

The mystery of Li_2O_2 formation pathways in aprotic Li– O_2 batteries

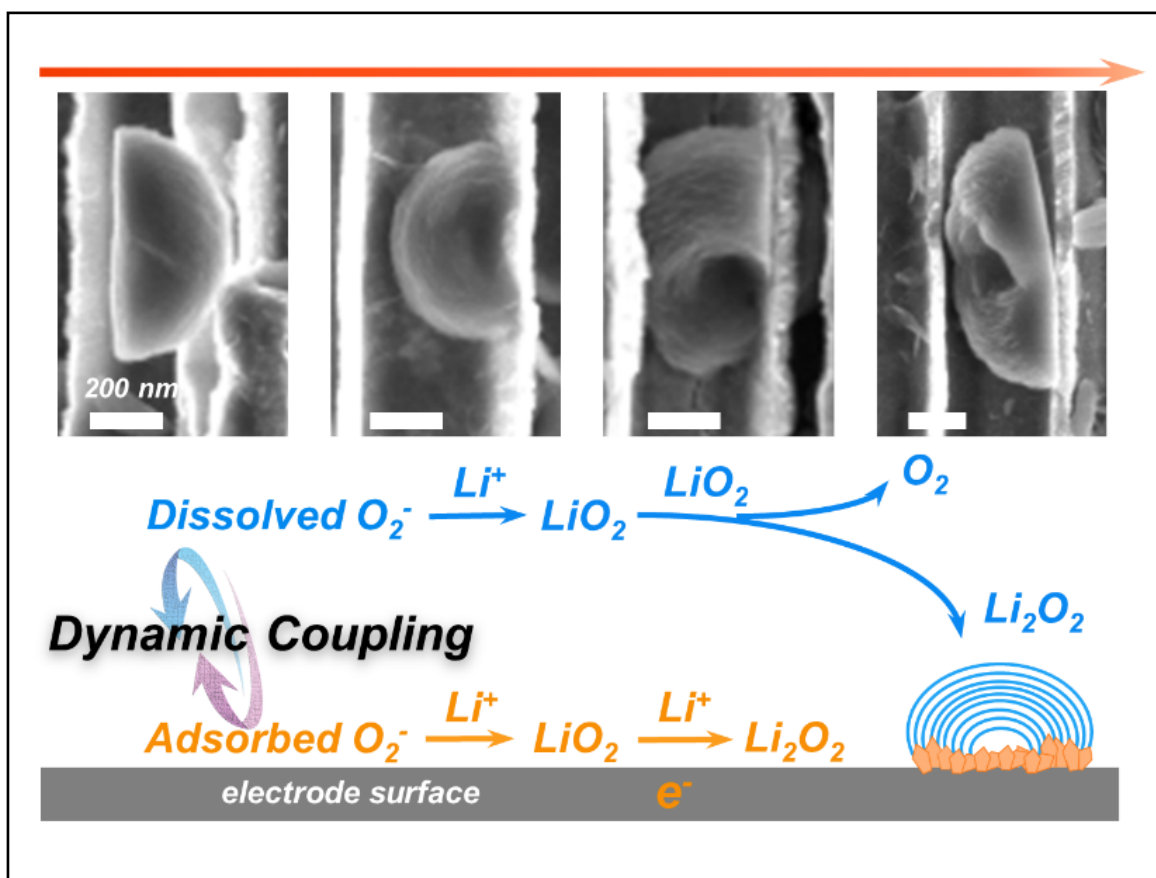
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Graphical abstract



A new possible Li_2O_2 formation pathway may couple the dynamic contribution of the solution and surface pathways.

Public summary

- Reviewing the understanding of Li_2O_2 formation over the past decade, including the variable morphologies, reaction pathways, and reaction interfaces.
- Revealing the nonadaptability of previous theories to the partly observed Li_2O_2 morphologies.
- Proposing a new possible reaction mechanism coupling the dynamic contribution of the solution and surface pathways to reveal the electrode-dependent Li_2O_2 .

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Abstract: The solid-state discharge product Li_2O_2 is closely related to the performance of $\text{Li}-\text{O}_2$ batteries, which exacerbates the concentration polarization and charge transfer resistance, leading to sudden death and poor cyclability. Although previous theories of the Li_2O_2 formation pathway help to guide battery design, it is still difficult to explain the full observed Li_2O_2 behaviors, especially for those with unconventional morphologies. Thus, the pathways of Li_2O_2 formation remain mysterious. Herein, the evolution of the understanding of Li_2O_2 formation over the past decades is traced, including the variable Li_2O_2 morphologies, the corresponding reaction pathways, and the reaction interfaces. This perspective proposes that some Li_2O_2 particles are strongly dependent on the electrode surface as a result of the dynamic coupling of solution and surface pathways and emphasizes a possible mechanism based on previous experimental results and theories. Further methods are expected to be developed to reveal complex Li_2O_2 formation pathways and spearhead advanced $\text{Li}-\text{O}_2$ batteries.

Keywords: $\text{Li}-\text{O}_2$ battery; Li_2O_2 morphology; formation pathway; reaction interface

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$\text{Li}-\text{O}_2$ batteries with high energy density have attracted extensive research attention in recent years. In particular, the aprotic system is investigated most due to its simple structure, which has a lithium negative electrode, separator, and porous positive electrode (air electrode) infiltrated by an organic electrolyte sequentially. During discharging, gaseous oxygen is first dissolved in the electrolyte, then diffuses to the electrode surface driven by the concentration gradient, and reacts electrochemically. The insulated solid discharge product Li_2O_2 is deposited on the boundaries between the electrolyte (liquid) and the active material (solid), which not only covers the active site but also causes electrode blockage, increasing the transport resistance of oxygen and Li ions. For a specific air electrode, the theoretical discharge capacity of a $\text{Li}-\text{O}_2$ battery is thought to be dependent on the maximum amount of Li_2O_2 that can be accommodated in the pores of this electrode. However, the pores cannot be fully utilized before sudden death due to a disrupted reaction interface or a surge in concentration polarization^[1]. As a result, the actual discharge capacity of a $\text{Li}-\text{O}_2$ battery is quite limited. In addition, the properties of the solid product are also intimately associated with the charging performance. Therefore, it is of profound significance to clarify the pathway of Li_2O_2 generation for its effective regulation and enhancement of battery performance.

In early experiments, researchers typically observed two kinds of morphologies of Li_2O_2 : particles (e.g., regular disc^[2], sheet^[2], and toroid^[3]) that are distributed in the electrode pores and films^[4] that completely encompass the electrode surface. The above morphologies have been included in Fig. 1a–d.

The evolution of toroidal Li_2O_2 morphologies with a carbon electrode at $0.1 \text{ mA}\cdot\text{cm}^{-2}$ is shown in Fig. 1e^[5], where the diameter and thickness of the toroids grow disproportionately with the discharge capacity and finally take on an ellipsoidal shape. In addition, when a higher current is applied, the morphology of the toroidal Li_2O_2 will change. Griffith et al.^[6] found that the particle size decreases as the current density increases from $0.1 \text{ mA}\cdot\text{cm}^{-2}$ to $1 \text{ mA}\cdot\text{cm}^{-2}$ using a similar carbon electrode, shifting from typical toroidal particles to needle-like shapes, as shown in Fig. 1e. The growth mechanism was proposed to be a chemical deposition process involving neutral species controlling the dimensions of the Li_2O_2 particles^[6]. Afterward, evidence for LiO_2 as an intermediate product of O_2 reduction was directed, and it was hypothesized that the final product Li_2O_2 came from a disproportionation reaction^[7,8]. For the film-like product, studies focused on how the product achieved electron conduction and how thick the product would cause insulation based on an electron tunneling effect^[9–11].

In response to the formation of these two morphologies, Bruce et al.^[12] suggested that two pathways exist, namely, the surface pathway and the solution pathway. Which pathway will occur depends on the adsorption of LiO_2 to the electrode surface and its solubility in the solution. The reaction processes are illustrated in Fig. 2a. This theory explains the behavior of Li_2O_2 in different electrolytes and provides guidance for enhancing battery performance. Since then, researchers have begun to tune the trade-off between capacity and reversibility by controlling the reaction pathways. Specifically, the

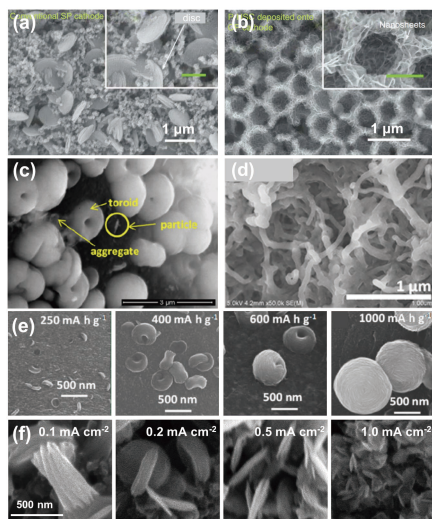


Fig. 1. Typical morphologies of Li_2O_2 : (a) disc; (b) sheet; (c) toroid; (d) film. (b) Reprinted with permission from Ref. [2]. Copyright 2013, Springer Nature Limited. (c) Reprinted with permission from Ref. [3]. Copyright 2015, American Chemical Society. (d) Reprinted with permission from Ref. [4]. Copyright 2016, American Chemical Society. (e) The evolution of toroidal Li_2O_2 morphologies with discharge capacity. Reprinted with permission from Ref. [5]. Copyright 2013, American Chemical Society. (f) The effect of current density on Li_2O_2 particles. Reprinted with permission from Ref. [6]. Copyright 2015, American Chemical Society.

toroidal Li_2O_2 formed by the solution pathway leads to higher capacity but undesired charging performance due to poor contact with the electrode; to obtain a lower charging overpotential and better reversibility, the surface paths can be enhanced. Typically, a high donor-number (DN) solvent enhances the solubility of LiO_2 in solution to promote toroidal Li_2O_2 growth. In addition to electrolyte replacement, electrode optimization methods are summarized to regulate the Li_2O_2 formation pathway: (i) Load efficient catalysts. For example, RuO_2 commonly used in $\text{Li}-\text{O}_2$ batteries transforms the toroid into a film via the surface pathway, significantly enhancing battery reversibility and even the formation of amorphous Li_2O_2 ^[5,13]. (ii) Carbon electrode surface modification. Increasing the content of oxygen-containing functional groups^[14] (e.g., C–O, C=O, and COO^-) or elemental doping^[15] (e.g., N and S) on the electrode surface can enhance the adsorption of LiO_2 . (iii) Control the subnanometer surface structure on the air electrode. Lu et al.^[16] precisely deposited size-selected Ag_n ($n = 3, 9, 15$) clusters on the carbon surface, where Ag_{15} exhibited the highest capacity and crystalline nanoparticles under the same conditions. The capacities of Ag_9 and Ag_3 decrease sequentially, showing elongated nanoparticles or nanorods and crystalline flat plates, respectively. According to the above theory and method, some new systems have been developed, such as batteries with LiO_2 as the discharge product, through a superior route^[17,18].

Although this theory seems to explain some phenomena in

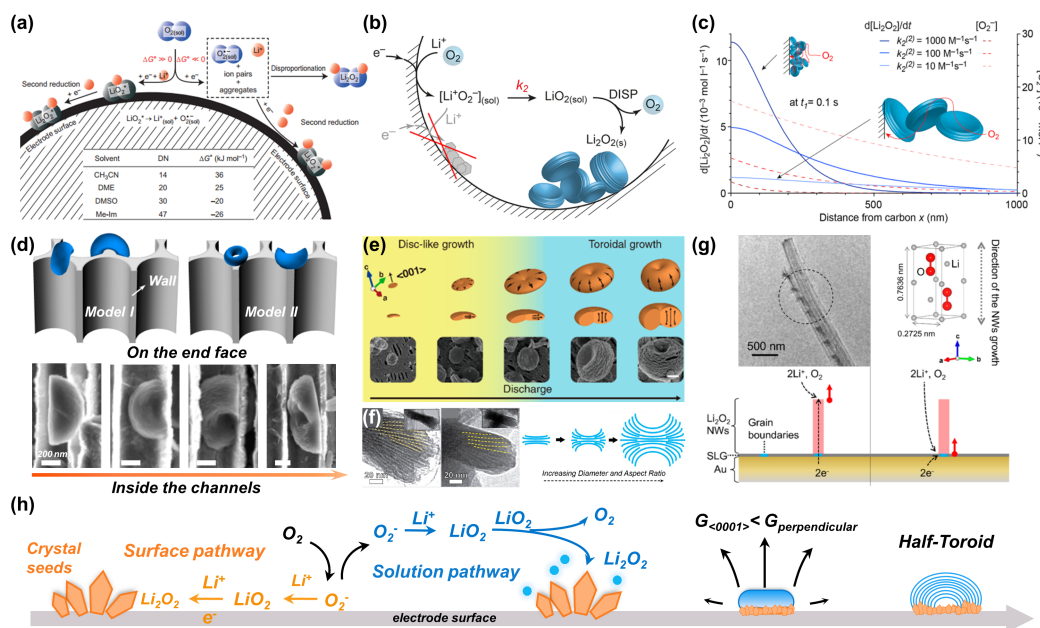


Fig. 2. Reaction pathways and growth models of Li_2O_2 . Schematic illustration of (a) the dual pathway (solution and surface pathways) and (b) the single solution pathway controlling Li_2O_2 formation. (a) Reprinted with permissions from Ref. [12]. Copyright 2014, Springer Nature Limited. (b) Reprinted with permissions from Ref. [20]. Copyright 2022, The Authors. Published by American Chemical Society. (c) Li_2O_2 formation rate and O_2^- concentration versus normal distance from the electrode surface via (b): Fast association (high k_2 , dark blue curve) causes fast Li_2O_2 formation close to the surface, steep O_2^- concentration gradients, high near-surface nucleation rates and a large number of small particles. Slow association (low k_2 , light blue curve) results in few, larger particles up to larger distances. Reprinted with permissions from Ref. [20]. Copyright 2022, The Authors. Published by American Chemical Society. (d) Irregular and surface-dependent particles on the end face and inside the channels of the C-AAO electrode. Reprinted with permission from Ref. [22]. Copyright 2022, American Chemical Society. The growth evolution of Li_2O_2 is proposed via different reaction pathways: (e) two consecutive stages of a toroidal and (f) its layer-by-layer growth model by the solution pathway; (g) the growth of Li_2O_2 nanowires (NWs) toward the $\langle 0001 \rangle$ direction by the surface pathway. (e) Reprinted with permissions from Ref. [24]. Copyright 2019, American Chemical Society. (f) Reprinted with permissions from Ref. [23]. Copyright 2013, American Chemical Society. (g) Reprinted with permission from Ref. [25]. Copyright 2020, American Chemical Society. (h) The possible growth process of half-toroids via a dynamic coupling mechanism.

the battery and has been considered a guideline to design electrodes or electrolytes for a long time, it is still difficult to correspond to the fully observed Li_2O_2 behaviors. First, based on the solution pathway, Li_2O_2 particles should be well crystallized and form regular shapes, while irregular morphologies are widely observed. Second, for a defined combination of electrolytes and electrodes, both reaction pathways are presented simultaneously in most cases^[19]. Recently, a new study by Prehal et al.^[20] concluded that the surface pathway is completely absent and that the solution pathway is the only pathway, as illustrated in Fig. 2b. They thought that the LiO_2 solvation energy is enhanced by increasing the rate to form associated $\text{LiO}_{2(\text{sol})}$ in the dissociation/association equilibrium ($\text{Li}^+_{(\text{sol})} + \text{O}_2^-_{(\text{sol})} \rightleftharpoons \text{LiO}_{2(\text{sol})}$) rather than the desorption/adsorption equilibrium between the electrode and solution ($\text{Li}^+_{(\text{sol})} + \text{O}_2^-_{(\text{sol})} \rightleftharpoons \text{LiO}_2^*$). Based on this premise, weakly solvating low DN electrolytes shift the dissociation equilibrium toward associated $\text{LiO}_{2(\text{sol})}$, in turn increasing the association rate constant k_2 . Additionally, superoxide was measured to have a faster disproportionation rate in electrolytes with low DN. Thus, the concentration distribution of superoxide determines the Li_2O_2 formation rate. The nucleation density and size of Li_2O_2 with different DN electrolytes and current densities can be explained by Fig. 2c. Assuming that such a mechanism of Li_2O_2 formation controlled by a single solution pathway is true, species transport (O_2 , LiO_2 , O_2^- , and Li^+) through the deposited Li_2O_2 is the only factor limiting the discharge capacity, and studies on Li_2O_2 film thickness, conductivity, and crystallinity are nonessential.

However, the conclusion seems to be contradicted by some experimental results: (i) Li_2O_2 film does provide a reaction interface for the second single electron transfer. Chen et al. used a rotate ring-disk electrode to exclude Li_2O_2 from disproportionation and deposit a dense Li_2O_2 film with a thickness of ~ 7 nm close to the ultimate transfer thickness^[21]. Time-of-flight secondary ion mass spectrometry is a powerful tool for tracking reactive interfaces, by which a final sandwich structure of $\text{Li}_2^{18}\text{O}_2|\text{Li}_2^{16}\text{O}_2|\text{Li}_2^{18}\text{O}_2$ was confirmed after the electrode alternately discharged into $^{16}\text{O}_2$ and $^{18}\text{O}_2$. The 25% $\text{Li}_2^{18}\text{O}_2$ was identified to be contributed by the Li_2O_2 /electrolyte interface. (ii) Many Li_2O_2 particles observed in the experiments are irregular or even half-toroidal, which is difficult to explain by the growth rule of minimum surface energy alone. Recently, we observed the growth of toroidal Li_2O_2 inside and on a carbon-coated anodic aluminum oxide (C-AAO) air electrode with highly ordered channels, as shown in Fig. 2d^[22]. On the end face with the honeycomb structure, the toroidal Li_2O_2 is incomplete and hugs the wall. While inside the channel, some Li_2O_2 shows only half a toroid, such as a “snail” shape clinging to the wall, and some are even half-disc. The above phenomena that the morphology of Li_2O_2 particles shows a strong dependence on the electrode surface is common and not accidental. The half-disc is perhaps the primary stage of the half-toroid, as the formation of a typical toroid after a disc has grown to a certain extent has been demonstrated^[23,24]. Park et al.^[24] revealed the evolution of a toroid composed of two consecutive stages using in situ liquid-phase transmission electron microscopy observations: initial lateral growth into the disc and subsequent vertical growth into the toroid, as

shown in Fig. 2e. During asymmetric vertical growth, the toroidal Li_2O_2 crystallites are indicated to grow by a layer-by-layer mechanism and be dominated by a large (0001) crystal face (Fig. 2f)^[23]. Thus, the half-toroid particles inside the channels of the C-AAO electrode may grow in the direction of the arrow in Fig. 2d.

Since toroidal and film-like Li_2O_2 coexist, why would a Li_2O_2 particle not be the product combining the two morphologies? We speculate that the irregular Li_2O_2 particles are the result of the dynamic coupling of the surface and solution pathways. Epitaxial growth is a possible reason for the Li_2O_2 particles attaching to the electrode surface. Uosaki et al.^[25] found that crystalline Li_2O_2 nanowires (NWs) preferentially grow along the c -axis at the grain boundaries (GBs) of a gold electrode covering single-layer graphene (SLG), with lengths up to 80 μm , as shown in Fig. 2g. Similarly, a few micron-long nanorod and nanowire morphologies were observed by Li et al.^[26]. For a complete toroid, Lu et al.^[27] suggested that the new deposition starts from the top edge of the discharge product, implying disproportionation reactions at the Li_2O_2 /electrolyte interface. Hence, we propose a new reaction pathway to explain the formation of half-toroids, as illustrated in Fig. 2h. During the early growth period, the surface pathway at the Li_2O_2 /electrode interface leads to crystal seeds on the electrode surface and preferential growth in one direction. Li_2O_2 at this stage is formed completely by electrochemical processes and can maintain a tight connection with the electrode. As the discharge proceeds, the increasing LiO_2 in the solution bulk disproportionates around the above Li_2O_2 rudiments via solution pathways and minimizes the total surface energy. Previous reports have shown that the total surface energy in the $\langle 0001 \rangle$ direction is higher than that perpendicular to $\langle 0001 \rangle$ at the early discharging stage^[24], as a result of which half-toroidal Li_2O_2 is formed initially and expands laterally. Then, the new Li_2O_2 grows heterogeneously in layers at the edges and center of the half-disc and forms a final half-toroid. Consequently, attachment to the electrode surface and toroidal morphology are exhibited concurrently. The predominant growth direction of Li_2O_2 and the dynamic contribution of the two pathways to the irregular Li_2O_2 particles could be correlated with the electrode material and structure, electrolyte DN, and growth degree. For example, in the case of NWs, the inertness of the basal plane (non-GBs) on the SLG/Au surface is not favored for the lateral growth of Li_2O_2 . In addition, the growth of Li_2O_2 is probably kinetically controlled. Thus, the oxygen conditions and temperature affect the dominant growth of Li_2O_2 ^[24,25,28]. One view is that the low oxygen diffusive condition leads to the high frequency of ledges and kinks in the peripheral regions of the particles, based on which the increased divergence of the surface energy contributes to the inhomogeneous expansion of the particles^[24]. A first-principles study indicated that preferential growth in the $\langle 0001 \rangle$ direction was favored in a Li-rich and oxygen-poor environment, and in this case, the energy of the (0001) surface of the Wulff shape was increased, while (1120) remained constant^[28].

Although great efforts have been devoted to the in situ and ex situ observations of Li_2O_2 , the reaction mechanisms and growth models of Li_2O_2 are still a mystery. More experiment-

al and theoretical approaches are expected to be developed to reveal these complex processes and provide guidance for the design of advanced Li–O₂ batteries toward practical applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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