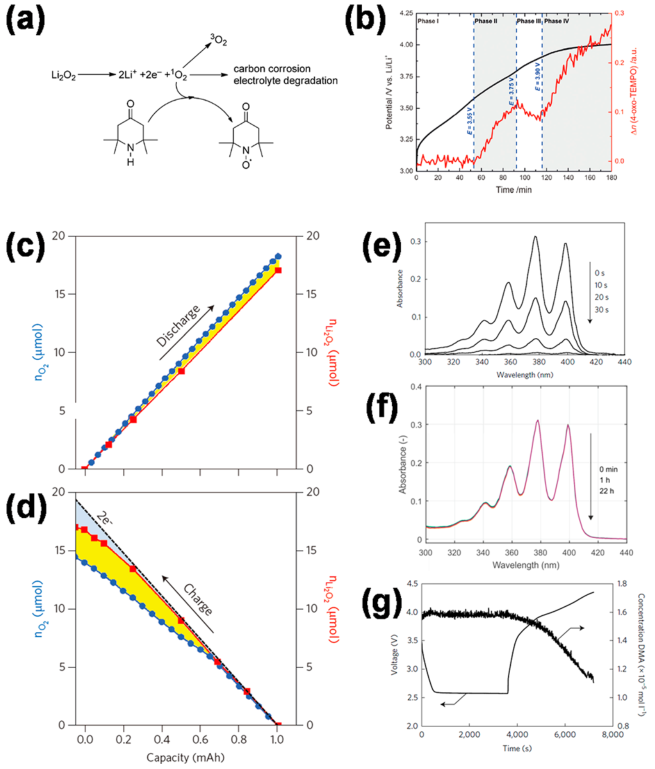

Figure 4. Origin of the side reactions in Li–O_2 batteries is singlet oxygen ($^1O_2$) rather than LiO_2 or O_2^-. (a) Schematic image for scanning the $^1O_2$, which can initiate the side reaction. Reaction of 4-oxo-TEMP with $^1O_2$ forms the stable 4-oxo-TEMPO radical. (b) Voltage profile and EPR signal amplitude of the 4-oxo-TEMPO formed during charging of Li_2O_2 with 0.1 M 4-oxo-TEMP as a spin trap. (c) Number of moles of O_2 consumed (blue) and Li_2O_2 formed (red) during discharging. (d) Number of moles of O_2 evolved (blue) and Li_2O_2 consumed (red) during battery recharging. (e) UV–vis absorption spectra with $^1O_2$ and 9,10-dimethylanthracene (DMA). $^1O_2$ was produced in situ by photogeneration with the sensitizer palladium(II) meso-tetra(4-fluorophenyl)tetrabenzoporphyrin. (f) UV–vis absorption spectra of DMA in contact with KO_2. (g) Operando fluorescence spectroscopy during galvanostatic discharging and charging with DMA as an $^1O_2$ trap. (Reprinted with permission from ref 30, Copyright 2016, Angewandte Chemie; ref 31, Copyright 2017, Nature Energy; ref 32, Copyright 2017, Nature Energy.)

that are strong nucleophiles and primarily destructive to cell components have not yet been clearly identified. Moreover, little is known about LiO_2, which readily decomposes to Li_2O_2 and is thus unavailable under usual laboratory conditions. Recently, Peng's group reported the synthesis of LiO_2 in liquid NH_3 at cryogenic temperatures to investigate the relative reactivity of a variety of oxygen species, as shown in Figure 3b.[24] They concluded that LiO_2 is the most reactive oxygen species in Li–O_2 batteries; thus, it can degrade Li–O_2 batteries.

On the basis of the degradation reactions initiated by superoxide, there are many reported approaches to mitigate this issue, as shown in Figure 3c–f. Owen's group reported that a redox molecule can catalyze the reduction reaction of oxygen to superoxide and superoxide to peroxide after reduction (Figure 3c).[25] Similar to the redox mediator for OER, which oxidizes to decompose Li_2O_2 during charging, ethyl viologen can facilitate and accelerate the ORR reaction and drastically decrease the lifetime of superoxide.

Huang and Chen's groups reported pthalocyanines and Co-salen, respectively, as mobile O_2 carriers[26,27] that bind O_2 before and after reduction to avoid the formation of aggressive superoxide intermediates (O_2^- or LiO_2) that readily decompose the organic electrolyte (Figure 3d).

Bruce's group reported 2,5-di*tert*-butyl-1,4-benzoquinone (DBBQ) as a carrier for Li^+ and O_2 to promote Li_2O_2 formation during discharging.[28] The main focus of this study was increasing the capacity by inducing the solution mechanism for Li_2O_2 formation in ether solvent in which Li_2O_2 is typically formed via the surface mechanism due to its low donor number character; however, another benefit of DBBQ is controlling the reactive soluble LiO_2 to potentially hinder the side reactions (Figure 3e).

Another method reported by Shao-Horn's group is controlling the concentration of electrolyte to decrease the solubility of LiO_2 in the electrolyte. In the highly concentrated solution (~3 M Li salt), LiO_2 is difficult to dissolve because the DMSO molecules are solvating Li^+; this suppresses the side reactions of LiO_2 to generate LiOH (Figure 3f).[29]

However, unlike many previous studies that reported that the side reaction in Li–O_2 batteries is related to reduced oxygen species like LiO_2,[19−29] recent papers have identified singlet oxygen ($^1O_2$) as the suspected origin of the irreversible parasitic reactions in Li–O_2 batteries, as shown in Figure 4.[30−33]

Wandt's group was the first to report the formation of singlet oxygen in Li–O_2 batteries during the charging process.[30] As shown in the schematic image in Figure 4a, 4-oxo-TEMP can trap the $^1O_2$ to form a stable 4-oxo-TEMPO radical, which is detected using operando electron paramagnetic resonance (EPR) spectroscopy. $^1O_2$ formed during charging, which was confirmed in the voltage profile with EPR data (Figure 4b); this correlates well with carbon corrosion and electrolyte degradation in Li–O_2 batteries.

Subsequently, Freunberger's group further elucidated the mechanism of $^1O_2$ generation during the discharge and charge processes and reported that the formation of $^1O_2$ is promoted by moisture.[31] As shown in Figure 4a−d, the occurrences of the production of singlet oxygen, i.e., during discharging, at the onset of charging and during charging at higher voltages correlate well with the extent of the side reactions during discharging and charging of Li−O_2 batteries. By comparative analysis using an $^1O_2$ trap (i.e., 9,10-dimethylanthracene, DMA), which selectively removes $^1O_2$ in a chemical reaction (but not O_2^-) (Figure 4e,f), it was confirmed that $^1O_2$ is produced primarily during galvanostatic charging, which matches well with the degree of the side reactions in Li−O_2 batteries, as shown in Figure 4c,d. Moreover, they suggested the addition of a quencher (i.e., 1,4-diazabicyclo[2.2.2]octane, DABCO), which deactivates $^1O_2$ by physical quenching via a temporary charge transfer complex, as an alternate method to remove $^1O_2$ from Li−O_2 batteries. Physical quenchers are preferable to traps because neither the quencher nor O_2 is consumed in physical quenchers, while traps irreversibly react with $^1O_2$ chemically. However, the suggested quencher, DABCO, is electrochemically unstable at voltages greater than 3.5 V; accordingly, this method would need to be developed with a more stable quencher.

Because reduced oxygen species, such as LiO_2, have been assumed to cause the side reactions in Li−O_2 batteries in many papers (as shown in Figure 3), the idea that $^1O_2$ is the origin of the side reactions is a highly unexpected and innovative result for Li−O_2 batteries. Therefore, many of the approaches to impede the side reaction that were suggested in previous reports should be considered again with a focus on $^1O_2$. In addition, further studies to elucidate the mechanism of the side reaction of the cell components (e.g., carbon cathode, binder, solvent, salt, etc.) with $^1O_2$ are also necessary. We believe that the presence and impact of $^1O_2$ in Li−O_2 batteries will receive significant attention from now on, which might enable vast improvements to this battery system.

In this Viewpoint, we discussed the controversial issues related to LiO_2 including the possibility of LiO_2 as a stabilized final discharge product and main inducing factor (origin) of the side reactions. First, the identification of LiO_2 as a final discharge product is incorrect. Second, the origin of the side reaction was also questioned as $^1O_2$ has been proposed to be the actual cause of the irreversible parasitic reaction in Li−O_2 batteries rather than reduced oxygen species such as LiO_2. Beyond identifying the correct and incorrect conclusions, we expect that the presentation of various perspectives will identify new research directions and contribute to the development of future Li−O_2 batteries. More active debate and discussion of these issues will hopefully lead to a more accurate understanding of the mechanism and fuel advances in Li−O_2 batteries.

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Notes

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