Understanding the Effect of Solid Electrocatalysts on Achieving Highly Energy-Efficient Lithium–Oxygen Batteries

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Nonaqueous lithium–oxygen (Li–O₂) batteries are regarded as a promising electrochemical energy storage technology because of largely defeating commercial Li-ion batteries on theoretical energy density. However, due to the electrically insulating property of Li₂O₂, a typical discharge product in Li–O₂ batteries, high overpotential is inevitable upon charge. Nonetheless, catalysts could regulate the electrochemical formation pathways of Li₂O₂, and its morphology is closely bound with the energy required to dissociate. Meanwhile, in addition to Li₂O₂, alternative discharge products with inherently low dissociation energy can be produced by specific catalysts. Here, fundamental oxygen reduction routes in Li–O₂ batteries are focused on, catalyst-dependent geometry formation of Li₂O₂ is presented, and geometry-related charge kinetics are discussed. Products formed under specific catalysts are further explored with an emphasis on LiO₂. Future directions to in situ study the electrocatalytic mechanism are subsequently proposed, and an energy system design based on oxygen redox reactions is conceived to provide new perspectives for future electrochemical energy technologies.

1. Introduction

The nonaqueous lithium–oxygen (Li–O₂) battery, as a promising electrochemical energy storage technology, has generated great research interest for decades due to its considerably high theoretical energy density. With the lightest metal, lithium, as the anode, and the readily available gas O₂ as the cathode, Li–O₂ batteries deliver a theoretical energy density as high as ≈3450 Wh kg⁻¹ according to the reversible electrochemical reaction equation (Equation (1)), which is about six times that of commercial LiCoO₂-based Li-ion batteries (≈580 Wh kg⁻¹).[1]

\[
2\text{Li} + \text{O}_2 = \text{Li}_2\text{O}_2, \quad \Delta E = 2.96 \text{V versus Li}^+ / \text{Li}
\]  

However, the development of Li–O₂ batteries faces several issues, such as low energy efficiency, poor rate capability, and limited cycle life.[2] Apart from the instability of the organic electrolyte and lithium anode caused by the chemical attack from oxygen-based species (e.g., superoxide radicals or singlet oxygen), the issue is closely related to the sluggish kinetics of the oxygen reduction reaction (ORR, the charge process) and oxygen evolution reaction (OER, the charge process), which highly depends on the electrical transport property of Li₂O₂.[2b] Though charge transport on Li₂O₂ is critical to the electrochemical performance of Li–O₂ batteries, Li₂O₂ is somewhat electrically insulating with an intrinsically large bandgap of 4.2–4.5 eV.[3] Moreover, with the increase of particle size and film thickness, the electrical transport capability of Li₂O₂ becomes worse.[4] Therefore, a high charge overpotential (>1.0 V) is typical for Li₂O₂ dissociation during the OER process, directly leading to extra energy consumption and parasitic reactions, resulting in the degradation of battery performance.[2b,5]

To tackle the aforesaid hurdles, researchers have primarily focused on designing efficient solid electrocatalysts to improve reaction kinetics in the cathode. In general, the solid catalysts could promote the ORR in different pathways: One is tuning the Li₂O₂ formation routes to induce different physical geometries (e.g., disc/toroid/sphere/flower-like particles and film-like morphology);[4b,4c,6] another is changing the cell chemistry to form easily degradable products, such as LiO₂, rather than Li₂O₂.[7] As the physical geometry and chemical composition of the discharge products are closely related to the energy to initiate product dissociation during the OER, morphology and composition control of discharge products via catalyst optimization is undoubtedly important in lowering the charge overpotential and enhancing the electrochemical performance of Li–O₂ batteries.[8] Therefore, to advance Li–O₂ technologies, it is necessary to understand how catalysts affect the formation of products with a specific geometry and composition during the ORR, and to correlate the product nature with electrochemical performance.[4a,9]
In this short Review, fundamental electrochemical reaction routes in Li–O2 batteries on the ORR are presented, along with the application of solid electrocatalysts. In particular, we focus on 1) discussing the effect of catalysts on the formation of particle-like and film-like Li2O2 during discharge and demonstrating the geometry-dependent charge reaction kinetics and 2) presenting alternative discharge products (such as lithium superoxide, LiO2) formed under specific catalysts, with an emphasis on the formation/dissociation mechanism. Future directions for further catalytic mechanism study in Li–O2 batteries and energy system design derived from oxygen-based reaction are subsequently proposed, thus to provide a new perspective in the development of electrochemical energy storage technologies.

2. Li2O2 Formation Pathways

A typical electrochemical reaction in nonaqueous Li–O2 batteries follows Equation (1): The forward describes the discharge reaction with oxygen reduction to form Li2O2, and the reverse describes the charge reaction with Li2O2 decomposition to release oxygen. In general, two pathways are commonly recognized during the formation of Li2O2 on discharge, i.e., the solution-mediated pathway and surface-mediated pathway.\[10]\]

Upon discharge, Li2O2 is formed as an intermediate either in the electrolyte (Equation (2)) or on the electrode surface (Equation (4)), which can be classified as soluble LiO2(sol) or surface-adsorbed LiO2(ads), respectively.\[4b,11]\]

For the solution-mediated pathway, particle-like Li2O2 with disc/toroid/sphere/flower geometry would be generated by the disproportionation reaction of LiO2(sol), simultaneously releasing oxygen (Equation (3))\[6,10a,10c]\]. In the solution-mediated pathway, LiO2(sol) is more likely to dissolve into the electrolyte, leaving the cathode surface continuously exposed, and thus a larger discharge capacity can be achieved than that in the surface-mediated pathway, where the cathode would be covered by intermediates/products to obstruct discharge reactions from going on.\[12]\] As for the solution-mediated pathway, two issues related to parasitic reactions cannot be ignored. First, similar to the OER process where oxygen is evolved, singlet oxygen (1O2; oxygen in its first excited state) as well as triplet oxygen (3O2; the most common and stable oxygen in its ground state) may be formed during the solution-mediated pathway.\[13]\] 1O2 is considered to be one of the possible culprits for parasitic reactions: In glyme-based electrolytes, ROOH, R, and ROO− would be generated via 1O2-induced electrolyte degradation.\[13]\] In addition, due to the inherent electrically insulating property of Li2O2, the difficulty to decompose Li2O2 increases with the increasing of particle size. High potential is required to decompose the large-sized Li2O2 formed during the solution-mediated pathway, and thus parasitic reactions including electrolyte degradation and cathode decomposition may be inevitable. As for the surface-mediated pathway, Li2O2 is the primary product (Equation (5)).\[10a,10c]\] The Li2O2 generated by the surface pathway has a film-like geometry, which is more likely to degrade during charge compared to particle-like Li2O2.\[12a,4b,11]\]

\[
\text{LiO}_2\text{(sol)} + \text{LiO}_2\text{(sol)} \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 / ^1\text{O}_2 \tag{3}
\]

**Surface-mediated pathway**

\[
\text{O}_2 + e^- + \text{Li}^+ \rightarrow \text{LiO}_2\text{(ads)} \tag{4}
\]

\[
\text{LiO}_2\text{(ads)} + e^- + \text{Li}^+ \rightarrow \text{Li}_2\text{O}_2 \tag{5}
\]

The formation pathway of Li2O2 is deeply related to the solvation capability of Li2O2 in the electrolyte. The solution-mediated pathway to form large-sized Li2O2 can be promoted in the following ways: 1) applying high donor number (DN) solvents\[14]\] to stabilize O2− in the electrolyte, 2) adding high acceptor number (AN) additives\[12a]\] to enhance dissolution of Li2O2(ads) adsorbed on the electrode surface, and 3) controlling the discharge process at a low rate.\[11]\] In addition to the effect from the solvents or additives, even in the conventional electrolyte, 1 M bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME), different morphologies of Li2O2 could also be obtained by using different catalysts\[4b,4c]\] suggesting that catalysts with certain properties can induce Li2O2 formation through different routes, and thus to affect the charge process, especially to influence the charge overpotential. Here, we will discuss the effects of catalysts on the formation route/geometrical shape of Li2O2 during the ORR.

3. Catalyst Effect on the Geometry of Li2O2

The morphological parameters such as shape and thickness of Li2O2 are expected to crucially influence electrochemical performance, including discharge capacity, charge overpotential, and cyclability.\[13]\] Various morphologies of Li2O2 have been widely observed in ether-based electrolytes in previous studies, including particles in the shapes of discs,\[6,10a,10c]\] toroids,\[4b,12a,17]\] spheres,\[13c]\] or flowers,\[5a]\] and thin film with rough surface.\[4a,19]\] The relationship between the geometry of Li2O2 and the electrochemistry was early discussed by Shao-Horn et al.\[4a]\] Using carbon nanotubes (CNTs) as the catalyst, small particles (<20 nm) and large discs (50–200 nm) are obtained at high and low discharge rates, respectively. Interestingly, small particles exhibit much lower overpotential than that of larger discs in the charging profiles. Similar phenomena have been broadly reported\[4a,4b,20]\] as smaller size can facilitate mass and electrical transport on Li2O2, thus generating fast kinetics of the OER. Apart from the effect of visualized geometries, Shao-Horn et al. found that surface oxygen of Li2O2 with different morphologies exhibits different electronic features, which could intrinsically influence the product decomposition upon charge.\[4a]\] Now that the electrochemical processes in Li–O2 batteries, especially the charging reaction, are closely related to the product geometry, it is essential to obtain insights into catalyst-dependent product formation.

As known, various cathode catalysts, such as carbon materials,\[11]\] noble metals,\[22]\] and metal oxides,\[20,23]\] have been demonstrated to reduce the charge overpotential in Li–O2 batteries. Although the behavior of catalysts varies in different electrolyte systems, their influence on product formation is undoubtedly linked to the physicochemical properties, including the surface structure of crystalline catalysts, optimized density distribution,

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**Equation (1):**

\[
\text{Li}_x\text{O}_2 + \text{e}^- \rightarrow \text{Li}_x\text{O}_2\text{(ads)} + \text{Li}^+ \tag{1}
\]
and the local electronic structure of catalytic sites. In addition to the regulation of intrinsic properties, electrochemical reaction routes and the product geometry can also be tuned with the aid of external driven force (e.g., photofield, thermal field, and magnetic field).\(^{24}\) Especially, photoassisted electrocatalysis will be specially presented and discussed as follows.

### 3.1. The Effect of Surface Structure

The role of exposed surfaces of crystals in many catalytic fields has been in depth studied, especially in the field of photocatalysis. For example, the early study on facet-dependent catalytic activity of anatase TiO\(_2\) shows that due to face-specific electron trapping, the probe molecule is preferentially located and reduced on \{101\} facets rather than \{001\}.\(^{25}\) Similarly, in Li-O\(_2\) systems, ORR and OER activation energies can be effectively regulated via the close interaction between exposed surfaces of catalysts and surrounding species (e.g., electrolyte and O\(_2\)), and thus affect the formation of Li\(_2\)O\(_2\) with specific geometry.

To figure out the effect of exposed surfaces of catalysts on the product geometry, our group\(^{26}\) designed two kinds of \(\beta\)-MnO\(_2\) crystals dominated by \{100\} and \{111\} facets, respectively (Figure 1a,b). Compared with pure carbon, both kinds of \(\beta\)-MnO\(_2\) crystals can reduce the discharge/charge overpotentials when adopted as the cathode catalyst, where the charge overpotential on \{100\}-dominant \(\beta\)-MnO\(_2\) is smaller than that on \{111\}-dominant \(\beta\)-MnO\(_2\) (Figure 1c). The discharge product catalyzed by \{100\}-dominant \(\beta\)-MnO\(_2\) exhibits a thin-film morphology, whereas the discharge product catalyzed by \{111\}-dominant \(\beta\)-MnO\(_2\) shows a toroidal shape (Figure 1d,e). As discussed in the aforementioned content, Li\(_2\)O\(_2\) formation generally follows two mechanisms: One is to form as thin films on cathode surface via the surface pathway; another is to form into large particles in the shape of discs/toroids/spheres via the solution pathway. It is noticeable that the products formed on \{100\}-dominant \(\beta\)-MnO\(_2\) and \{111\}-dominant \(\beta\)-MnO\(_2\) are governed by the surface pathway and solution pathway, respectively, which is mainly related to the balance between the dissolution of Li\(_2\)O\(_2\) in the electrolyte and its adsorption on catalysts.\(^{7a,12b}\) According to density functional theory (DFT) results (Figure 1f), the adsorption energy of Li\(_2\)O\(_2\) on the \{100\} surface is \(-1.80\) eV, much more negative than that on the \{111\} surface \((-0.77\) eV). It indicates that the \{100\} surface provides stronger binding with Li\(_2\)O\(_2\) than the \{111\} surface, and more Li\(_2\)O\(_2\) can be adsorbed on \{100\}-dominant \(\beta\)-MnO\(_2\) during the ORR process, to thus promote surface formation of Li\(_2\)O\(_2\). Specifically (Figure 1g), the intermediate LiO\(_2\)(ads) formed via Equation (4) adsorbs on the \{100\} surface and then is reduced by the second electron to form thin-film-like Li\(_2\)O\(_2\) (Equation (5)). \(\beta\)-MnO\(_2\) dominated with \{111\} facets facilitates the solution pathway, where the intermediate LiO\(_2\)(ads) formed though Equation (2) prefers to dissolve in the electrolyte, and subsequently transforms into Li\(_2\)O\(_2\) toroids through disproporionation (Equation (3)). The geometry of Li\(_2\)O\(_2\) regulated by the crystal surface has a direct influence on the charge overpotential, mainly due to the difference in electrical transport capability. The decomposition of thin-film-like Li\(_2\)O\(_2\) is generally more facile than that of toroidal Li\(_2\)O\(_2\) with large particle size; thus, the lower charge overpotential can be achieved on \{100\}-dominant \(\beta\)-MnO\(_2\) compared to \{111\}-dominant \(\beta\)-MnO\(_2\).

Recent works published by Lu’s group suggest that bonding stabilization between catalyst surface and intermediates of Li\(_2\)O\(_2\) oxidation plays a key role for OER activity.\(^{8,26}\) It is believed that

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**Figure 1.** Scanning electron microscopy (SEM) images of \(\beta\)-MnO\(_2\) crystals with a) \{100\}-dominant facets and b) \{111\}-dominant facets. c) Charge-discharge profiles at first cycle of i-O\(_2\) cells based on pure carbon and \(\beta\)-MnO\(_2\) crystals. SEM images after discharge in Li-O\(_2\) batteries of d) \{100\}-dominant \(\beta\)-MnO\(_2\) crystals and e) \{111\}-dominant \(\beta\)-MnO\(_2\) crystals. f) The adsorption energy of LiO\(_2\) and g) the proposed reaction mechanism on the surface of \{100\} and \{111\} of \(\beta\)-MnO\(_2\), respectively. Reproduced with permission.\(^{26}\) Copyright 2019, American Chemical Society.
surface reactivity of the catalyst is strongly correlated with its bonding chemistry: Crystal facets with low atom coordination demonstrate higher surface energy and thus greater reactivity than facets with lower surface energy.\cite{25} Under this guidance, Cr$_2$O$_3$ catalysts with different fractions of high-energy facets were controllably constructed by Lu’s group.\cite{26} As proof, charge overpotentials decrease with increasing fraction of high-surface-energy facets of Cr$_2$O$_3$, and Cr$_2$O$_3$ with the highest fraction of high-energy facets even outstrips a Ru-based catalyst by >120 mV in average charge potential.

The surface effect of crystals also applies to noble metal catalysts.\cite{9,22a} Kang et al.\cite{22a} revealed that anisotropic Pt exposed with {411} facets revealed the formation of sheet-like Li$_2$O$_2$ during the ORR, and showed considerably enhanced electrocatalytic performance with significantly low OER potential (3.1 V @ 200 mA g$^{-1}$) when compared to commercial Pt/C. Anisotropic crystals provide facets with high surface energy and rich step atoms. As for high-index facets, e.g. {411} facets on Pt crystals, coordination numbers of step atoms are lower than those of low-index facets, and more nucleation sites can thus be offered to Li$_2$O$_2$. Benefitting from the step atoms, sheet-like Li$_2$O$_2$ would grow up on anisotropic Pt exposed with {411} facets, whereas large-sized Li$_2$O$_2$ particles are inevitably formed with commercial Pt/C. As has been previously proved, the sheet-like Li$_2$O$_2$ can be easily dissociated due to its facile ionic/electronic transport, which guarantees a reduced overpotential during the OER. Further, the correlation between the surface structure of the noble catalyst Au and the nucleation/growth/decomposition of the discharge product Li$_2$O$_2$ was directly observed via in situ electrochemical atomic force microscopy by Shen et al.\cite{9} As reported, the surface structure of Au is closely related to the catalytic activity of the ORR and OER: Au catalyst with specific particle size and porous structure can promote the formation of Li$_2$O$_2$ with large size at a relatively high discharge potential, and densely stacked Au nanoparticles could fully decompose Li$_2$O$_2$ with lower overpotential.

Therefore, due to the arrangement and coordination of exposed atoms as well as the surface morphologies, catalysts do exhibit great influence on the geometry of Li$_2$O$_2$. The correlation between the surface structure of catalysts and product geometry–dependent electrochemical performance in Li–O$_2$ batteries has been well documented, especially for metal oxides\cite{4b} and noble metals.\cite{9} Meanwhile, physiochemical properties of catalytic sites such as electronic structure and density distribution would also present a huge impact on Li$_2$O$_2$ formation.

### 3.2. The Effect of Catalytic Sites

Significant differences exist in catalytic sites among different types of catalysts, especially in terms of activity, distribution, and local electronic structure of sites.\cite{29} Strategies to optimize catalysts mainly involve composition regulation and structure engineering. No matter what strategy is adopted, catalysts with engineered catalytic sites will affect the electrochemistry in Li–O$_2$ batteries. As mentioned earlier, high overpotential in Li–O$_2$ batteries is attributed to undesirable intrinsic properties of Li$_2$O$_2$, including low electrical conductivity and slow mass transport kinetics. The revealing of the basic relationship between catalytic sites and Li$_2$O$_2$ formation will provide guidance to catalyst optimization, which is closely associated with the battery electrochemical performance.

To uncover the relationship between Li$_2$O$_2$ structural evolution and catalysts optimized via composition regulation, strategies of surface coating and bulk doping were used by our group\cite{4c} to regulate catalytic site composition. Original Co/CoN$_x$@graphene along with Pt surface-coated and Pt bulk-doped catalysts were achieved (Figure 2a–c). The approaches of surface coating and bulk doping via Pt would produce significantly different catalytic sites, which may induce distinct electocatalytic properties. It is noticeable that the main catalytic sites of these three catalysts lie in Co/CoN$_x$, Pt, and Pt/Co$_3$O$_4$, respectively. During discharge, Li$_2$O$_2$ with morphologies of disc, toroid, and sphere were generated on different catalytic sites (Figure 2d–f). DFT calculations show that intermediate conformations are different among these three catalyst surfaces: Li$_2$O$_2$* on Co/CoN$_x$, Li$_2$O$_2$* on Pt, and Li$_2$O$_2$* on Pt/Co$_3$O$_4$ (Figure 2g), resulting in different nucleation processes during discharge, leading to different morphologies of bulk Li$_2$O$_2$, and influencing their charge overpotentials. Compared to disc-like and toroidal Li$_2$O$_2$ formed on Co/CoN$_x$- and Pt-dominated catalysts, respectively, spherical Li$_2$O$_2$ formed on Pt/Co$_3$O$_4$-dominated catalytic sites demonstrates a much lower decomposition overpotential of 0.4 V (Figure 2h,i). Particularly, the spherical Li$_2$O$_2$ formation on noble metal–based catalysts (Ru-CNTs) was in situ observed using environmental transmission electron microscopy by Luo et al.\cite{30} As demonstrated, the spherical Li$_2$O$_2$ has a hollow structure, which could promote the mass/electrical transport in the OER process, thus reducing the charge overpotential.

Single-atom catalysts (SACs), with atomically dispersed metal centers as active catalytic sites, demonstrate maximized atomic utilization and unique electronic structure, which greatly differ from their counterparts: micro/nanocrystal catalysts.\cite{31} In addition, due to the single-atom nature of the active site, SACs with a low-coordination environment and enhanced substrate–support interaction have displayed forceful catalytic performance in a series of catalytic reactions, including photocatalytic reactions, hydrogen evolution reaction, and carbon dioxide reduction.\cite{32} Particularly, SACs with a definite structure of catalytic sites would benefit researchers to study the formation mechanism of Li$_2$O$_2$ in more detail. With this in mind, hollow N-doped carbon spheres with isolated single Co sites (N-HP-Co SACs) were fabricated by Song et al. (Figure 3a–c),\cite{33} and the catalytic site of “Co$^+$” was clearly revealed. Clear advantages can be observed when N-HP-Co SACs are applied as the cathode catalyst in Li–O$_2$ batteries: The conductive carbon framework expedites transport of electrons/electrolyte/O$_2$, and the well-dispersed catalytic sites guarantee homogeneous nucleation/growth of isolated Li$_2$O$_2$. Different from commercial Pt/C on which toroidal Li$_2$O$_2$ particles are formed (Figure 3d) upon discharge, N-HP-Co SACs promise not only an enhanced ORR potential (2.51 V vs 2.48 V) with the formation of nanosheet-like Li$_2$O$_2$ (Figure 3e), but also a reduced OER polarization (3.37 V vs 4.31 V), as shown in the CV profiles (Figure 3f). Theoretical calculation results illustrate that, due to the specific electronic structure of CoN$_x$, more electrons can transfer to catalytic sites of N-HP-Co SACs than Pt/C during discharge. Clearly, the geometry formation of nanosheet-like Li$_2$O$_2$ closely correlates with the local
electronic structure at CoN₄ sites. As shown in Figure 3g, compared to Pt/C, more nucleation sites can be provided by N-HP-Co SACs, which are beneficial to nanosheet formation and further assembly of large sheets based on enhanced solution-mediated mechanism.\[6\] Furthermore, such a product formation mechanism to generate nanosheet-like Li₂O₂ is also in favor of the OER process, leading to enhanced mass/charge transport capability of the discharged product and acceptable low charge overpotential. Coincidentally, an atomically dispersed cobalt catalyst anchored on N-doped carbon nanosheets (Co-N-C SACs), with the same local catalytic site structure of CoN₄, was also studied in Li–O₂ batteries by Wang et al.\[34\] Obviously, Co-N-C SACs can provide plentiful homogeneously distributed accommodation sites for the adsorption, nucleation, and growth of Li₂O₂. Under the catalysis of Co-N-C SACs during discharge, the morphology of Li₂O₂ is tailored into nanocrystals with the size of 2–3 nm, and the charge overpotential is obviously reduced mainly due to the aforesaid geometry-dependent electrical transport of Li₂O₂.

3.3. The Effect of Photoassisted Catalysts

Despite structure engineering on catalyst surface and electronic structure optimization at local catalytic sites, catalysis performance can also be manipulated in the presence of a photofield, thermal field, and magnetic field.\[135\] Particularly, photoassisted electrochemistry in Li–O₂ batteries was first reported by Yu et al.,\[36\] where triiodide ions (redox mediator) were first generated on a photoelectrode and then oxidized Li₂O₂ at a reduced overpotential. Different from generating a photoinduced redox mediator, photoenergy can directly assist in the oxidation of Li₂O₂ through photovoltage compensation. TiO₂ nanotubes integrated with Au nanoparticles were designed by Tong et al.\[24c\] Upon irradiation, positively charged holes with strong oxidizing capability could be effectively created on TiO₂, which subsequently promoted the decomposition of Li₂O₂ at a reduced oxidation potential as low as 2.67 V. Apart from lowering the overpotential upon charging, photoenergy also involves the discharge process through photogenerated electrons.

Figure 2. Transmission electron microscopy (TEM) images of a) Co/CoN@graphene, b) Pt surface-coated catalyst (Pt/Co/CoN@graphene), and c) Pt bulk-doped catalyst (Pt/Pt₃Co/Co/CoN@graphene), which are denoted as sample A, sample B, and sample C, respectively. TEM images of Li₂O₂ formed on d) sample A, e) sample B, and f) sample C with morphologies of disc, toroid, and sphere, respectively. g) Optimized structure of ORR-induced intermediate Li₄O₄ on the surface of sample C. h) Calculated and experimental charge overpotentials based on different catalysts. i) Discharge/charge profiles at first cycle. Reproduced with permission.\[4c\] Copyright 2019, Wiley-VCH.
Interestingly, formation route and geometry of Li$_2$O$_2$ can be modulated under the function of photo-energy. A hierarchical TiO$_2$-Fe$_2$O$_3$ heterostructure was purposely designed by Li et al. Under illumination, film-like Li$_2$O$_2$ was formed on the cathode surface, while in the absence of illumination, Li$_2$O$_2$ appears as a toroid. It indicates that the surface-mediated pathway dominates in the photoassisted ORR process, whereas the solution-mediated pathway proceeds without photoassistance. The film-like morphology not only favors the mass transfer of oxygen and the charge transport of ions/electrons during the ORR process, but also facilitates the low-overpotential dissociation of Li$_2$O$_2$ upon charging. As a result, an ultralow overpotential of 0.19 V between charge and discharge plateaus was achieved. The mechanism of the different reaction behaviors mainly lies in the electron density on the surface of the cathode catalyst: Tremendous photoexcited electrons with high conductivity would overflow onto the catalyst surface under illumination, and thus the generation rate of LiO$_2$ under illumination was faster than that without illumination, resulting in the accumulation of LiO$_2$ species in the near-surface area of the catalyst. Extrapolating the concept of photoassistance in Li–O$_2$ batteries, electrocatalytic reactions in Li–O$_2$ batteries may also be regulated other than by a photofield, such as by a thermal field and a magnetic field, and thus thermal and magnetic effects on the electrocatalytic behaviors in Li–O$_2$ batteries may be the focus of future research.

4. Alternative Products

Due to the unfavorable dissociation of Li$_2$O$_2$ caused by its inherent electrically insulating property, researchers have also sought for solutions on changing reaction pathways to produce more desirable lithium/oxygen-based species. Extrapolating the concept, alternative products in the form of LiOH and LiO$_2$ have also been reported in nonaqueous Li–O$_2$ systems.
In particular, Grey et al.\textsuperscript{18c} demonstrated an impressive reversible reaction in Li–O\textsubscript{2} batteries with LiOH as the main discharge product. Under the function of a soluble redox mediator, LiI, and the promotion of H\textsubscript{2}O (purposedly added or unavoidable trace water in the original electrolyte), an ultralow charge potential of 3.0 V (vs Li\textsuperscript{+}/Li) is achieved during LiOH decomposition. Though LiOH is a promising product candidate in terms of its favorable dissociation process, the application of LiI is bound to promote internal shuttle, resulting in low Coulombic efficiency. More importantly, the reversible LiOH/O\textsubscript{2} chemistry is still under debate due to the issues of LiOH on thermodinamics. To get around the issues from LiI, our group reported a mechanically different strategy to achieve reversible LiOH by simply adding sodium ions (Na\textsuperscript{+}) into the conventional organic electrolyte in Li–O\textsubscript{2} batteries, where a low charge potential of 3.4 V (vs Li\textsuperscript{+}/Li) was observed with LiOH as the solely detected product. The "solvation mechanism" tuned by Na\textsuperscript{+} is proposed in this work: Via adding Na\textsuperscript{+} into the electrolyte, the solvation environment of Li\textsuperscript{+} is changed, and the electrolyte degradation would be facilitated in the initial ORR process to form H\textsubscript{2}O, which is the essential reactant in the following formation of LiOH. It should be pointed out that although no apparent electrolyte decomposition during the subsequent cycles is observed and a remarkable cycling performance is obtained, the participation of H\textsubscript{2}O will indisputably corrode the lithium anode and accelerate battery failure. Other than the formation of LiOH, Li\textsubscript{2}O is considered another promising product due to its excellent chemical stability in Li–O\textsubscript{2} systems.\textsuperscript{19} Unfortunately, due to its tough cleavage of the O–O bond, Li\textsubscript{2}O faces a prodigiously high overpotential during the oxidation process even with state-of-the-art catalysts.\textsuperscript{19,41} As reported by Xia et al., only at an elevated temperature can Li–O\textsubscript{2} batteries deliver a reversible redox reaction to form Li\textsubscript{2}O.\textsuperscript{19} Therefore, a Li–O\textsubscript{2} cell with molten salt as the electrolyte was designed: With Li\textsubscript{2}O as the reversible product, a low charge overpotential, suppressed parasitic reactions, and a theoretical Coulombic efficiency of \( \approx 100\% \) were achieved. Ignoring the excellent performance, the high operating temperature may impede the development of Li–O\textsubscript{2} batteries to be practical energy storage devices. As a result, the research focus has also shifted to other alternative products.

Different from LiOH and Li\textsubscript{2}O, Li\textsubscript{2}O formed via the one-electron oxygen reduction process may be the best choice as an alternative product because LiO\textsubscript{2} can be achieved via catalyst optimization without changing any other components in Li–O\textsubscript{2} systems. As known, LiO\textsubscript{2} is an intermediate observed in conventional Li–O\textsubscript{2} batteries, which is highly active and unstable, and will transform into Li\textsubscript{2}O or induce parasitic reactions via attacking cell components. Regardless, it is uphill work to make Li\textsubscript{2}O as a stable product; our group\textsuperscript{7a} successfully achieved the reversible formation and decomposition of the product Li\textsubscript{2}O in Li–O\textsubscript{2} batteries, specifically under the catalysis of the noble metal Ir supported on reduced graphene oxide (Ir–rGO). As revealed, Li\textsubscript{2}O can be stabilized on the catalyst surface, mainly due to its similar crystallographic lattice to that of lithiated Ir (Ir\textsubscript{x}Li), which may potentially induce Li\textsubscript{2}O epitaxial growth (Figure 4a,c). DFT calculations confirm the half-metallic nature of Li\textsubscript{2}O, which is in favor of its dissociation during the OER process. Li\textsubscript{2}O shows a fairly low charge overpotential upon charge, with an average

\begin{figure}[h]
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\caption{a) Schematic presenting lattice match between Li\textsubscript{2}O and Ir\textsubscript{x}Li, and showing discharge processes of Ir–rGO in oxygen and in Ar gas. b) Voltage profiles of Li–O\textsubscript{2} batteries using Ir–rGO as the cathode catalyst. The inset shows capacity as a function of cycle number. c) SEM image and (inset in (c)) TEM image of discharge product formed on Ir–rGO. Reproduced with permission.\textsuperscript{17a} Copyright 2016, Springer Nature.}
\end{figure}
potential around 3.25 V versus Li+/Li (Figure 4b). Irrespective of numerous characterizations, including Raman spectra to identify the formation of LiO₂, it is suspected that the binder polyvinylidene fluoride binder (PVDF) may generate similar Raman signals to those of LiO₂,[42] thus interfering with the confirmation of LiO₂. However, it should be emphasized that, apart from numerous evidence from differential electrochemical mass spectrometry (DEMS), X-ray diffraction (XRD), etc., Halder et al. have pointed out that Raman peaks attributed to LiO₂ can reversibly appear and disappear as discharge and charge processes proceed,[40] which strongly excludes the effect of PVDF. Although LiO₂ may be a promising product candidate in Li–O₂ batteries, especially due to its low-energy-consumption charging process, and despite subsequent work based on the reversible reaction of LiO₂ under the catalysis of Pd–rGO reported by Gao et al.,[79] it is still a tough task to excavate efficient catalysts that can generate more stable LiO₂.

5. Conclusion

As the primary discharge product in conventional nonaqueous Li–O₂ batteries, LiO₂ exhibits poor electrical transport capability due to its inherent large bandgap, and a high overpotential is thus inevitable for its dissociation upon charge, which may further induce battery degradation. The solution to conquer the issue lies in the application of efficient electrocatalysts, which can regulate reaction pathways of product formation/decomposition. Particularly, various morphologies of LiO₂, correlated with charge overpotential and electrochemical stability, can be engineered via crystal surface control and catalytic site regulation of catalysts. In addition, under specific catalysts, alternative products can be produced. As elaborately discussed, LiO₂ with inherent low dissociation potential can be reversibly generated and stabilized on Ir- or Pd-based catalysts.

Li–O₂ batteries are complex electrochemical systems, whose practical application requires meticulous consideration of anode protection, electrolyte optimization, and cathode design. Among the system complexity, the cathode catalyst still plays the most crucial role in Li–O₂ battery electrochemistry. Though the effect of catalysts on geometry regulation and composition tuning of products have been studied in depth, many identified challenges still remain unsolved; especially, few works have focused on physicochemical state changes of catalysts during the ORR/OER in Li–O₂ batteries. Therefore, in situ characterization platforms, such as in situ surface-enhanced Raman spectroscopy, X-ray absorption spectroscopy, atomic force microscopy, and environmental transmission electron microscopy, are suggested to be built, thus to gain real-time information regarding catalyst evolution during electrocatalyzing processes. This will directly elucidate how catalysts work during electrochemical processes in Li–O₂ batteries, and in turn provide guidance on optimal catalyst design.

Apart from focusing on catalysts, battery systems can also be redesigned based on the oxygen redox. Extrapolating the oxidation state of O in the valence of 0, −0.5, −1, and −2, which is achievable and reversible in Li–O₂ battery electrochemistry, a closed system based on oxygen redox reactions of O⁻⁰·⁵ ≡ O⁻¹ ≡ O⁻² may be designed, which may potentially increase the practicality of batteries, without participation of gaseous oxygen. Actually, based on the aforementioned idea, battery reactions based on LiO₂/ LiO₂ ≡ LiO have been early reported by Zhu et al.[43] Though the catalyst (cobalt oxides) seems to be indispensable in the work, practical reversible capacity of 587 mAh g⁻¹ with a voltage plateau of 2.55 V (vs Li⁺/Li) was achieved. Based on the tactic, reversible reaction between LiO₂ and LiO₂ was also realized under the catalyst effect of Ir–rGO by Qiao et al.[44] Noticeably, a high specific capacity of 400 mAh g⁻¹ with a low round-trip overpotential (0.12 V) and 99.5% Coulombic efficiency over 2000 cycles can be achieved. Based on a few but significant studies, closed battery systems under reversible redox reactions of oxygen can be alternative promising electrochemical energy technologies.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalyst properties, lithium–oxygen batteries, lithium peroxide, lithium superoxide, product geometry

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