

## REVIEW

# Advances and Challenges on Cathode Catalysts for Lithium-Oxygen Batteries

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## Abstract

Aprotic lithium-oxygen batteries (LOBs) with high theoretical energy density have received considerable attention over the past years. However, the oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) at cathodes suffer from slow kinetics for large overvoltages in LOBs. Significant advances on catalysts have been achieved to accelerate cathode kinetics, but understanding on the formation/decomposition processes of  $\text{Li}_2\text{O}_2$  is limited. Herein, this review highlights the fundamental understanding of the correlation between catalysts and formation/decomposition of  $\text{Li}_2\text{O}_2$ . Various types of cathode catalysts are discussed to reveal the mechanism of formation/decomposition of  $\text{Li}_2\text{O}_2$ , aiming to present the prerequisites for the design of highly efficient cathode catalysts. Future prospects of comprehensive consideration on introduction of light or magnetism, protection of Li metal anode, and electrolyte engineering are presented for the further development of LOBs.

**Keywords:** Aprotic lithium-oxygen batteries; Cathode catalysts; Reaction kinetics; Overvoltage; Formation/decomposition of  $\text{Li}_2\text{O}_2$

## 1. Introduction

Aprotic LOBs (lithium-oxygen batteries) with high theoretical energy density of ca.  $3600 \text{ Wh}\cdot\text{kg}^{-1}$  have received tremendous attractions in the field of high-performance energy storage devices [1,2]. Since LOBs working at room temperature have been reported by Abraham in 1996, extensive efforts have been devoted to constructing high-performance LOBs [3,4]. Typical LOBs include lithium metal anodes,  $\text{O}_2$  cathodes, and non-aqueous  $\text{Li}^+$  containing electrolytes. The cathode is usually composed of porous conductive substrate to facilitate  $\text{O}_2$  diffusion, ensuring sufficient contact between  $\text{O}_2$  and  $\text{Li}^+$  in electrolytes. In a discharge process,  $\text{O}_2$  is reduced at a cathode to form insoluble discharge product  $\text{Li}_2\text{O}_2$ . It is later decomposed in the porous cathode to release  $\text{O}_2$  during the charge process [5,6]. However, this simple cathode reaction faces substantial challenges, involving high overvoltages

during discharge/charge process, low round-trip efficiency, and inferior cycle stability. Up to now, abundant progress has been achieved in LOBs to circumvent these inevitable dilemmas, including designing efficient electrocatalysts [7–9], optimizing electrolyte composition [10], and protecting lithium metal anode [11], etc. Among these, employing selective cathode catalysts for LOBs can directly tune the formation of  $\text{Li}_2\text{O}_2$  during discharge and its reversible decomposition during charge, reducing the discharge/charge polarization [12–15]. Although some reviews have focused on the development and reaction mechanism of LOBs [4,6], the summary on recent advances on cathode catalysts, especially their features and mechanism of formation/decomposition of  $\text{Li}_2\text{O}_2$ , has not yet been reviewed systematically. A comprehensive review on recent progress of designing cathode catalysts and their influence on discharge/charge process in LOBs is highly in demand.

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This review will spotlight the challenging issues of cathode and the recent research progress on cathode catalysts. We highlight the key challenges of cathode and present the design principles of cathode catalysts in LOBs. The various types of cathode catalysts are classified and discussed, including understanding adsorption behavior between intermediate  $\text{LiO}_2$  and active sites on cathode catalysts, mechanism of formation/decomposition of  $\text{Li}_2\text{O}_2$ , and evaluating the development of various cathode catalysts in LOBs. Some perspectives into the development of LOBs for practical application are presented.

## 2. Challenges of cathode in LOBs

### 2.1. Sluggish cathode kinetics

In theory, the high specific energy of LOBs is attributed to the electrochemical reaction between  $\text{Li}^+$  and  $\text{O}_2$  occurring on the cathode surface ( $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 = \text{Li}_2\text{O}_{2(\text{solid})}$ ,  $E^0 = 2.96 \text{ V vs. Li}^+/\text{Li}$ ) [16]. The reversible redox behavior involves ORR and OER processes [17]. It is reported that two reaction mechanisms of  $\text{Li}_2\text{O}_2$  formation pathways occur via the surface-adsorption or the solution-mediated model [6,18,19], as depicted in Fig. 1. Toroid-shaped  $\text{Li}_2\text{O}_2$  can be directly produced on the cathode surface via the disproportionation of dissolved intermediate  $\text{LiO}_2$  in the solution-mediated model. In virtue of the strong affinity between the intermediate  $\text{LiO}_2$  and cathodes, film-like  $\text{Li}_2\text{O}_2$  will be generated through surface-adsorption model [20,21]. Toroid-shaped  $\text{Li}_2\text{O}_2$  usually delivers higher discharge capacity than that of film-like  $\text{Li}_2\text{O}_2$ . Although the equation for formation/decomposition of  $\text{Li}_2\text{O}_2$  is quite simple, the three-phase interface reactions

between  $\text{O}_2$ , cathode and electrolyte are complex during the real  $\text{O}_2$ -electrode reaction process [22].

The insoluble and insulating discharge product  $\text{Li}_2\text{O}_2$  will be accumulated on the cathode surface, passivating catalytic sites, further hindering the charge and mass transfers [23]. The high interfacial contact impedance causes sluggish kinetics of the ORR and OER processes. This results in high discharge/charge overvoltages, aggravating the performance of LOBs [24]. Previous researches have revealed that these restrictions can be overcome by utilizing cathodes with modulated electronic structure and enhanced catalytic activity [25]. During OER process, Li vacancies can be first formed at the  $\text{Li}_2\text{O}_2$ -catalyst interfaces by  $\text{Li}^+$  extraction. This encourages  $\text{Li}^+$  from the outer part of the  $\text{Li}_2\text{O}_2$  particle moving to the vacant sites created by  $\text{Li}^+$  and triggers  $\text{O}_2$  evolution at the outer part of the  $\text{Li}_2\text{O}_2$  particle. The continuous contact between  $\text{Li}_2\text{O}_2$  and catalysts promotes  $\text{Li}_2\text{O}_2$  oxidation kinetics. It is vital to design a high-efficiency catalyzed cathode with intrinsic electrocatalytic activity to improve  $\text{O}_2$  redox kinetics for ORR and OER processes in LOBs. Although catalyzed cathode has significant effect on the formation of  $\text{Li}_2\text{O}_2$ , the deposition/decomposition site of  $\text{Li}_2\text{O}_2$  is not clear. These issues are unavoidable challenges for catalyzed cathode design for LOBs. These catalyst materials would be discussed in the subsequent section.

### 2.2. Design principles of cathode in LOBs

The role of cathode in LOBs is to provide catalytically active sites and accommodation for  $\text{Li}_2\text{O}_2$ . The cathode must not only have an open pore structure to accelerate  $\text{O}_2$  diffusion, but also possess high electrocatalytic activity to regulate the

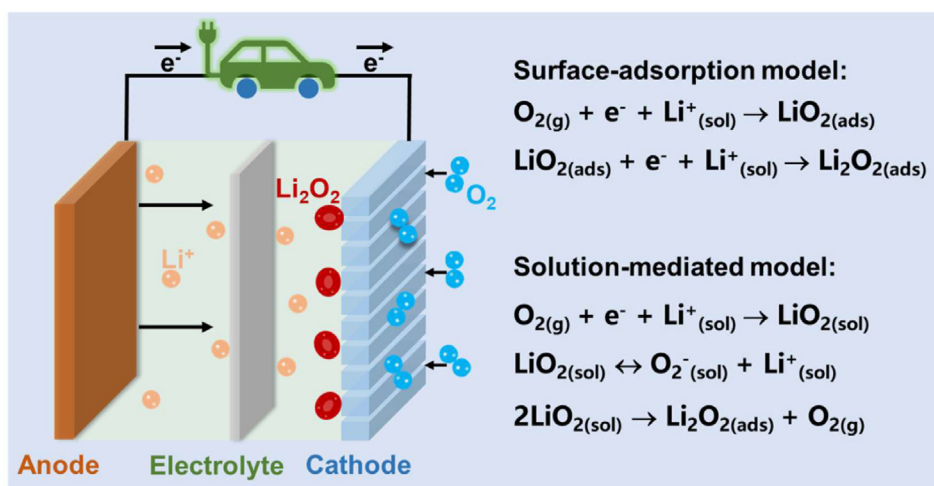


Fig. 1. Schematic presentation of Li-O<sub>2</sub> battery.

formation and decomposition of  $\text{Li}_2\text{O}_2$ . The use of catalysts for LOBs can lower charging overvoltages and improve battery reversibility compared to the case without catalysts [26–28]. Nazar et al. proposed that  $\text{Co}_3\text{O}_4$  catalysts could promote mass transport of  $\text{Li}_x\text{O}_2$  species on electrode surfaces by reducing their binding energies with the surface, which in turn facilitate both further oxidation and reduction of  $\text{Li}_x\text{O}_2$  [29]. It should be noted that the design principles of cathode catalysts have the following features: (1) Selective catalytic characteristics, organic electrolytes tend to decomposition in the presence of catalysts, and this means that cathode catalysts need to be inert to decomposition of organic electrolytes and reduce the formation of byproducts; (2) Intrinsic catalytic activity and high stability, a highly efficient cathode catalyst can not only ensure the formation/decomposition of  $\text{Li}_2\text{O}_2$  at low overvoltages, but also is thermodynamically stable in oxidative environment; (3) Tunable catalytic sites, strategies for increasing catalytic sites usually involve doping, facet engineering, surface modification, nanostructure, etc.; (4) Optimizing intermediate species adsorption behavior, this distinctly alters the geometric morphology and distribution of discharge product  $\text{Li}_2\text{O}_2$ ; (5) Facilitating decomposition of byproducts, the continued formations of  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$  byproducts need to be removed to improve the reversibility of LOBs. Recently, abundant attentions have been devoted to designing catalyst materials in LOBs, including carbon cathodes and noncarbon cathodes. These cathode catalysts are collectively shown in Fig. 2.

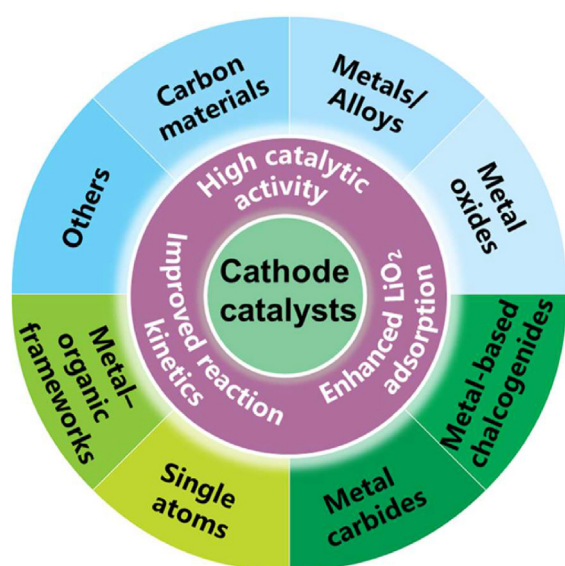


Fig. 2. Various types of cathode catalysts and a summary for their functions.

### 3. Cathode catalysts

#### 3.1. Carbon cathodes

The carbon materials, due to low weight, high conductivity, and low cost, have attracted much interest as cathodes for LOBs in recent years. A range of traditional carbon materials have been widely employed in LOBs, such as Super P, carbon nanotubes, graphene, Vulcan XC 72R [4,30]. But the overvoltages of ORR/OER reactions are still high on these carbon cathodes due to their limited catalytic activity. How to design carbon materials with high catalytic activity is the focus of carbon cathodes in LOBs. To address this issue, various modifications including heteroatom doping, hierarchical structure, and designing defects have been suggested. These strategies can significantly regulate the surface electronic state of carbon materials, reducing the reaction barrier and corresponding low overvoltages [31]. Heteroatom doping has been most widely studied to boost the reaction kinetics because of the electronegativity difference between carbon substrate and the heteroatom. Wong et al. confirmed that O-doped carbon nanotube can directly influence the surface-binding affinity of  $\text{O}_2$  and  $\text{LiO}_2$ , leading to the predominant surface-adsorption-based  $\text{Li}_2\text{O}_2$  growth and low overvoltages for  $\text{Li}_2\text{O}_2$  decomposition [32]. In addition, carbon doping usually involves a variety of heteroatoms at the same time to further regulate electronic structure of carbon materials. Ma et al. doped F into a carbon matrix together with N, O, S with suitable content to regulate the morphology of film-like  $\text{Li}_2\text{O}_2$  with granular inclusion in Fig. 3a, thus favorable to  $\text{Li}_2\text{O}_2$  decomposition in the charge process. Density functional theory (DFT) results indicate that C–F bond has strong adsorption energy to Li and O in  $\text{Li}_2\text{O}_2$ , and the strong interaction enhances the electron transfer from  $\text{Li}_2\text{O}_2$  to the carbon matrix to generate hole polaron. The separation of electron and hole at the interface of  $\text{Li}_2\text{O}_2$  and cathode reduces the energy barrier for the interfacial charge transfer presented in Fig. 3b, thus accelerating decomposition of  $\text{Li}_2\text{O}_2$  [12].

Although heteroatom doping can improve the electrocatalytic kinetics of carbon cathodes, they usually suffer from the harsh oxidative environment because of the reaction intermediate superoxide, leading to electrode inactivation and passivation. As a result, combining increased kinetics and stability is necessary for heteroatom-doped carbon cathodes. Qian et al. highlighted the high activity of C–Se–C bond in Se-doped carbon can effectively scavenge superoxide radical [33]. The antioxidants prevent free radicals from

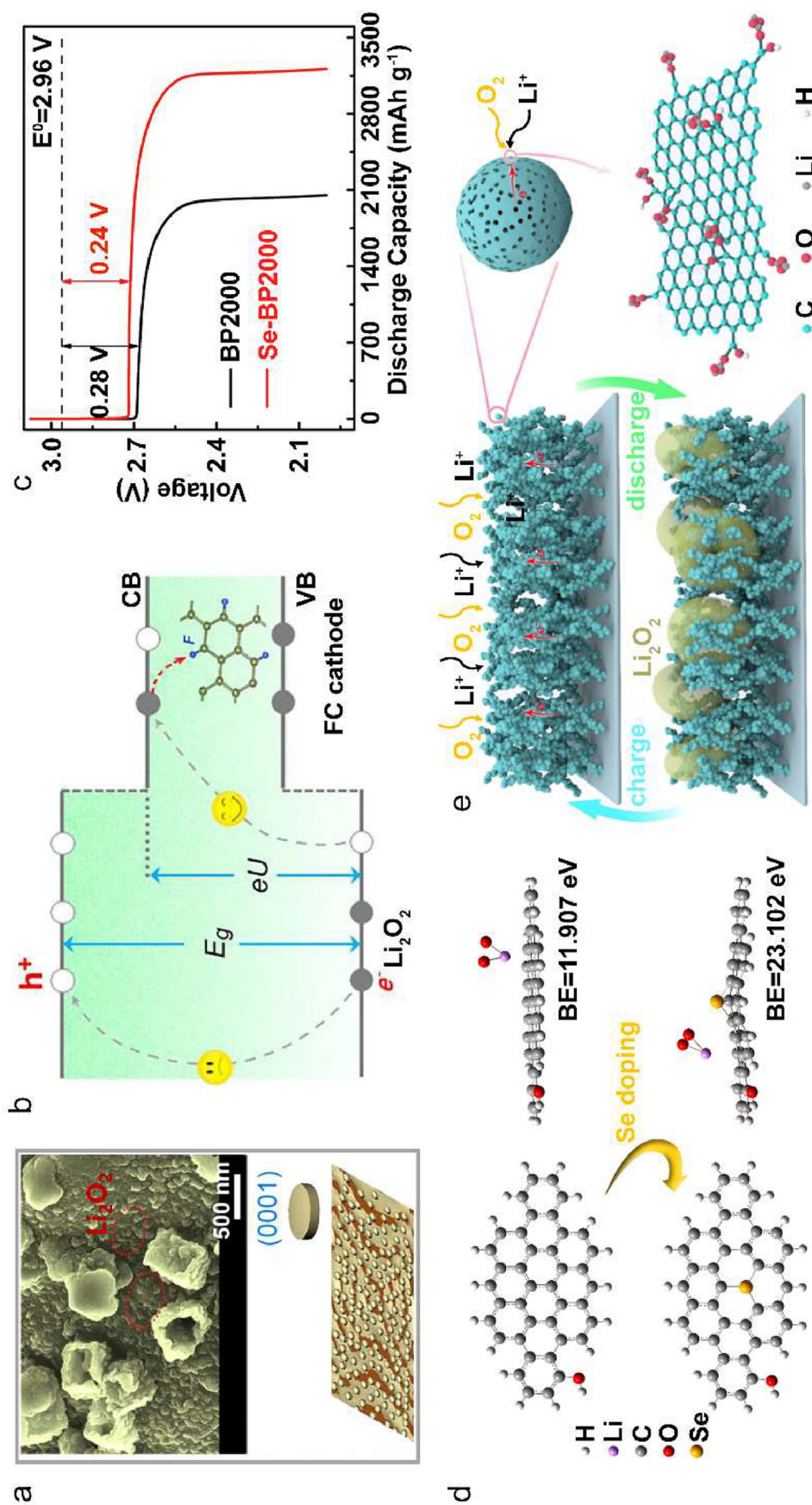


Fig. 3. (a) SEM image of discharge product  $\text{Li}_2\text{O}_2$  on the surface of F-doped carbon, (b) Corresponding energy barrier reducing mechanism,  $E_g$  is the intrinsic excitation energy of  $\text{Li}_2\text{O}_2$ ,  $eU$  is the interfacial charge transfer (CT) barrier. Reproduced with permission [12]. (c) Discharge curves of Se-doped carbon cathode at  $200 \text{ mA g}^{-1}$ , (d) Binding energy change of  $\text{Li}_2\text{O}_2$  species on carbon material after Se doping. Reproduced with permission [33]. (e) Schematic of the cathode with carbon nanosphere clusters in a working LOBs. Reproduced with permission [34].

attacking electrolyte and alleviate side reactions to some extent. Se-doped carbon exhibited higher discharge capacity of  $3213 \text{ mAh} \cdot \text{g}^{-1}$  and decreased overvoltage in Fig. 3c. The positive binding energy of  $\text{LiO}_2$  on Se-doped carbon in Fig. 3d affirms that  $\text{LiO}_2$  intermediates prefer to dissolving in the electrolyte. This means that the solution-mediated model plays a dominant role in the formation of  $\text{Li}_2\text{O}_2$ .

In addition to heteroatom doping, other carbon materials are also designed in LOBs. Lu et al. demonstrated that biomass-derived carbon nanoparticles with open slit-shaped hierarchical pore structure can act as a cathode for LOBs described in Fig. 3e [34]. The porous carbon nanomaterial facilitates the interfacial contact between electrolyte and electrode, and can accommodate more  $\text{Li}_2\text{O}_2$  products. Owing to the open and stable hierarchical pore structure, the sample delivers superhigh specific capacity of  $20300 \text{ mAh} \cdot \text{g}^{-1}$ , and excellent long-term stability with capacity retention of 100% for 543 cycles.

Carbon cathodes as a host for  $\text{Li}_2\text{O}_2$  can not only provide high electrical conductivity to realize fast electron transport, but also further reduce the mass of electrode to increase energy density. One issue is that these cathodes may not tolerate extremely oxidizing environment, especially at high overvoltages [35–37]. The reactive oxygen species during discharge, including superoxide and singlet oxygen, can react with defects to form  $\text{Li}_2\text{CO}_3$  [38]. It was also reported that carbon materials may undergo parasitic reactions to form the byproduct  $\text{Li}_2\text{CO}_3$  via the reaction:  $\text{Li}_2\text{O}_2 + \text{C} + 1/2\text{O}_2 \rightarrow \text{Li}_2\text{CO}_3$  [35]. To solve these dilemmas, improving the crystallinity of carbon and lowering charging voltages could be considered for truly efficient carbon-based cathodes in LOBs.

### 3.2. Noncarbon cathodes

In addition to carbon cathodes, other noncarbon cathode catalysts, such as metals/alloys, metal oxides, metal-based chalcogenides, carbides/nitrides, metal organic frameworks (MOFs), single atoms, etc., have also been widely studied to facilitate the decomposition of  $\text{Li}_2\text{O}_2$  in recent years. This section will briefly introduce reaction mechanism of these various types of cathode catalysts for LOBs.

#### 3.2.1. Metals/alloys

Metals or alloys have been intensively studied and used as cathodes in LOBs because of high intrinsic activity and good conductivity. Shen et al. revealed that the nanostructured Au is directly related to the catalytic activity toward ORR and

OER reactions [39]. They showed that nanoporous Au with sizes of ca. 14 nm and ca. 5 nm for nanopores boosts the nucleation and growth of toroidal  $\text{Li}_2\text{O}_2$  with large size at a high discharge voltage. In contrast, Au nanoparticles with a size of ca. 15 nm could catalyze the toroidal  $\text{Li}_2\text{O}_2$  being fully decomposed via the top to bottom approach at a low charge potential in Fig. 4a. On the nanoparticles/nanoporous Au composite electrode, the  $\text{Li}_2\text{O}_2$  tends to concentrate on the nanoporous Au with superior ORR activity, but it restricts the OER activity because of densely packed Au nanoparticles. This means that the nanostructure of electrode has an impact on interfacial reaction between  $\text{Li}_2\text{O}_2$  and catalysts. The PtIr multipod cathode catalyst reported by Guo's group demonstrated the confined growth of  $\text{Li}_2\text{O}_2$  during the discharge process [40], thus leading to formation of  $\text{Li}_2\text{O}_2$  cones with a small diameter compared to Pt cathodes in Fig. 4b. The abundant  $\text{Li}_2\text{O}_2$ /PtIr contact interfaces ensure adequate electron transport channels and improve OER kinetics for  $\text{Li}_2\text{O}_2$  decomposition. Theoretical calculation discloses the electron transfer from Ir to Pt owing to higher electronegativity of Pt than that of Ir, which results in lower Lewis acidity of Pt atoms on the PtIr surfaces than that on the pure Pt surfaces. The low Lewis acidity causes down-shifting of d-band center for Pt atoms in PtIr alloys, leading to low adsorption strength towards  $\text{LiO}_2$ . Although metals or alloys catalysts appear rapidly on catalyzing ORR and OER, surface oxidation of metals or alloys occurs when exposed to the air. The stability of these materials must be considered in LOBs.

#### 3.2.2. Metal oxides

Metal oxides are capable of catalyzing the formation and decomposition of  $\text{Li}_2\text{O}_2$  in LOBs, and their catalytic activity can be further improved via facet engineering and heterostructure. Metal oxides applied in LOBs mainly include single metal oxide [8,41], multimetal oxides [42], and perovskites [43], etc. Hou et al. found that  $\text{CeO}_2$  nanocubes with exposed (100) facets ensure high active catalytic properties [8]. The  $\text{CeO}_2$ /C matrix showed lower overpotentials and higher specific capacity because of the super catalytic performance in Fig. 5a. They revealed dissociative  $\text{O}_2$  adsorption on the  $\text{CeO}_2$  (100) surface to form surface-adsorbed  $\text{LiO}_2$ , resulting in loosely stacked  $\text{LiO}_2$  films. The matching of lattice distance between  $\text{Li}_2\text{O}_2$  (100) surface (2.72 Å) and  $\text{CeO}_2$  (100) surface (2.74 Å) can promote the epitaxial growth of  $\text{Li}_2\text{O}_2$  films on  $\text{CeO}_2$ , accelerating the decomposition of loose  $\text{Li}_2\text{O}_2$  films during OER. In addition,  $\beta\text{-MnO}_2$

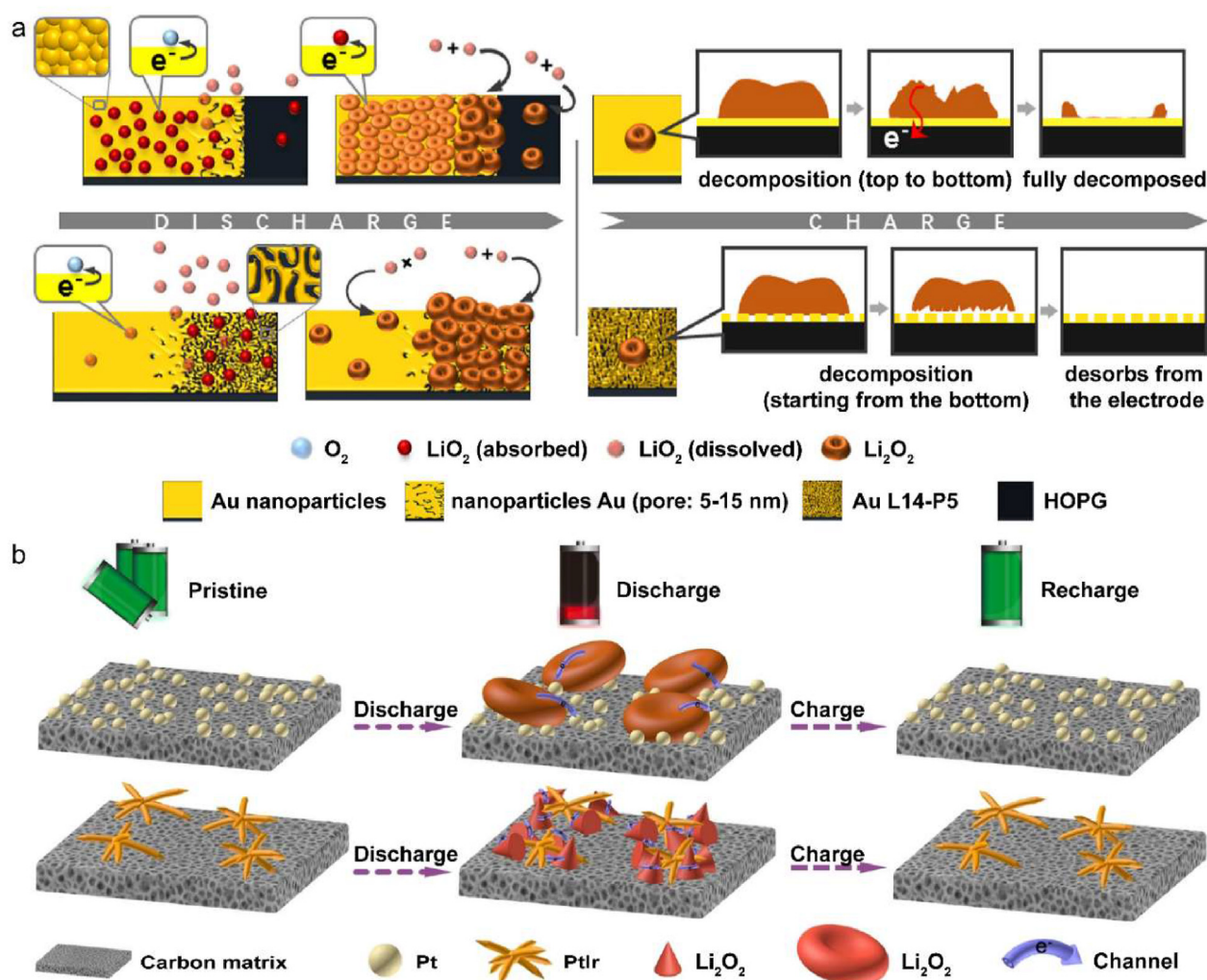


Fig. 4. (a) Schematic illustration of the proposed Li-O<sub>2</sub> interfacial processes on Au nanoparticles. Reproduced with permission [39]. (b) Schematic illustrations of the discharge-charge mechanisms for the Pt and PtIr cathodes. Reproduced with permission [40].

crystals with high occupancy of (111) or (100) facets were found to affect  $Li_2O_2$  formation [41]. The  $Li_2O_2$  morphology was related to different adsorption energies of the  $LiO_2$  intermediate on different facets. As displayed in Fig. 5b, the (111) facets of  $\beta$ - $MnO_2$  catalyzed the solution routes to form toroid-shaped  $Li_2O_2$ , while the (100) facets facilitated the surface routes for the formation of  $Li_2O_2$  films. Sun et al. developed amorphous/crystalline heterostructure acting as a cathode electrocatalyst for LOBs with a low voltage gap of only about 0.95 V [42]. The unique trimetallic CoFeCe oxide was confirmed to expose more intrinsic highly active sites and enhance adsorption of intermediate  $LiO_2$  on the surface.

### 3.2.3. Metal-based chalcogenides

Metal-based chalcogenides, including sulfides and selenides, exhibit good electrocatalytic property and high chemical stability.  $MoS_2$  usually

shows favorable electrocatalytic performance in LOBs [44]. He et al. found that the exposed (002) facet of layered  $MoSe_2$  offered abundant active sites to improve ORR and OER activity [45].  $MoSe_2$  has strong interaction with adsorbates, in which  $Li_2O_2$  forms a more stable bond with the substrate in Fig. 6a. The exposed  $MoSe_2$  crystal facet (002) acts as surface seeds for  $Li_2O_2$  growth from tiny particles to dense plates. This is attributed to the tiny lattice mismatch between the (001) facet of  $Li_2O_2$  and (002) of  $MoSe_2$ . The intrinsic catalytic capability of 2D layered  $MoSe_2$  can directly form/decompose  $Li_2O_2$  in Fig. 6b, avoiding the formation of  $LiO_2$  intermediate. The strategy of exposing active crystal facet was also applied in  $SnSe$  [46]. Also, sulfur vacancy-rich  $Ni_3S_2$  can act as a bifunctional catalyst for LOBs [25]. DFT confirmed that uniform sulfur vacancies on the surface are the active sites, enhancing adsorption capacity of the  $LiO_2$  intermediate. Although structure design and

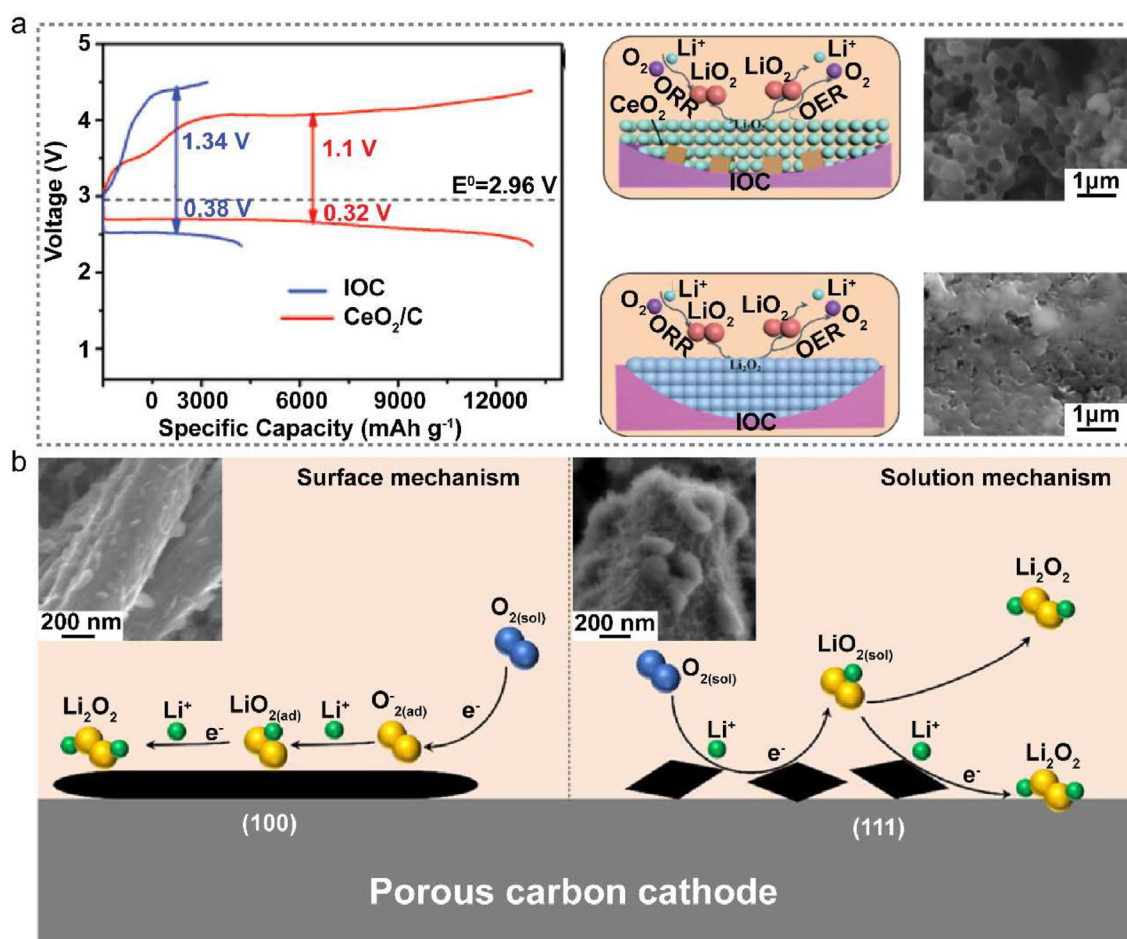


Fig. 5. (a) Schematic of the reaction mechanism for  $\text{CeO}_2$  nanocubes during cycling and the corresponding experimental results. Reproduced with permission [8]. (b) Proposed  $\text{Li}_2\text{O}_2$  formation mechanisms on  $\beta\text{-MnO}_2$  bipyramidal prism (100) and octahedron (111) crystals, the inserted SEM images showing the morphologies of the discharge products on the surface. Reproduced with permission [41].

surface modification are usually used to expose more catalytic active sites of metal-based chalcogenides, whether these sites can be maintained after decomposition of  $\text{Li}_2\text{O}_2$  needs to be further characterized.

### 3.2.4. Metal carbides

Due to the high electrical conductivity and high oxidation resistance, metal carbides have attracted intense attention as cathode materials in LOBs. Li et al. revealed that the  $\text{Nb}_2\text{C}$  MXene nanosheets cathode with uniform O anchored surface exhibited most stable surface structure compared to bare  $\text{Nb}_2\text{C}$  or F and OH anchored surfaces [47]. In initial ORR process, nonstoichiometric discharge product  $\text{Li}_{2-x}\text{O}_2$  is formed when the intermediate species  $\text{LiO}_2$  is accumulated on the electrode surface. Porous  $\text{Li}_2\text{O}_2$  is the main product due to the weakened adsorption ability of the electrode surface for  $\text{Li}^+$  and  $\text{O}_2$  in Fig. 6c. Wang et al. further exploited crystal defects in  $\text{Ti}_3\text{C}_2$  MXene quantum dot clusters to induce coordination environment

modification of Ti-C, coordination number and bonding length, and thus modulate electron structure and expose more unsaturated coordinative sites [48]. The crystal defects function as  $\text{O}_2$  adsorption sites, enhancing the  $\text{LiO}_2$  intermediate adsorption energies.

### 3.2.5. Single atoms

The size of catalysts has vital effect on the utilization of active atoms. Relative to bulk materials, the single-atom species will exhibit the super-high atomic utilization and uniform active sites. Wang et al. synthesized Co single atoms embedded in nitrogen-doped carbon matrix (Co-SAs/N-C) as a dual-catalyst in LOBs [49]. They found that rich Co- $\text{N}_4$  moieties as catalytic sites not only enhance the affinity of intermediate  $\text{LiO}_2$ , but also reduce both the  $\text{Li}_2\text{O}_2$  formation and oxidation overpotentials. Compared to Co-NPs/N-C and N-C cathodes, the voltage gap of Co-SAs/N-C is as small as 0.4 V at  $200 \text{ mA} \cdot \text{g}^{-1}$  with a limiting capacity of  $1000 \text{ mAh} \cdot \text{g}^{-1}$  in Fig. 7a. The discharge/

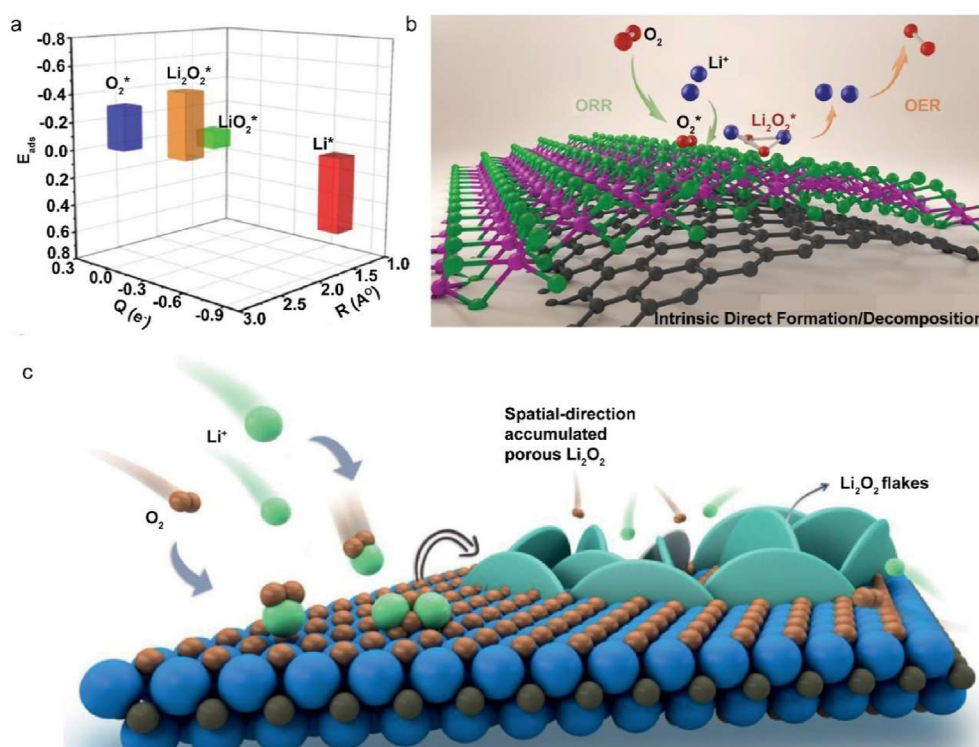


Fig. 6. (a) Adsorption energy ( $E_{ads}$ ), Bader charge transfer ( $Q$ ), and distance ( $\text{\AA}$ ) between different adsorbates and  $MoSe_2$ , (b) Schematic illustration of the direct formation/decomposition of  $Li_2O_2$  on the surface of  $MoSe_2$ . Reproduced with permission [45]. (c) Illustration of ORR and OER pathways for  $Li_2O_2$  formation/decomposition on  $Nb_2C$  surfaces. Reproduced with permission [47].

charge profiles of Co-SAs/N-C show long cycle stability at  $400 \text{ mA} \cdot \text{g}^{-1}$  in Fig. 7b. The higher affinity between  $LiO_2$  and Co- $N_4$  centers induces homogeneously distributed  $Li_2O_2$  by surface-adsorption model, as depicted in Fig. 7c. During recharge, the decomposition of densely packed  $Li_2O_2$  with nanosize easily occurs due to the intimately contacted catalytic centers of Co- $N_4$ . In order to avoid single atoms aggregation, carbon matrix is usually used to confine single atoms by metal-N bonds, which will affect the mass loading of single atoms. Hu et al. revealed that increased number of Ru- $N_4$  moieties are more active/stable for ORR/OER in LOBs [9]. This will encourage more efforts on increasing the number of single atoms to improve redox kinetics for LOBs.

### 3.2.6. MOFs

MOF materials have attracted attention as electrocatalysts due to porous structure and various metal junctions. When MOFs are directly employed as electrocatalysts, the problems of inferior conductivity and limited active metal sites will cause sluggish reaction kinetics. Li et al. modulated the spin state of  $Ni^{2+}$  sites of a two-dimensional conductive MOF of  $Ni^{II}$ -NCF to produce  $Ni^{III}$ -NCF as a bifunctional catalyst, which enhances the oxygen redox kinetics in LOBs [7].

The higher  $LiO_2$  adsorption energy on  $Ni^{III}$ -NCF reveals a strong interaction between the intermediate oxygen species and  $Ni^{3+}$  sites in Fig. 7d. The high-valence  $Ni^{3+}$  sites promote  $LiO_2$  adsorption and formation of the densely packed  $Li_2O_2$  nanosheets shown in Fig. 7e. Porous MOF materials can promote oxygen adsorption and desorption processes. The improvement of electrical conductivity and modification of active sites of MOF materials will promote its application in LOBs.

### 3.2.7. Other catalysts

Except for the materials mentioned above, there are other types of cathode catalysts applied in LOBs [50], including metal nitrides [51]/phosphides [52], and organics [53]. For example, Liu et al. found that CoN cathode facilitated the appropriate adsorption and facile charge transfer between  $Li_2O_2$  and CoN [51]. The high intrinsic catalytic activity of CoN facilitates the reaction kinetics during ORR/OER. The specific porous nanowire arrays architecture enables the compact contact between  $Li_2O_2$  and CoN catalyst, thus lowers the electrode resistance. Kim et al. studied antioxidant organogermanium polymer to suppress solvated superoxide and induce strong surface-adsorption reaction, enhancing surface-induced growth/decomposition of  $Li_2O_2$  [53].

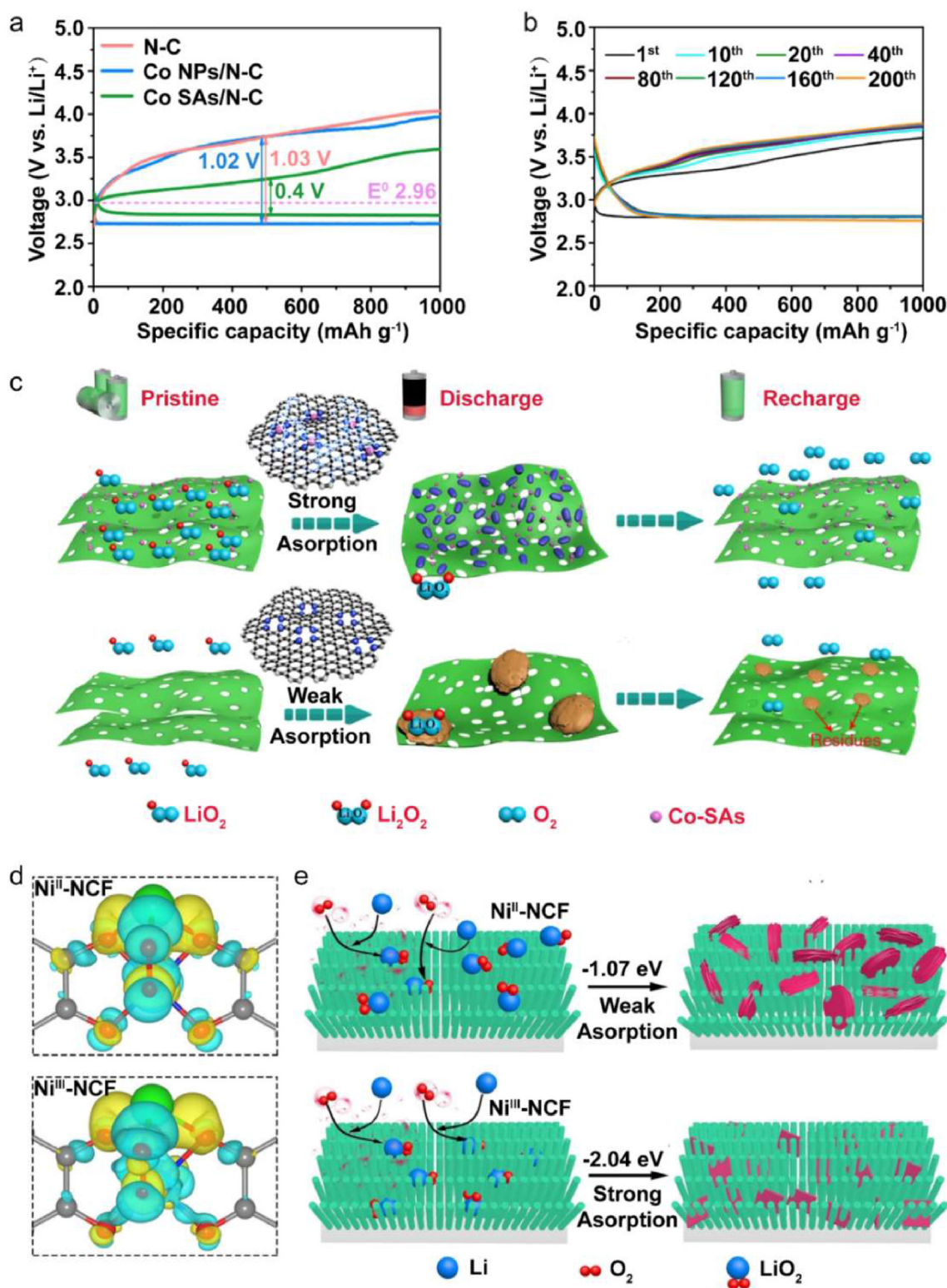


Fig. 7. (a) Discharge-charge curves of Co-SAs/N-C, Co-NPs/N-C, N-C electrodes at  $200 \text{ mA}\cdot\text{g}^{-1}$ . (b) Discharge-charge profiles of Co-SAs/N-C at  $400 \text{ mA}\cdot\text{g}^{-1}$ . (c) Schematic of the working mechanism for the Co-SAs/N-C and N-C electrodes. Reproduced with permission [47]. (d) Differential charge densities of  $\text{LiO}_2$ -adsorbed  $\text{Ni}^{\text{III}}\text{-NCF}$  and  $\text{Ni}^{\text{II}}\text{-NCF}$ . Cyan and yellow represent charge depletion and accumulation, respectively. The isosurface value is set to  $0.003 \text{ e}\cdot\text{bohr}^{-3}$ . (e) Discharge mechanism on  $\text{Ni}^{\text{III}}\text{-NCF}$  and  $\text{Ni}^{\text{II}}\text{-NCF}$  cathodes. Reproduced with permission [7].

Organics have poor conductivity and are easy to dissolve into the electrolyte. Improving conductivity and inhibiting dissolution of organics can further improve electrochemical performance in LOBs.

#### 4. Conclusions and outlooks

Aprotic LOBs have garnered extensive interest because of their high theoretical energy density. Great efforts have been focused on promoting the reaction kinetics and suppressing the side reactions on cathodes. This review mainly analyzes the challenging issues of cathodes and summarizes the current advances on cathode catalysts, including carbon materials, metals/alloys, metal oxides, metal-based chalcogenides, MOFs, single atoms, and other catalysts. Adopting catalysts for LOBs effectively lowers overvoltages of ORR/OER and improves rechargeability compared to the case without catalysts. The active sites in these catalysts can regulate the affinity for  $\text{LiO}_2$  and promote the charge transfer between the electrode and discharge product  $\text{Li}_2\text{O}_2$ . However, in-depth understanding of the correlation between catalysts and formation/decomposition of  $\text{Li}_2\text{O}_2$  is urgently required. Although cathode catalysts make great contribution to the development of LOBs, other challenges about lithium dendrites and electrolyte decomposition are also inevitable. For the further development of LOBs, various issues and corresponding strategies are discussed as follows:

(1) The use of catalysts in LOBs can effectively reduce overvoltages by modulating the interaction between the catalyst surface and reaction intermediates. Although plenty of catalysts have been designed as cathodes in LOBs, there is an argument that catalysts only catalyze the part in direct contact. The catalysts may be passivated by insulating and insoluble  $\text{Li}_2\text{O}_2$  coating. It is questioning whether the catalytic sites remain after cycling. On the one hand, searching for a highly efficient cathode catalyst with intrinsic activity is necessary. The adsorption energy of intermediate species on the cathode surface, nanometer structure and facet orientation of the catalyst govern the  $\text{Li}_2\text{O}_2$  growth mechanism. In addition, advanced computational and *in situ* characterization techniques can be adopted to quantitatively describe the catalytic mechanism and evolution of active sites. For example, *in situ* atomic force microscope (AFM) can reveal the nucleation, growth, and decomposition of the discharge product  $\text{Li}_2\text{O}_2$  against the operating voltages. The stretching vibrations of O–O in  $\text{LiO}_2$  and  $\text{Li}_2\text{O}_2$  can be detected

via *in situ* Raman during cycling. *In situ* differential electrochemical mass spectrometry (DEMS) is adopted to analyze the  $\text{O}_2$  consumption in the discharge, and release during the charging process. This understanding will facilitate the development of cathodes in LOBs via rational catalyst design.

(2) It was demonstrated that the introduction of light or magnetism into LOBs could improve the reaction kinetics during discharge/charge [54–59]. Li's group conducted a series of investigations, like plasma mediated oxygen redox [58], built-in electric fields for carrier separation [59], and semi-conducting metal-organic framework cathodes [57], to generate photoelectrons and holes to promote  $\text{Li}_2\text{O}_2$  oxidation, reducing electric energy loss in charging processes. Recently, they dissected the mechanism and summarized the recent progress of photoelectrochemistry of oxygen in LOBs [60]. These strategies may open up a new pathway for highly efficient oxygen cathode materials for LOBs.

(3) There are three main parts including air cathode, Li metal anode, and electrolyte in LOBs. The problems of Li dendrites and organic electrolyte decomposition are unavoidable. For Li metal anodes, the formation of solid electrolyte interface (SEI) films and the side reactions on Li metal surface will lead to low Coulombic efficiency and Li dendrites. Stabilizing the SEI on Li metal surface and designing electrolytes are effective approaches to mitigate these issues [61–64]. Of note, the electrolyte in LOBs needs not only to stabilize the lithium anode, but also to withstand the attack of superoxide and decomposition promoted in the presence of catalysts. To improve the air stability of LOBs, developing efficient selective gas scrubbers can remove  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to reduce  $\text{LiOH}$  and  $\text{LiCO}_3$  byproducts.

Despite the improved electrochemical performance has been achieved with effective cathode catalysts, it is required to further understand intrinsic catalytic mechanism and rational design of high-performance cathode catalysts. Finally, the overall view on cathodes, Li anodes, electrolytes, and separators should be comprehensively considered to design LOBs for practical applications.

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## 锂-氧气电池：正极催化剂的最新进展与挑战

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### 摘要

非质子锂-氧气电池具有高理论能量密度, 在过去几年里受到了广泛关注。然而, 动力学缓慢的氧还原反应 (ORR) /氧析出反应 (OER) 和放电产物  $\text{Li}_2\text{O}_2$  导电性差导致锂-氧气电池过电位大, 放电容量有限, 循环寿命短。开发有效的锂-氧气电池正极催化剂可以调控放电与充电过程中  $\text{Li}_2\text{O}_2$  的形成和可逆分解, 减小放电/充电极化。尽管提升 ORR/OER 动力学的正极催化剂已经取得了一系列重要进展, 但是对正极在放电和充电中  $\text{Li}_2\text{O}_2$  生成和分解过程的理解依然是不足的。这篇综述聚焦于锂-氧气电池正极催化剂的最新进展, 总结了催化剂与  $\text{Li}_2\text{O}_2$  生成/分解的作用关系, 本文首先指出了锂-氧气电池正极面临的科学问题, 包括动力学缓慢的 ORR/OER 过程和导电性差的反应产物  $\text{Li}_2\text{O}_2$  钝化电极, 并提出了锂-氧气电池正极设计准则。通过对最近报道的正极催化剂进行分类讨论, 明晰调控催化剂活性位点策略, 理解在正极反应过程中不同催化剂的活性位点对反应中间产物的吸附状态, 以及对  $\text{Li}_2\text{O}_2$  生成和分解的作用机制, 评估了不同类型正极催化剂在锂-氧气电池的潜在应用。最后总结了锂-氧气电池正极催化剂依然存在的挑战, 例如阐明正极催化剂活性位点与附着的  $\text{Li}_2\text{O}_2$  界面在充放电过程中的变化, 并揭示了设计高效正极催化剂的决定因素, 展望了通过光/磁协助、负极保护以及电解液设计等策略, 进一步推动锂-氧气电池的应用。

**关键词:** 非质子锂氧电池; 正极催化剂; 反应动力学; 过电压;  $\text{Li}_2\text{O}_2$  的形成与分解