



Review

Recent Progress on Catalysts for the Positive Electrode of Aprotic Lithium-Oxygen Batteries [†]

Yichao Cai [‡], Yunpeng Hou [‡], Yong Lu and Jun Chen ^{*}

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, Tianjin 300071, China; nankaicaiyichao@mail.nankai.edu.cn (Y.C.); houyp0727@mail.nankai.edu.cn (Y.H.); 2120150622@mail.nankai.edu.cn (Y.L.)

^{*} Correspondence: chenabc@nankai.edu.cn

[†] Dedicated to the 100th anniversary of Nankai University.

[‡] These authors contributed equally.

Received: 29 April 2019; Accepted: 24 May 2019; Published: 28 May 2019



Abstract: Rechargeable aprotic lithium-oxygen (Li-O₂) batteries have attracted significant interest in recent years owing to their ultrahigh theoretical capacity, low cost, and environmental friendliness. However, the further development of Li-O₂ batteries is hindered by some ineluctable issues, such as severe parasitic reactions, low energy efficiency, poor rate capability, short cycling life and potential safety hazards, which mainly stem from the high charging overpotential in the positive electrode side. Thus, it is of great significance to develop high-performance catalysts for the positive electrode in order to address these issues and to boost the commercialization of Li-O₂ batteries. In this review, three main categories of catalyst for the positive electrode of Li-O₂ batteries, including carbon materials, noble metals and their oxides, and transition metals and their oxides, are systematically summarized and discussed. We not only focus on the electrochemical performance of batteries, but also pay more attention to understanding the catalytic mechanism of these catalysts for the positive electrode. In closing, opportunities for the design of better catalysts for the positive electrode of high-performance Li-O₂ batteries are discussed.

Keywords: Li-O₂ batteries; positive-electrode catalysts; carbon materials; noble metals; transition metals

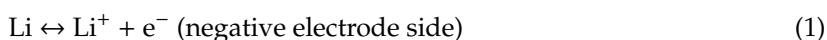
1. Introduction

Since their successful commercialization in the 1990s, lithium-ion batteries (LIBs) have fulfilled the expectation of becoming a qualified energy storage system and are widely used in peoples' daily lives [1,2]. In the meantime, sodium ion batteries (SIBs) are also intensively studied due to their higher abundance and lower cost of the sodium element [3]. However, LIBs and SIBs, which are based on transition-metal oxide positive electrode and carbon negative electrode, are gradually unable to meet the requirement of high-energy-density applications. To cater to the need of developing novel high-energy-density rechargeable batteries, the so-called “beyond Li-ion batteries” such as lithium-sulfur (Li-S) and metal-air (e.g., Li-O₂, Na-O₂) batteries have attracted intensive interest in recent years. Among them, rechargeable aprotic Li-O₂ batteries are considered one of the most promising candidates owing to their ultrahigh theoretical energy density of approximately 3600 Wh·kg^{−1} [4–6], which is comparable to that of gasoline.

The concept of an Li-O₂ battery was first proposed by Littauer and Tsai in 1976 [7]. With the hypothetical discharge product Li₂O, the battery could reach a high energy density with an approximate output voltage of 3 V. After two decades, Abraham and Jiang demonstrated the first Li-O₂ battery

with only three cycles by using a lithium metal negative electrode, carbonate-based gel polymer electrolyte, and a carbon positive electrode containing Co catalyst [8]. The discharge product is Li_2O_2 rather than Li_2O according to the Raman spectra. Subsequently, the cycling life of aprotic Li- O_2 batteries was prolonged to 50 cycles by using an electrolytic manganese dioxide catalyst accompanied with liquid carbonate electrolyte. Unfortunately, the carbonate-based electrolyte was reported to be unstable during discharge and no signal of Li_2O_2 was detected in an ethylene carbonate/diethyl carbonate-based electrolyte. Thus, ethers were introduced as relative stable solvent for the electrolyte of Li- O_2 batteries with an solidly evidenced discharge product of Li_2O_2 [9]. Therefore, the ether-based electrolyte was intensively studied as a universal electrolyte for rechargeable aprotic Li- O_2 batteries in subsequent works.

As illustrated in Figure 1a, a rechargeable aprotic Li- O_2 battery usually consists of a lithium metal negative electrode, aprotic electrolyte, a separator and a porous catalyzed positive electrode, where the following reversible electrochemical reactions occur [10]:



During discharge, Li metal in the negative electrode is oxidized to form Li^+ and e^- . While at the positive electrode side, the dissolved O_2 is reduced by electron and reacts with Li^+ in electrolyte to form insoluble Li_2O_2 discharge product. For the charging progress, Li_2O_2 is reversibly decomposed in the porous positive electrode. Meanwhile, Li^+ is reduced with e^- and deposited on the negative electrode as Li metal. However, owing to the insulating nature of discharge product Li_2O_2 , the charging process always shows sluggish oxygen evolution reaction (OER) dynamics and high charging voltage plateau. The huge voltage gap could not only lead to a low energy and Coulombic efficiency, but also bring about numerous side reactions initiated by high charging potential, thus resulting in a poor cycling life [11–13]. As reported by Bruce's group [14], carbon materials were only stable under a charging potential lower than 3.5 V, especially for the hydrophobic carbon. Recently, Freunberger et al. [15] proposed the formation of highly reactive singlet oxygen when charging above 3.55 V, which should be responsible for a major fraction of side reactions. Therefore, it's of great necessity to lower the charging potential under 3.5 V in order to reach a more rechargeable Li- O_2 battery with a prolonged cycling life. To achieve this goal, one of the most effective and direct solutions is to develop positive-electrode catalysts with highly catalytic activity toward the decomposition of Li_2O_2 [16]. The reported positive-electrode catalysts for Li- O_2 batteries can be mainly divided into three categories, carbon materials, noble-metal-based materials, and transition-metal-based materials [17–20]. In recent years, tremendous efforts have been devoted to the development of positive-electrode catalysts with better performance and remarkable progress being made, not only with respect to the catalytic performance, but also more importantly, on understanding the recondite electrochemical reactions during battery cycling. Thus, it's necessary to comprehensively summarize the orientational strategies for improving the catalytic performance of positive-electrode catalysts and the newly developed in-depth understanding of the electrochemical mechanism in Li- O_2 batteries.

In this review, we mainly discuss three types of positive-electrode catalysts, namely carbon materials, noble-metal-based materials, and transition-metal-based materials. We highlight the design strategies to develop catalysts with enhanced performance. Moreover, the catalytic mechanisms of the positive electrode are discussed in detail. In addition, the future perspectives toward developing high-performance positive-electrode catalysts for aprotic Li- O_2 batteries are also proposed.

2. Overview of Li-O₂ Batteries

To better understand the function mechanism of catalysts and to pave the way for expanding a new catalytic strategy, it's essential to understand the underlying reaction mechanism during charge and discharge. However, reactions that actually take place during battery cycling are much more complicated than the chemical equation described in Equations (1–3). There are two different growth modes of the discharge product Li₂O₂ [21]. As schematically shown in Figure 1b, in the first step, the solvated O₂ molecule is reduced by one electron, forming a solvated O₂^{•−} intermediate. While divergence occurs in the second step, if the adsorption toward the intermediate is strong enough, the solvated O₂^{•−} intermediate can be adsorbed on the electrode surface, attracting a Li⁺ to neutralize the negative charge, and being further reduced or undergoing a disproportionation on the electrode surface to form Li₂O₂ in the surface pathway. Alternately, if the electrolyte shows a high enough donor number (DN) and the electrode adsorption toward O₂^{•−} intermediate is weak enough [22], the solvated O₂^{•−} intermediates keep accumulating in electrolyte, and disproportionate to generate a bulk or toroid Li₂O₂ product through the solution pathway [23–25].

To verify the previously mentioned steps for Li₂O₂ formation, efforts were made to detect the existence of O₂^{•−}/LiO₂ intermediates during discharge, which are very unstable and possess only limited lifetime. Luckily, with the help of in-situ surface-enhanced Raman spectroscopy (SERS), Bruce's group [26] directly detected the existence of LiO₂ during the discharging progress. As shown in Figure 1c, in the very beginning period of discharging, peak with short lifetime arose at 1137 cm^{−1} which was associated with the O–O bond vibration in LiO₂. Such a result directly proved the formation of unstable LiO₂ discharge intermediate which underwent a quick disproportionation to form the final discharge product Li₂O₂. Similar results were also found in the following works by various characterization methods such as transmission X-ray microscopy (TXM), electron paramagnetic resonance, and selected-area electron diffraction (SAED) [27–33].

Compared with the intensively studied oxygen reduction reaction (ORR) mechanism in the discharging progress of Li-O₂ batteries, the reaction mechanism of OER remained quite elusive. Only a SAED ring of LiO₂ intermediate phase during charge was detected with the help of an environmental transmission electron microscope (TEM). However, such testing conditions could not fully reconstruct the situation of Li-O₂ batteries under real operation [33]. Later on, Lu et al. [34] proposed that the oxidation mechanism of Li₂O₂ is closely related to the DN of electrolyte solvent. Through rotating ring-disk electrode (RRDE) and X-ray absorption near-edge structure, they confirmed the different OER mechanisms of Li-O₂ batteries using different solvent varied in DN as described in Figure 1d. In a high DN solvent, the oxidation of Li₂O₂ followed a solution way with the formation of soluble LiO₂ intermediate (e.g., dimethyl sulfoxide, 1-methylimidazole), while for the low DN solvent (e.g., acetonitrile (ACN), tetraethylene glycol dimethyl ether (TEGDME)), the oxidation of Li₂O₂ proceeded by way of solid delithiation, pretty similar to the behavior of the positive electrode in LIBs under charging. Interestingly, if we look back to the research carried by Bruce's group, when they studied the LiO₂ intermediate in the ORR progress with in-situ SERS, they detected no signal of LiO₂ during charging, and proposed a direct two electron oxidation mechanism for charging in Li-O₂ batteries. Note that the solvent of electrolyte they used is ACN (low DN solvent), it's reasonable that no LiO₂ signal could be collected during charging process. In fact, in 2013, Shao-Horn and Lu had proposed a surface delithiation pathway in TEGDME electrolyte for Li₂O₂ oxidation but without further experimental proof [35]. Thus, we can conclude that the charging and discharging process shared a common intermediate, LiO₂, whose solubility was greatly depended on the DN of solvents. Moreover, there are competition interactions between electrolyte and positive electrode surface toward LiO₂ intermediate. Different degree of solubility and the attraction of positive electrode toward LiO₂ would thus decide the solution or surface pathway toward the formation and decomposition of discharge product.

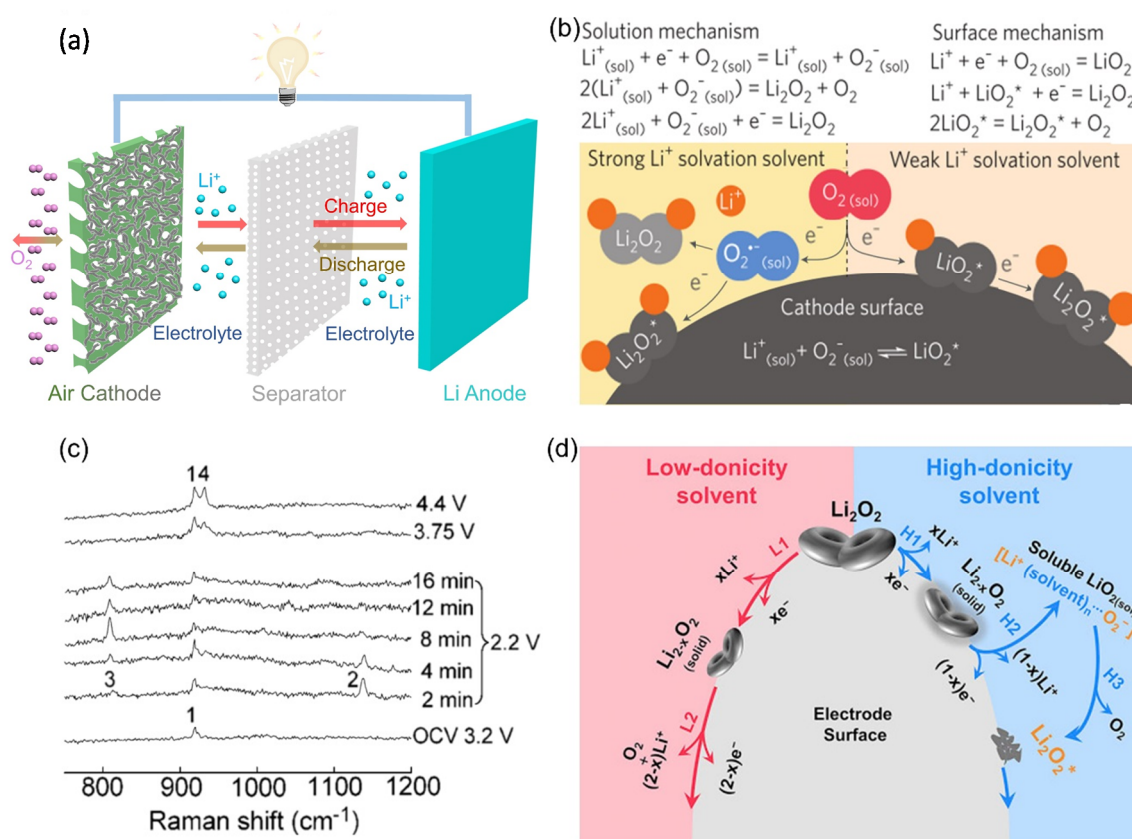


Figure 1. (a) Schematic illustration of rechargeable aprotic Li-O₂ battery system. (b) Proposed mechanisms for Li₂O₂ growth in Li-O₂ batteries. (c) In situ SERS during O₂ reduction and re-oxidation on Au positive electrode. (d) Proposed solvent-controlled Li₂O₂ decomposition mechanism. (b) Reproduced with permission from Ref. [25], copyright 2016, Nature Publishing Group. (c) Reproduced with permission from Ref. [26], copyright 2011, Wiley-VCH. (d) Reproduced with permission from Ref. [34], copyright 2018, Elsevier.

Furthermore, the morphology of Li₂O₂ also shows a great impact on the battery performance. According to previous conclusion, there are two pathways for Li₂O₂ to deposit on the electrode, i.e., solution pathway and surface pathway, corresponding to a bulk morphology and an amorphous morphology, respectively. In general, an amorphous product always contains more defects than a crystalline one. When there coexist a mixture of crystalline and amorphous products in the same positive electrode, the amorphous part is much more prone to be decomposed when charging owing to its better contact with electrode and faster electron transfer [36]. Several subsequent researches demonstrated that the improved Li⁺ ionic conductivity and increased Li⁺ vacancies resulted in lower charging potentials [37,38]. A theoretical calculation further revealed that the amorphous Li₂O₂ showed a twelve order of magnitude higher ionic conductivity, and a four order of magnitude higher electronic conductivity as compared with the crystalline one [39], which was directly proven by alternating current impedance and direct current polarization in the subsequent work [38]. In addition to the inherent improved ionic conductivity in film-like products, the film-like structure always means a compact contact with conductive electrode surface and thus enhances electron transfer. Furthermore, the direct access of Li⁺ to the uncovered part of the conductive electrode surface could be maintained. Only at the very end of discharge do the last holes in those films close up and the cell voltage visibly drops [40]. Numerous works have reported that the characteristics of positive-electrode catalyst surface could greatly influence the formation pathway of Li₂O₂ and lead to a film-like product that benefits battery performance, which will be intensively discussed in the later chapters. Thus, to achieve high-performance Li-O₂ batteries, the positive-electrode catalysts shall be highly valued. In the

following part, we will successively discuss the recently studied catalysts, including carbon materials, noble-metal-based materials, and transition-metal-based materials.

3. Carbon

Carbon materials generally possess many merits such as excellent electrical conductivity, good chemical and thermal stability, light weight, high surface area, sufficient resources, and low cost [41,42]. As a result, various carbon materials, including activated carbon [43], carbon paper [44,45], carbon nanotubes (CNT) [46–49], graphene [42,50–54], and mesoporous carbon [55–58], have been used as the positive electrode for Li-O₂ batteries. In this section, various strategies to design high-performance carbon positive-electrode catalysts are discussed, including structural design, heteroatom doping, defect modification, and synergy of the above three strategies.

3.1. Structural Design

Considering the cathodic process is an intricate redox reaction taking place in the triple-phase of gas, liquid, and solid, the structural design of positive electrodes is critical to achieve high-performance Li-O₂ batteries. It has been found that the morphology and quantity of discharge products can be regulated by controlling the pore sizes and porosity of carbon electrodes [59]. For example, Zhao et al. [60] reported a novel screen-printing method for preparing positive electrode materials, which could induce the generation of evenly distributed large crack-like pores (~10 μm). During discharge, such large pores facilitated the uniform deposition of Li₂O₂ products without pore clogging and electrical passivation. Compared with conventional slurry-coating method, the positive electrode fabricated by the screen-printing method doubled the battery's discharge capacity. In addition, by a simple dry compression molding method, Hu's group [42] prepared binder-free holey graphene-based air electrodes with mass loadings as high as 10 mg·cm⁻². Li-O₂ batteries with the as-prepared ultra-thick electrodes exhibited unexpected areal capacity values (up to ~40 mAh·cm⁻²) and superior cycling stability which are better than that of their thinner counterparts.

Inspired by eddy current effects in nature, Bae and co-workers [44] used an imprinting process with a micro-scale metal mold to prepare patterned carbon papers as air electrodes of Li-O₂ batteries. The patterned positive electrode not only enhanced the transport velocity of oxygen due to the intensified eddy current effect, but also increased reaction active sites due to a larger roughness factor (Figure 2a). Insulated, insoluble and bulky Li₂O₂ is difficult to decompose during recharge, which leads to high overpotentials and even blocks the pores of electrodes after several cycles. A unique mesoporous carbon electrode, which could guide the formation of one-dimensional (1-D) and amorphous Li₂O₂ (Figure 2b), was successfully employed as the positive electrode for Li-O₂ batteries [55]. In contrast to bulk Li₂O₂, the 1-D and amorphous Li₂O₂ with high specific surface area was much easier to decompose and thus led to an improved round-trip efficiency of ~80% (Figure 2c–e). In order to improve superoxide solubility and oxygen diffusivity, Balaish et al. [61] designed perfluorocarbons (PFCs)-CNTs hybrid air electrodes for Li-O₂ batteries. The free-standing CNTs with a meso-pore structure enabled better miscibility of PFCs and electrolyte (Figure 2f). Consequently, the advantages of PFCs as oxygenated-species' mediators and providers could be fully utilized. Integrating the strategies for promoting the diffusion of oxygen, regulating the growth of Li₂O₂ discharge products, as well as facilitating the wettability of electrolytes, a variety of carbon materials with hierarchical porous structures, such as carbon nanotubes-Ni foam composites [46], mesoporous nano-cubes [56], and wood-derived, free-standing porous carbon [62], have been successfully prepared and applied in high-performance Li-O₂ batteries.

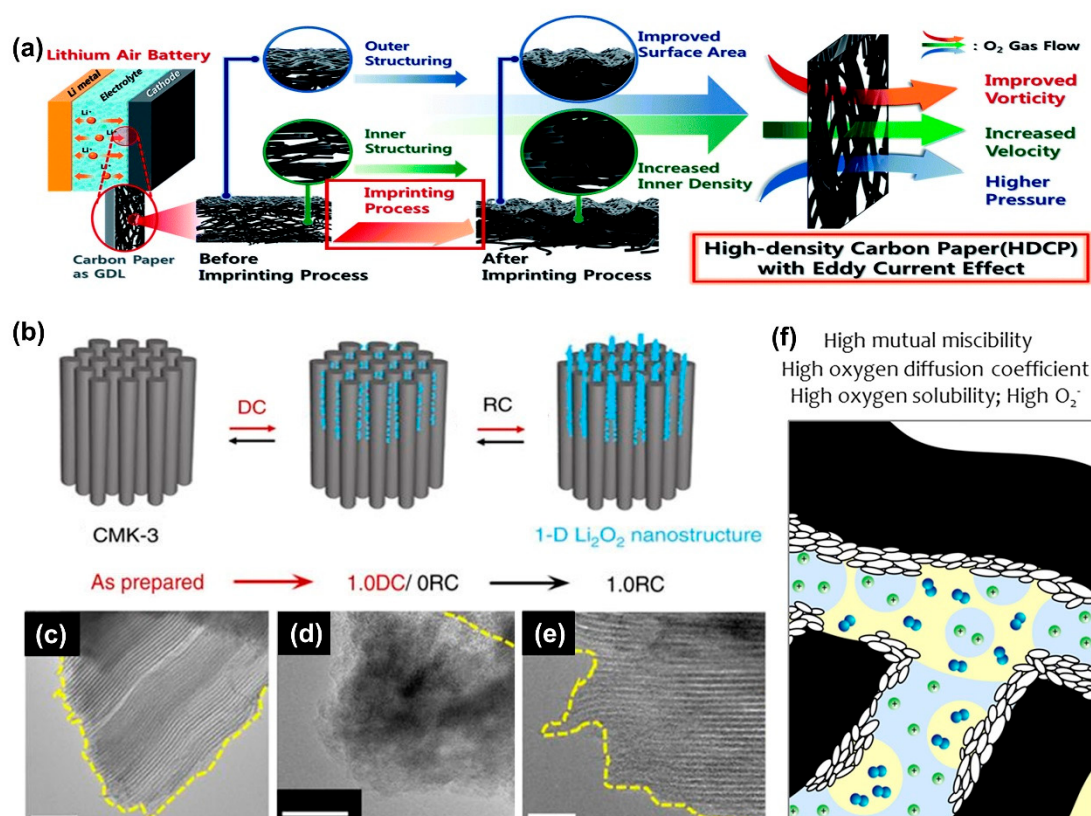


Figure 2. (a) Schematic illustration of the high-density carbon paper. (b) Schematic illustration of the growth and decomposition of Li_2O_2 (blue) induced by CMK-3. TEM images of (c) as-prepared, (d) fully discharged (marked as 1.0 DC or 0 RC), and (e) fully recharged (marked as 1.0 RC) CMK-3 electrodes. The scale bars are 50 nm. The corresponding capacity and current density are 1.0 mAh and $50 \text{ mA} \cdot \text{g}^{-1}_{\text{carbon}}$, respectively. The yellow dashed lines indicate the surface of CMK-3. (f) Schematic illustration of high mutual miscibility of PFCs (yellow) and electrolyte (blue). (a) Reproduced with permission from Ref. [44], copyright 2018, The Royal Society of Chemistry. (b–e) Reproduced with permission from Ref. [55], copyright 2018, Nature Publishing Group. (f) Reproduced with permission from Ref. [61], copyright 2018, Elsevier.

In addition to the electrochemical performance discussed above, operational safety, environmental adaptability, and environmental friendliness are also significant factors that have great impacts on the practical application of Li-O_2 batteries. Compared with liquid electrolyte, non-flammable and non-volatile solid electrolyte can greatly strengthen the safety of batteries. However, the use of solid electrolyte generally suffers from huge ohmic resistance and limited triple-phase boundaries [63,64]. To solve this problem, Zhao et al. [65] designed a seamless electrolyte-electrode structure, in which a top dense $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) layer served as the electrolyte and a bottom porous LATP scaffold coated with carbon nanoparticles (CNPs) and carbon nanofibers (CNFs) served as the electrode. A high-performance and high-security Li-O_2 battery was realized due to the reduced ceramic electrolyte layer (from several hundred micrometers to only $20 \mu\text{m}$) and the expanded electrode/electrolyte interface area (330 times). For Li-O_2 systems, even traces of water can cause destructive blows to both the positive and negative electrodes, so there still remain enormous challenges to achieve the long-term stable operation of Li-O_2 batteries under ambient conditions. Duan's group [50] reported a three-dimensional (3-D) hydrophobic graphene membrane with a highly cross-linked network which was efficiently selective for oxygen and water due to the tortuous hydrophobic channels. Moreover, the membrane could accelerate the transport of electrons, oxygen, and ions, and offer sufficient spaces for the deposition of Li_2O_2 discharge products. A Li-O_2 battery using this membrane as the positive electrode displayed exceptional performance under ambient conditions, including a high capacity

(>5700 mAh·g⁻¹ over 20 cycles) and repeated discharge/recharge behaviors (>2000 cycles with 140 mAh·g⁻¹, and >100 cycles with 1425 mAh·g⁻¹). Waste recycling is an important embodiment of the concept of sustainable development in nowadays society. By special treatment (e.g., carbonization), the organics are able to become inorganic carbon materials with unique 3-D network structures. Therefore, some organic wastes such as waste citrus peel [66], poplar inflorescence [43], yellow pine wood [62], and vacuum residue of ultra-heavy oil [67] have been employed as precursors for carbon positive electrode materials of high-performance Li-O₂ batteries.

3.2. Heteroatom Doping

To further improve the catalytic activity of carbon materials, heteroatom doping is considered as a valid strategy because it can activate the π electrons of carbon and thus speeding up reaction kinetics and reducing charge/discharge overpotentials [68]. Nitrogen is the most common doping element of this modification strategy. A lot of nitrogen-doped carbon materials such as mesoporous N-doped onion-like carbon [57], binder-free N-doped carbon paper [45], 3-D porous N-doped graphene aerogels [51], and C_xN_y particles@N-doped porous graphene [69] have been fully investigated.

With the help of density functional theory (DFT) computations, Zhou et al. [70] systematically investigated the ORR mechanism and initial nucleation processes of Li₂O₂ discharge products by selecting pristine and N-doped graphene as the research objects. This theoretical study demonstrated that pyridinic N-doped graphene facilitated the nucleation of Li₂O₂ clusters more effectively than pristine and graphitic N-doped graphene (Figure 3a). The superior catalytic properties of pyridinic N-doped graphene can be attributed to the powerful electron-withdrawing ability of N, which can make its neighboring carbon atoms be active to adsorb Li⁺ and O₂. In order to more systematically investigate the effects of heteroatom doping on carbon materials, Zhou's group [53] prepared pristine, N-doped, and S-doped bi-continuous nano-porous graphene electrodes for Li-O₂ batteries, respectively. The ORR catalytic activities of the three graphene electrodes were carefully studied. In the range of 2.4–2.7 V, the N-doped graphene electrode delivered maximum current at any potential as compared with the other two graphene electrodes. At a current density of 0.2 mA·cm⁻²_{geo}, the corresponding potentials were determined to be 2.49, 2.60, and 2.63 V for the pristine, S-doped, and N-doped graphene electrodes, respectively (Figure 3b). Furthermore, compared with the N-doped graphene electrode, the S-doped graphene electrode in Li-O₂ batteries exhibited better cycling stability at the controlled capacity of both 1000 and 2000 mAh·g⁻¹ (Figure 3c). The results revealed that the N-doped graphene can enhance the ORR kinetics more effectively while the S-doped graphene is more stable, and they are both more superior than the pristine graphene. In addition to nitrogen and sulfur, boron is also a doping element for the optimization of carbon materials. A 3-D porous B-doped reduction graphite oxide (B-rGO) electrode was successfully prepared by a simple freeze-drying method [71]. On account of its cross-linked structure and pore-forming property, boric acid contributed to form the 3-D hierarchical porous structure of the B-rGO. More importantly, as the boron source, boric acid helped to generate the B-O functional groups, which could serve as the catalytic active sites, resulting in much lower overpotentials for the ORR and OER processes (Figure 3d,e). With the B-rGO as a positive electrode, the Li-O₂ battery possessed a high discharge capacity and outstanding performance rate.

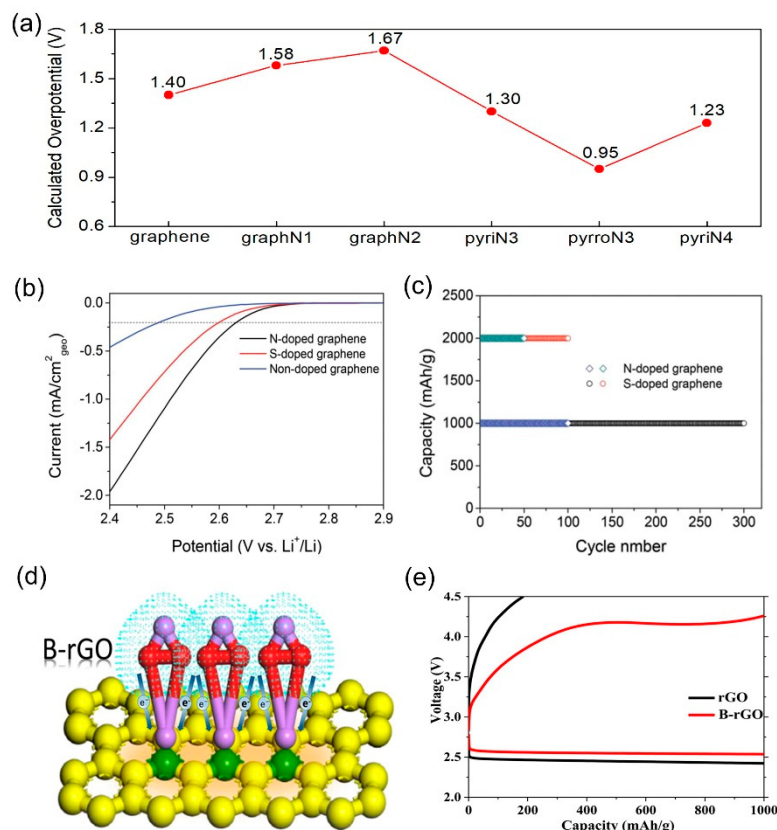


Figure 3. (a) The curve of calculated overpotentials (for the initial nucleation of Li_2O_2 at $U = 2.92$ V) versus graphene species. GraphN1 and graphN2 represent the graphitic N content of 2.33 wt % and 4.64 wt %, respectively. PyriN3 and pyriN4 represent the pyridinic N content of 7.07 wt % and 9.59 wt %, respectively. PyrroN3 represents the pyrrolic N content of 7.07 wt %. (b) Background-corrected ORR polarization curves of pristine, S-doped, and N-doped graphene electrodes collected in O_2 -saturated 1.0 M LiTFSI/TEGDME at $50 \text{ mV}\cdot\text{s}^{-1}$. (c) Cycling performance of S-doped and N-doped graphene electrodes at the current density of $300 \text{ mA}\cdot\text{g}^{-1}$ in Li-O_2 batteries. (d) Schematic illustration of B-rGO as the substrate capturing electrons from Li_2O_2 . The yellow, green, purple, and red spheres represent C, B, Li, and O atoms, respectively. (e) The first discharge-recharge curves of B-rGO and rGO at the current density of $2000 \text{ mA}\cdot\text{g}^{-1}$ in Li-O_2 batteries. (a) Data from Ref. [70]. (b,c) Reproduced with permission from Ref. [53], copyright 2015, Wiley-VCH. (d,e) Reproduced with permission from Ref. [71], copyright 2016, American Chemical Society.

3.3. Defect Modification

Surface defects of carbon materials may lead to undesired side reactions under high charging overpotential, which is one of the main reasons for the capacity fading of Li-O_2 batteries. In order to settle or weaken the drawback of carbon materials, coating surface and decreasing defect as two effective methods have been extensively investigated. For instance, Wang et al. [58] prepared a 3-D ordered mesoporous (3DOM) carbon material as the positive electrode of Li-O_2 batteries. Furthermore, for the sake of covering up the defects and preventing them from contacting with the reactive intermediates (e.g., O_2^-), the researchers also fabricated a rather thin layer of FeO_x on the 3DOM carbon surface via atomic layer deposition. Guo and co-workers [47] reported a Ru-IL (ionic liquid)-CNTs composite positive electrode, in which Ru, IL, and CNTs served as the catalyst, the carbon protection additive, and the substrates of the electrode, respectively. The sub-nanometer IL cation linker could availably seal up the surface defects of CNTs without retarding the charge transfer of Li^+/e^- , thus significantly inhibiting the emergence of side reactions. The optimization of the synthesis methods can effectively decrease surface defects of carbon materials. Dong et al. [48] prepared ultra-long, highly ordered, and vertically

arranged CNTs on permeable tantalum foil substrates (VACNTs-Ta) by using the thermal chemical vapor deposition technique. The well-crystallized CNTs on Ta foil had less surface defects ($I_D/I_G = 0.83$) as compared with the powder CNTs. Liu and co-workers [54] employed the plasma-enhanced chemical vapor deposition method to prepare a vertically arranged graphene nano-walls on Ni foam with an even lower I_D/I_G value of 0.85 at ambient temperature.

3.4. Synergy Strategies

Obviously, structural design, heteroatom doping, and defect modification have important effects on the performance of carbon materials in different aspects. Combining different modification strategies would result in further better results. Actually, some researchers have already made extensive attempts. For instance, in the report of Zhang et al. [49], the interpenetrative hierarchical N-doped CNTs were in situ grown on the surface of stainless steel mesh (N-CNTs@SS), generating a self-supporting, binder-free, flexible, and low-cost electrode. Due to the synergistic effects of structural design and heteroatom doping, the Li-O₂ batteries equipped with the N-CNTs@SS positive electrode displayed a high discharge capacity ($9299 \text{ mAh}\cdot\text{g}^{-1}$ at $500 \text{ mA}\cdot\text{g}^{-1}$), a superior rate capability, and excellent cycling stability (as long as 232 cycles). The combination of carbon modification and catalyst loading has also been extensively studied, and will be depicted later.

4. Noble Metals and Their Oxides

To develop catalysts with higher performance beyond carbon materials, researches paid attentions to noble metal catalysts which have shown high activity toward breaking and rebuilding O–O bond in water splitting and fuel cell. Except the intrinsic catalytic activity toward decomposing discharge product, many catalysts play their part in Li-O₂ batteries by inducing the deposition of Li₂O₂ and controlling the morphology of Li₂O₂ into an amorphous, and in most cases, presenting a film-like morphology rather than a bulk crystalline Li₂O₂. As mentioned before, those amorphous film-like products always show compact contact with electrode surface and enhanced ionic conductivity due to the abundant Li⁺ vacancies. Moreover, such thin film-like products could also guarantee the convenient Li⁺ pathway toward the conductive electrode surface.

4.1. Adsorption of Discharging Intermediate LiO₂

As mentioned above, the morphology and crystallinity of Li₂O₂ could greatly influence the electronic and ionic conductivity and thus the battery performance. For example, Zhuang et al. [72] investigated the relationship between battery performance and discharge product morphology by a planar model electrode method. The performance of the positive electrode with wormlike Li₂O₂ product always surpass those with large Li₂O₂ particles. They found the formed Li₂O₂ could be divided into two types of morphologies which strongly depended on the surface type of positive electrode (Figure 4a). By correlating the DFT calculation result and charge/discharge voltage plateau, it was found that the adsorption energy of LiO₂ on the catalyst and the charging potential presented a volcano shaped curved relationship (Figure 4b). With the adsorption energy increased from 0 eV, the charging overpotential decreased. But when the adsorption energy exceeded 4 eV and keep increasing, the overpotential started to increase instead. Such results are correlated with the product morphology. An appropriate LiO₂ adsorption energy could benefit the fast nucleation of newly formed discharging intermediate LiO₂, leading to smaller particles and eventually thin film- or worm-like products instead of bulk crystal products. However, when the adsorption became too strong, the absorbed particle would become too large. This work clearly revealed how the discharge product morphology changed when the adsorption energy differed, and thus impacted the battery performance.

Following the above strategy, there are plentiful of catalysts reported function in the way of inducing the deposition of Li₂O₂ and enhancing battery performance by forming amorphous or film-like products. As illustrated in Figure 4c, a Pd nanoparticle-loaded graphene positive electrode shows the obviously changed morphology of amorphous Li₂O₂ thanks to the stronger interaction

between the Pd electrode and LiO_2 . In contrast, a nearly perfect crystalline Li_2O_2 was observed on the pure graphene model positive electrode [73]. Such amorphous product-loaded positive electrodes presented higher ionic conductivity accompanied with low charge overpotential. In other works, small and vacancy-rich products were obtained with the help of catalysts [74–77]. By interacting with LiO_2 intermediate, the deposition site of Li_2O_2 could be regulated. The uniform growth of discharge product was observed with the help of SEM in a Pd coated anodic aluminum oxide as a comparison with the migrated and aggregated Li_2O_2 products owing to the lack of anchoring ability toward discharge product [78]. A similar phenomenon was also observed by Yang et al. [79], with the help of Au nanoparticles, which possessed stronger adsorption ability according to the DFT calculation results. The discharge products were prior to growth inside the carbon tube arrays and presented an amorphous film-like morphology under SEM observation. In the Au nanocrystals decorated MnO_2 sheets positive electrode, with the help of SEM the discharge product was observed to formed only inside the porous MnO_2 where Au particles were loaded [80]. In order to lower the cost on the positive electrode, compositing with carbon materials is highly recommended by researchers. Moreover, the highly porous structure of carbon materials could be fully utilized with a boosted exposure surface area of noble-metal-based catalysts and lead to increased active sites number on catalyst surface that could definitely benefit battery performance. Furthermore, catalyst component docking on the carbon surface could effectively avoid the direct contact between vulnerable carbon defects and highly reactive reduced oxygen species [81–83].

4.2. Stabilization of Discharging Intermediate LiO_2

Since the catalysts could adsorb the unstable discharging intermediate LiO_2 , what if we take measures to adsorb and further stabilize this intermediate to make it the final product? The crystalline LiO_2 exhibits half-metal characteristics and could present much higher electronic conductivity compared with the insulating characteristics of general discharge product Li_2O_2 . With such a vision, Lu's group [84] proposed a unique Li-O₂ battery with a stable LiO_2 crystal as the final discharge product for the first time. The high-energy X-ray diffraction (HE-XRD) result in Figure 4d indicated that this unique crystalline discharge product was stable enough to be stored for at least one week, and showed a high repeatability during the following battery cycling. This indicated that the sole discharge product in this unique secondary Li-O₂ battery system was crystalline LiO_2 . Since the LiO_2 crystal was so stable that it could be called as the discharge product rather than an intermediate. Moreover, such discharge product could be reversibly cycled for about 40 cycles, showing a low charging potential of 3.65 V during cycling under current density of $100 \text{ mA}\cdot\text{g}^{-1}$. The Ir nanoparticle-loaded rGO positive electrode played a critical role in this newly proposed reaction system. After the first discharge, the surface of Ir particles occurred an intermetallic phase of Ir_3Li sharing similar crystallographic lattice of LiO_2 (orthorhombic lattice). As shown in Figure 4e, the good lattice matches between the crystalline faces of Ir_3Li and LiO_2 demonstrated that the Ir_3Li could act as a template for the epitaxial growth of LiO_2 crystals, which was considered as the root cause for the formation of novel discharge product for Li-O₂ battery. Furthermore, the calculation results revealed that the LiO_2 was rather stable in crystalline state, while a small cluster of LiO_2 molecules would undergo a quick disproportionation. After that, Liu et al. [85] reported amorphous LiO_2 discharge products stabilized by positive electrode of Pd nanoparticles loaded 3D rGO. With the unique discharge product of Li-O₂ battery, the battery presented an even lower charging potential of 3.25 V as compared with that reported by Lu's group under the same current density of $100 \text{ mA}\cdot\text{g}^{-1}$ (3.6 V vs. 3.25 V). The good performance can be attributed to the enhanced electronic and ionic conductivity of amorphous LiO_2 . However, the stability of LiO_2 is weakened in the form of amorphous phase, such phenomenon is quite consistent with the previous calculation result [84].

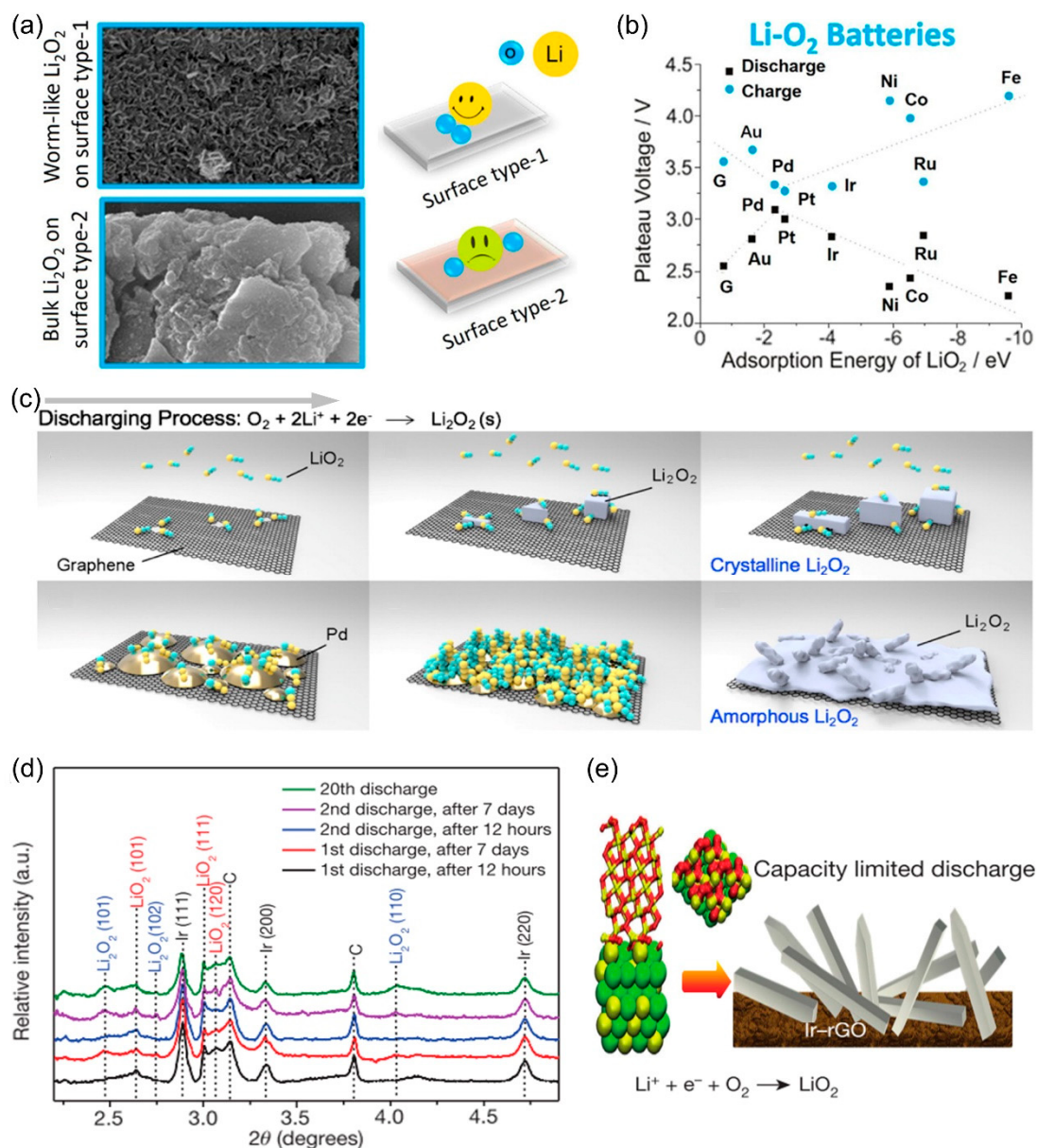


Figure 4. (a) Li_2O_2 with different morphologies formed on different positive electrode surface types. (b) The volcano shape relationship between charge/discharge voltage plateau and adsorption energy of LiO_2 on the positive electrode surfaces. (c) The growth model of Li_2O_2 on graphene and Pd coated graphene. (d) The HE-XRD patterns of discharge product on Ir-rGO as a function of ageing time. (e) Schematic illustration for the lattice matching between Ir_3Li and Li_2O_2 . (a,b) Reproduced with permission from Ref. [72], copyright 2017, American Chemical Society. (c) Reproduced with permission from Ref. [73], copyright 2016, American Chemical Society. (d,e) Reproduced with permission from Ref. [84], copyright 2016, Nature Publishing Group.

4.3. Utilisation of Bi-Metallic Catalysts

As the studies on noble metal catalysts for $\text{Li}-\text{O}_2$ batteries go deeper, the weaknesses of mono-component noble metal catalyst such as high cost and limited catalyst activity arise. In addition to the strategies like nanocrystallization and compositing with other materials to form a heterogeneous composite material with increased exposure surface to achieve better performance, forming bi-metallic materials with low content of noble-metal is another way to improve the performance without weakening the inherent advantages and effectively lowering cost. According to the theoretical D-band center model, by alloying with another metal element, the D-band center of catalyst could be adjusted in

a wide scope, while the catalytic activity is tightly associated with the electronic band of catalyst [86]. In some reported cases, the catalytic activity was elevated for several times by using such a strategy [87,88]. Standing on the shoulders of those pioneers, calculations to reveal the catalytic mechanism of bi-metallic in Li-O₂ batteries were performed [89,90]. With the increasing Li⁺ adsorption energy, the overpotential of ORR could be reduced, but the OER overpotential was increasing with the increasing of LiO₂ adsorption energy. However, the obtained results were contrary to those of Xiao's [72]. In recent works on the bi-metallic catalysts, some details on the changes occurred on catalysts were discovered, which might help us to further understand the working mechanism of bi-metallic catalysts. For instance, in a Pd-Cu bi-metallic positive electrode, the partially oxidation of Cu on the surface could influence the coordination structure and thus the catalytic activity of the material [91]. A similar Cu oxidation phenomenon was also observed in a Pt-Cu core-shell structure bi-metallic catalyst, accompanied with partially oxidized Pt. The well stabilized surface Cu(I) benefiting from the unique structure of the core-shell bimetallic catalyst served as the key to improved OER catalytic performance [92].

5. Transition Metals and Oxides

Considering the high cost and scarce reserves in the earth, the noble-metal-based catalysts seem not to be a good choice for the commercialized positive-electrode catalysts of Li-O₂ batteries. In this regard, the transition metals contained catalysts would be preferable, which could exhibit excellent performance in catalyzing the redox reactions due to the non-full outer D band orbitals. There are always many single electrons that could easily lost and empty orbitals that could easily accept foreign electrons. In recent years, remarkable progress has been made with respect to transition-metal-based catalysts, including not only their performance but also working mechanism in the pursuit of a better Li-O₂ battery.

5.1. Adsorption of Discharging Intermediate LiO₂

As discussed above, the morphology and physicochemical property of discharge product can effectively influence the charging performance of Li-O₂ batteries. Some pioneer works have revealed that catalysts determined the deposition process and finally affected the morphology of discharge product by the different adsorption ability toward LiO₂ intermediate [93–96]. Adopting such strategy, several relative works were published. For example, by calculating the adsorption energy of LiO₂ on different positive electrode surfaces, researchers found out that the CoO surface showed the highest adsorption energy of LiO₂. The formation of amorphous Li₂O₂ showed a high recharge reversibility and this benefited Li⁺ transportation toward positive electrode. As comparison, the bare carbon positive electrode presented the bulk Li₂O₂ after discharge, where lots of bulk products were still remaining on the positive electrode surface after charging. This indicates the poor rechargeability of the pristine positive electrode (Figure 5a,b). Such a strong interaction with LiO₂ could moderate the distribution of this highly reactive intermediate, and thus reduce the direct contact with carbon, preventing unwanted side reactions [97]. The calculation on the whole process of LiO₂ adsorption during discharge was completed by studying Co₂CrO₄ as the positive-electrode material [98]. Another calculation was conducted by investigating the relationship between the oxygen adsorption energy on the positive electrode surface and the morphology product. As expected, the stronger adsorption energy the positive electrode possessed, the smaller product and a better battery performance could be obtained. The strong adsorption of oxygen species on the Co₃O₄ surface was then powerfully evidenced by the RRDE measurement. As shown in Figure 5c, in the surface growth model of Li₂O₂ on the Co₃O₄ positive electrode surface, the O₂ was strongly adsorbed on the surface and trapped one electron to form a surface adsorbed O₂^{•−} or LiO₂ via the inner-sphere electron transfer pathway, forming a surface adsorbed LiO₂ intermediate in the inner Helmholtz plane. While for the CNT positive electrode, the solution model was introduced considering the weak adsorption of O₂ on the CNT surface. The dissolved O₂ could directly accept one electron to form a soluble O₂^{•−} or a solution nucleated LiO₂ via the out-sphere electron transfer route in the range of outer Helmholtz plane. In

RRDE measurement, the $\text{O}_2^-/\text{LiO}_2$ in solution could be oxidized at the ring, while the oxidation current of the surface adsorbed $\text{O}_2^-/\text{LiO}_2$ could only be collected from the disc. The plain curve of ring current for Co_3O_4 positive electrode indicated the very small amount of dissolved oxygen species in solution. While a significantly higher ring current was recorded for CNT positive electrode, indicating the existence of large amount of $\text{O}_2^-/\text{LiO}_2$ in solution. As shown in Figure 5d, such a deposition inducing ability was not affected by the changing morphology of catalyst, suggesting that it's the inherent adsorption ability towards the O_2 molecule, rather than the catalysts' morphology, dominates the deposition behavior of the discharge product [99].

On the basis of the behavior of oxygen adsorption, researchers proposed that the oxygen vacancy could adsorb oxygen species (O_2 , O_2^- , O_2^{2-}) during discharging on the catalyst surface, promoting the surface growth of Li_2O_2 to a film-like product. To further prove this opinion, they added a trace amount of water into electrolyte which is known for elevating solution free energy to enhance the solvating of LiO_2 , and found that the film-like discharge product was thickened. Comparing the toroid discharge product on the carbon surface and the thin or thick film-like product on CeO_2 surface, they concluded that the nucleation of solvated LiO_2 via a surface inducing process could lead to a smaller product particle with low crystallinity, which enhances the charging process of batteries [100]. To further utilize the catalytic activity of oxygen vacancies, numerous oxygen vacancies were introduced to a high surface TiO_2 thin film by decorating Co_3O_4 nanoparticles. Benefiting from the unique porous structure with highly exposed oxygen vacancies, Li_2O_2 product with amorphous film-like morphology was obtained, resulting in enhanced battery performance [101]. As shown in Figure 5e,f, the oxygen vacancies always indicated the exposure of positive valence atom, which, in some cases, are catalytic active transition metal atom. Such a structure could combine the deposition and in situ catalyzation of Li_2O_2 decomposition which was called self-catalyze. Such material showed a significant low charging overpotential when served as the positive-electrode catalyst of Li- O_2 battery [102]. Thanks to the oxygen vacancies on NiFeO_x surface, Li 2a vacancy rich products with little crystal accumulating into a film-like Li_2O_2 was achieved accompanied with high ionic conductivity enabled by those Li^+ vacancies. They found such a highly conductive product resulted in a thick film of 19 nm, much higher than those reported 7 nm. Such a positive electrode presented a high specific capacity of $25,000 \text{ mAh}\cdot\text{g}^{-1}$ [103], suggesting that film-like products do not always lead to lower capacities than that with bulk products. The results pave new ways to design high performance positive electrode for Li- O_2 batteries.

The Li^+ vacancy rich product presents some characteristics of the discharging intermediate LiO_2 , such as higher electronic conductivity and the high tendency to be decomposed during charging. Such intermediate-like product could be stabilized by the nano-size effect of ZnO nanoparticles. As illustrated by Figure 6a, the pristine VACNTs showed the formation of classical aggregated bulk Li_2O_2 discharge product, while the ZnO/VACNTs positive electrode showed a greatly depressed disproportionation of LiO_2 intermediate which was enabled by restricting LiO_2 in the nano-size space between ZnO and CNT, leading to ultra-small crystalline products of LiO_2 , Li_3O_4 and Li_2O_2 (Figure 6b,c). As a result, the batteries with ZnO coated CNT positive electrode showed low charge potential and long cycling life [104]. Such an intermediate stabilizing strategy was also applied in lithium carbon dioxide batteries and significantly reduced the charging over potential [105]. More and more catalysts based on the intermediate adsorption effect and deposition-morphology controlling were reported [106–108]. Such synergy strategy seems a viable path to further promote the catalytic activity of catalysts, resulting in Li- O_2 batteries with better performance.

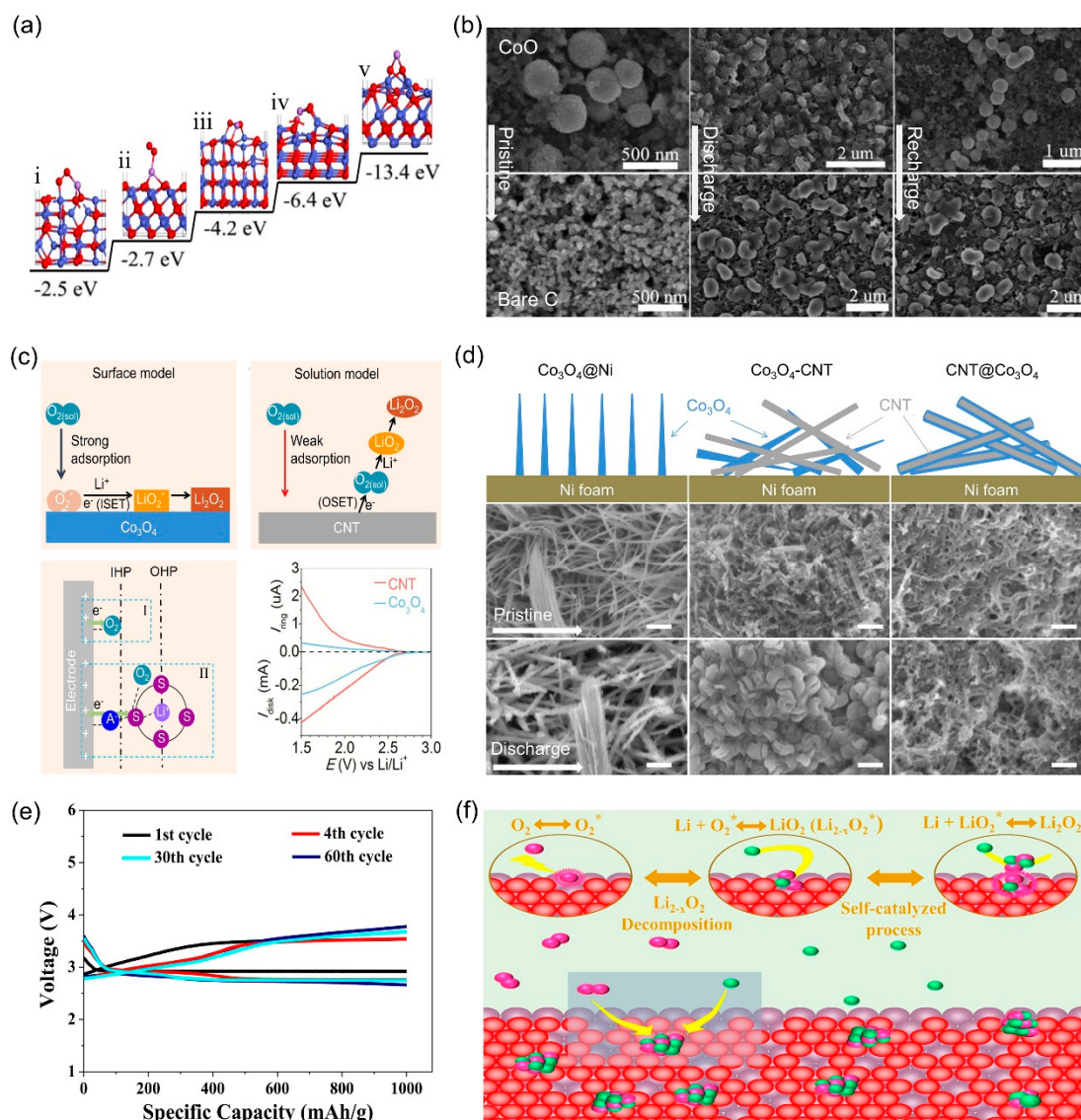


Figure 5. (a) The most stable configurations of Li_2O_2 adsorption on the positive electrode surfaces of (i) Co_3O_4 (110), (ii) O-CoO (111), (iii) CoO (200), (iv) CoO (220), and (v) Co-CoO (111). (b) The morphology comparison of different positive electrode and their discharge/charge states. (c) The illustration of Li_2O_2 growing on different positive electrode surfaces with varied O_2 adsorption ability and the collected RRDE curves. (d) Schematics and SEM images of designed positive electrode materials. (e) Discharge/charge voltage profiles of the Li-O_2 batteries with MoO_{3-x} positive electrode. (f) Schematic diagram of the proposed electrochemical mechanism of the reversible formation of the discharge products on the surface oxygen vacancies of MoO_{3-x} positive electrode. (a,b) Reproduced with permission from Ref. [97], copyright 2015, Nature Publishing Group. (c,d) Reproduced with permission from Ref. [99], copyright 2017, Elsevier. (e,f) Reproduced with permission from Ref. [102], copyright 2017, Elsevier.

5.2. Composite with Carbon

It is known that the major fraction of transition metal oxides are not good electronic conductors. The electron transfer during OER would be limited due to the lacking of good electronic conductivity, leading to enlarged polarization. Therefore, it's urgent to improve their electronic conductivity. Considering the cost and structural adjustability, carbon materials seem to be the optimal candidates to composite with transition metal oxides. The protection of the surface defects of carbon materials provided by a coating layer helps to depress the parasitic reaction and prolong the cycling life of

batteries. Moreover, the inherent high conductivity and porosity of carbon-based skeleton accelerate electron conducting and mass transfer in the positive electrode. In addition, the highly porous carbon skeleton could provide abundant docking sites for catalysts and thus could definitely increase the exposure area of catalysts and the exposed catalytic active sites. The composite of nano ZnO particles with a carbon coating was reported for the protection of carbon surface defects and the suppression of side reactions between carbon and Li_2O_2 . By using isotope labeling method, they found a significant decrease in carbon dioxide releasing after the ZnO decorating [109]. Thus, a prolonged cycling life of 100 cycles was presented by this stabilized carbon positive electrode. While the pristine carbon positive electrode only showed a short cycling number of 40 under the same cycling rate of $0.1 \text{ mA}\cdot\text{cm}^{-2}$. However, this method couldn't completely prevent the decomposition of carbon positive electrode because the formed discharge products could cause the detachment between carbon and ZnO particles. Thus, a better coating material or upgraded coating strategy need to be developed to further improve the performance of Li- O_2 batteries. Note that the morphology and the stoichiometric ratio of discharge product have significant influence on the battery performance. There are also some other reported works utilizing the synthesis strategy of carbon protection and deposition modulation in order to achieve high performance Li- O_2 batteries with low charging overpotentials accompanied by prolonged cycling lives [110–116]. For example, a magnetron sputtering n-type Si nanoparticle on CNT composite positive electrode presented discharge product in the form of low crystalline accompanied with large amounts of defects and vacancies inside, which was in a striking contrast to the large toroid products formed on the bare CNT surface. Furthermore, the side reactions were inhibited by the Si coating, resulting in ultra-low cycling voltage gap of 0.72 V. While for the pristine CNT positive electrode, the gap was increased to 1.7 V under the same testing condition of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ (Figure 6d,e) [117]. The battery with a highly ordered hierarchically porous honeycomb-like structured carbon skeleton could work under an ultrahigh discharging rate because of the greatly enhanced mass transfer. The loaded MnO_2 provided the positive electrode with the controlled formation of amorphous film-like Li_2O_2 product and led to a low charging potential [118].

5.3. Lithiation Enhanced Catalytic Performance

Although the transition metal oxides have been widely used in catalyzing ORR and OER, their activities remain to be promoted in some cases. There were some reported works utilizing valence moderating strategy to enhance the OER catalytic activity. Things seem to work well when some lower valence fraction was introduced into the pristine transition metal oxides [119,120]. As a controllable and convenient way to exquisitely moderate the valence and electronic structure of transition metal in their oxides. It was found that the band gap of the oxides could be narrowed by lithiation, suggesting an elevated electronic conductivity. Moreover, the adsorption energy toward LiO_2 intermediate could be strengthened by lithiation. By limiting the lithiation voltage, the lithiation level and the valence of transition metal could be easily controlled. In this way, the adsorption energy could be exquisitely moderated to an appropriate value according to the volcano plot [121]. Besides the valence change during lithiation, morphology evolution also occurs after lithium insertion, mainly from the pulverization of origin particles to smaller ones. Hence, ultrasmall sized Ni and Co nanoparticles ($\sim 2 \text{ nm}$) were obtained after the lithiation of cobalt-nickel layered double hydroxide (Co-Ni LDH). Compared with the pristine double hydroxide, the surface area of catalyst was greatly enhanced owing to the freshly formed Ni and Co metal nanoparticles after lithiation reaction. The catalyst with highly exposed active site showed significant improvement in lowering charging polarization for Li_2O_2 decomposition compared to the pristine Co-Ni LDH (Figure 6f–h) [122]. Similar strategies were applied in some other works with enhanced battery performance, indicating that the valence moderating strategy by electrochemically inserting cations could serve as a viable method to further enhance the catalytic performance of catalysts [123,124].

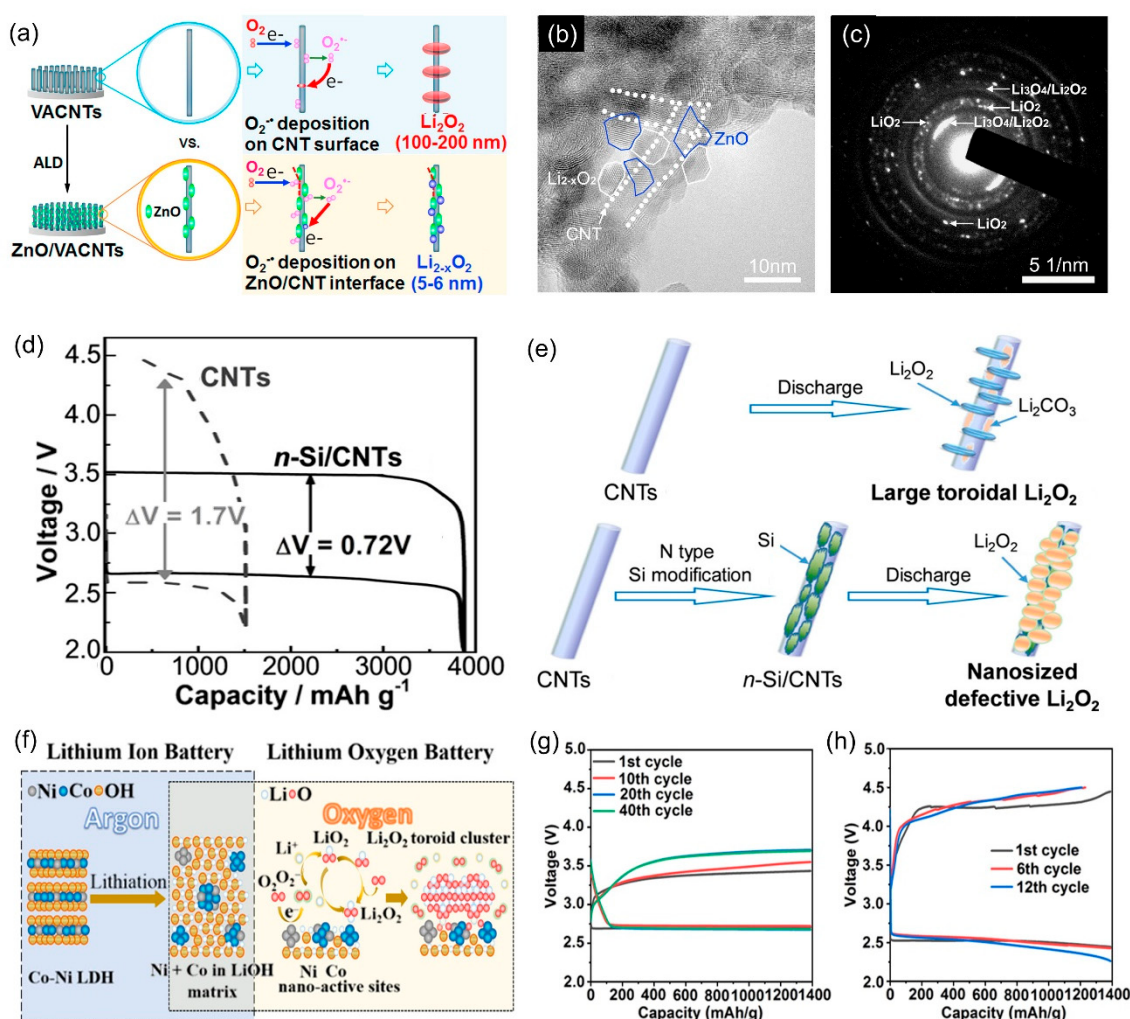


Figure 6. (a) Proposed mechanisms for electrochemical growth processes of discharge product on two different positive electrode (VACNTs and ZnO/VACNTs). (b) The high-resolution transmission electron microscopy (HRTEM) image along with (c) the corresponding SAED of the discharge products on ZnO/VACNTs. (d) The electrochemical performance of Li-O₂ batteries with CNTs positive electrode and n-Si coated CNTs positive electrode. (e) The schematic illustration of the product moderation and carbon protection by introducing n-type Si modification. (f) Schematic diagram of lithiated Co-Ni LDH with enhanced electrical conductivity network and highly exposed active sites. The cell performance of Li-O₂ batteries with (g) the lithiated Co-Ni LDH positive electrode and (h) the pristine Co-Ni LDH positive electrode. (a–c) Reproduced with permission from Ref. [104], copyright 2016, Elsevier. (d,e) Reproduced with permission from Ref. [117], copyright 2018, American Chemical Society. (f–h) Reproduced with permission from Ref. [122], copyright 2018, American Chemical Society.

The transition metals contain a large group of elements, and each element could function in a different way with a variety of mechanisms. Thus, it is challenging to regulate all the transition-metal-based catalysts in one article. Some other alternative mechanisms were also suggested, such as the epitaxial growth of nanosized Li₂O₂ enabled by Fe₂O₃ positive electrode [125], quite a similar concept to the Ir₃Li as the template for the epitaxially induced nucleation and growth LiO₂ in Lu's work [84]. Additionally, an optimized sp²/sp³ carbon bond was proposed by introducing CuCeO₃ nanorods to graphene nanosheet, together with the stabilized Cu⁺/Cu²⁺ redox pair enabled by the solid support of Ce element. The synergistic effect could contribute to improved battery performance [126].

6. Conclusions and Perspectives

In summary, this review provides an overview on the different positive-electrode catalysts for Li-O₂ batteries and the effective strategies to elevate their performance. The electrochemical performance of Li-O₂ batteries with different positive electrode materials are summarized in Table 1. The morphology moderating and vacancy introducing strategy, through the interaction with LiO₂, show high feasibility in both noble-metal and transition-metal-based catalysts. Moreover, lithiation and bi-metallic strategies via moderating the electronic structure of catalysts are effective to further elevate their catalytic activity. In addition, other strategies, such as introducing porous carbon skeletons to enhance the electronic conductivity of the positive electrode, are also widely adopted to improve the performance. Among all the reported positive-electrode catalysts, transition-metal-based catalysts would be the most promising candidate for large-scale Li-O₂ battery applications with regard to the balance of catalytic performance and cost.

Although much progress has been made, there are still some challenges which need to be addressed properly before the practical use of positive-electrode catalysts in Li-O₂ batteries. First, fundamental research about the battery reaction mechanism is still needed, which could speed up the oriented design and optimization of catalysts. Second, the electronic structure moderating strategy could be applied to subtly adjust the interaction intensity between electrochemical intermediates in order to achieve a fine regulated battery performance. Third, to ensure the good conductivity and large exposure surface area of catalysts, the synthesis of nanocrystallized catalysts and porous electrode structures shall be highly recommended. Finally, to realize the commercialization of Li-O₂ batteries, the large-scale production of positive electrodes with high performance, low cost, environmental friendliness and high safety should be considered.

Table 1. A summary on electrochemical performance of Li-O₂ batteries with different positive electrode materials.

Positive Electrode	Cycle Number/Capacity (mAh·g ⁻¹)/Rate (mA·g ⁻¹)	The First Charge Potential (V) ¹	Maximal Capacity (mAh·g ⁻¹)	Maximal Rate (mA·g ⁻¹)/Corresponding Charge Potential (V) ²	Electrolyte	Ref.
Carbon materials						
C-800 (nearly 96% microporous)	120/1000/200	3.51	6003	-/-	1.0 M LiNO ₃ in DMAc	[59]
CMPACs (citrus maxima peel)	466/500/-	~4.05	7800	-/-	1.0 M LiTFSI in TEGDME	[66]
N-PIACs (poplar inflorescence)	220/1000/-	~3.5	12060	-/-	1.0 M LiCF ₃ SO ₃ in TEGDME	[43]
Screen-printed cathode	40/1000/-	4.06	6840	-/-	1.0 M LiTFSI in TEGDME	[60]
P-CNF/CP	30/1000/200	~4.28	5312.51	500/~4.38	1.0 M LiTFSI in TEGDME	[44]
NCPE (N-doped carbon paper)	30/480/~35	~3.47	8040	~140/~3.7	1.0 M LiClO ₄ in DMSO	[45]
CNTs/NF	110/2000/200	3.4	12960	2000/4.4	1.0 M LiTFSI in TEGDME	[46]
VACNTs-Ta	>65/1000/200	~4.3	>10000	1000/~4.3	1.0 M LiTFSI in TEGDME	[48]
N-CNTs@SS	232/500/500	~3.75	9299	2000/-	0.5 M LiTFSI in PMIMTFSI	[49]
Dry-pressed hG	20/200/20	~4.15	~4000	-/-	1.0 M LiTFSI in TEGDME	[42]
3-D graphene membrane	>2000/140/2800	~3.5	>5700	-/-	1.0 M LiNO ₃ in DMAc	[50] ³
CB-H (graphene hollow spheres)	104/500/300	3.9	16805	1000/~4.05	1.0 M LiNO ₃ in DMAc	[67]
NPGAs (N-doped graphene aerogels)	72/1000/300	4.12	10081	3200/-	1.0 M LiTFSI in TEGDME	[51]
C _x N _y @NPG	200/1000/1000	4.1	16705	1000/~4.25	1.0 M LiTFSI in TEGDME	[52]
S-doped graphene	300/1000/300	~4.4	4920	1000/~4.55	1.0 M LiTFSI in TEGDME	[53]
N-doped graphene	100/1000/300	4.25	10400	-/-	1.0 M LiTFSI in TEGDME	[53]
VA-G/NF	10/280/140	3.4	-	-/-	1.0 M LiTFSI in TEGDME	[54]
B-rGO	35/1000/100	~3.88	~18000	2000/~4.15	1.0 M LiTFSI in TEGDME	[71]
CMK-3	19/500/50	3.2	-	2000/3.8	0.5 M LiTFSI in TEGDME	[55]
MCCs (meso-porous carbon nanocubes)	5/1000/400	3.75	26100	2000/-	0.1 M LiClO ₄ in DMSO	[56]
N-OLC (N-doped onion-like carbon)	194/1000/1000	3.51	12180	2000/-	1.0 M LiTFSI in TEGDME	[57]
CNPs/CNFs-LATP	1174/~141.5/~94.3	~3.9	-	-/-	LATP (Li _{1.3} Al _{0.3} -Ti _{1.7} (PO ₄) ₃)	[65]
Noble metals and their oxides						
Pt-HGNs	10/1000/100	3.1	~5600	500/3.35	1.0 M LiTFSI in TEGDME	[77]
Pt-Cu (2.5% Pt + 5% Cu)	35/500/100	3.15	2376	-/-	1.0 M LiCF ₃ SO ₃ in TEGDME	[91]
Pt ₃ Co NCs	65/1000/200	3.1	11000	2000/-	1.0 M LiCF ₃ SO ₃ in TEGDME	[86]
MmC@Ru	100/1000/400	3.4	12400	1000/3.55	0.5 M LiClO ₄ in DMSO	[81]
VACNT@RuO ₂	100/~1613/~806.5	3.6	9050	~1613/~4	1.0 M LiTFSI in TEGDME	[83]
RuO _x -CNp@In ₂ O ₃	165/1000/400	~4	~20000	2000/~4.6	1.0 M LiTFSI in TEGDME	[114]

Table 1. Cont.

Positive Electrode	Cycle Number/Capacity (mAh·g ⁻¹)/Rate (mA·g ⁻¹)	The First Charge Potential (V) ¹	Maximal Capacity (mAh·g ⁻¹)	Maximal Rate (mA·g ⁻¹)/Corresponding Charge Potential (V) ²	Electrolyte	Ref.
Pd/UPC	231/1000/300	3.35	-	500/3.95	1.0 M LiCF ₃ SO ₃ in TEGDME	[82]
RuO ₂ /UPC	150/1000/300	3.6	-	500/3.7	1.0 M LiCF ₃ SO ₃ in TEGDME	[82]
MGP-20 (MnO _x -GeO _y -Pd)	163/1000/300	3.1	10900	500/3.5	1.0 M LiCF ₃ SO ₃ in TEGDME	[76]
Pd-rGO	100/500/1000	3.25	18687	2000/-	1.0 M LiTFSI in TEGDME	[85]
Co ₃ O ₄ NAs/Pd NCs	258/500/100	3.75	5337	-/-	1.0 M LiClO ₄ in DMSO	[75]
Ir-rGO	~40/1000/100	~3.62	~9500	-/-	1.0 M LiCF ₃ SO ₃ in TEGDME	[84]
Au@CST	112/500/400	3.8	5488	1000/~4.4	1.0 M LiClO ₄ in DMSO	[79]
Au-δMnO ₂	165/500/400	3.8	10600	1600/3.9	1.0 M LiClO ₄ in TEGDME	[80]
Transition metals and their oxides						
Mixed-valent MnO _x spheres	320/1000/100	3.5	9709	800/3.6	1.0 M LiCF ₃ SO ₃ in TEGDME	[119]
Li _{0.50} MnO ₂	197/1000/200	3.6	10823	2000/4	1.0 M LiTFSI in TEGDME	[121]
Co ^{II} -salen/MCNTs@MnO ₂	300/1000/500	3.7	13050	500/3.7	5 mM Co ^{II} -salen/1.0 M LiTFSI in TEGDME	[113]
MnO ₂ /HPC	300/1000/350	3.5	~9200	5000/-	1.0 M LiTFSI in TEGDME	[118]
Holey 2-D Mn ₂ O ₃ nanosheets	33/1000/200	4.0	3600	-/-	1.0 M LiTFSI in TEGDME	[120]
CMO-4 (CoMn ₂ O ₄)	41/500/200	~4	~5860	400/-	0.5 M LiTFSI in TEGDME	[107]
Co-CoO/N-CNR	86/1000/100	3.9	10555	1000/-	1.0 M LiTFSI in TEGDME	[111]
CoO mesoporous spheres	300/1000/40	~3.6	4849	-/-	1.0 M LiTFSI in TEGDME	[97]
Co(OH) ₂ @CNS	40/715/150	3.8	5403	-/-	1.0 M LiCF ₃ SO ₃ in TEGDME	[116]
CCO (Co ₂ CrO ₄ yolk-shell nanospheres)	236/1000/200	3.25	8554	500/3.85	1.0 M LiTFSI in TEGDME	[98]
p-CNT/Co ₃ O ₄ [M]	116/500/200	3.65	4331	1100/4.35	1.0 M LiCF ₃ SO ₃ in TEGDME	[93]
Co ₃ O ₄ -TiO ₂ (B)	200/1000/100	3.8	11000	500/-	1.0 M LiTFSI in TEGDME	[101]
NCO@N-rGO (NiCo ₂ O ₄ nanoparticles)	112/1000/200	3.44	6716	1000/~3.9	1.0 M LiTFSI in TEGDME	[110]
Ni-MOFs	170/600/1200	~3.7	9000	1440/~3.95	1.0 M LiTFSI in TEGDME	[96]
NiFeO _x /CNT	126/1000/200	~3.75	16987	2000/-	0.5 M LiTFSI in TEGDME	[103]
Fe ₃ O ₄ -Fe nanohybrids	100/1000/500	~3.87	13890	2000/~4.3	1.0 M LiNO ₃ in DMAc	[95]
3DOM FePO ₄	300/1000/250	3.95	9923	500/~4.2	1.0 M LiTFSI in TEGDME	[124]
LFO-900 (α-Fe ₂ O ₃ -LaFeO _{3-x})	108/500/100	~3.6	7183.3	500/-	1.0 M LiTFSI in TEGDME	[106]
LNON/4 h (N-doped LaNiO ₃)	50/500/250	3.9	5910	400/-	1.0 M LiTFSI in TEGDME	[108]
G/meso-LaSrMnO	50/500/125	3.4	6515	1000/~4.1	1.0 M LiTFSI in TEGDME	[112]
Red-CuGeO ₃ -G (reduced CuGeO ₃ -G)	50/2000/1000	4.2	10030	-/-	1.0 M LiNO ₃ in DMAc	[126]
ZnO/VACNTs	112/1000/50	3.55	4580	-/-	0.9 M LiTFSI in TEGDME	[104]
MoO ₂ /graphitic foam	>55/500/1000	~4.18	5500	1000/~4.18	1.0 M LiTFSI in TEGDME	[115]
MoO _{3-x} NSs-2	60/1000/100	3.45	10825	-/-	1.0 M LiClO ₄ in DMSO	[102]

¹ The first charge potential corresponds to the voltage at half of the first charge capacity in the second column. ² Corresponding charge potential corresponds to the voltage at half of the first charge capacity at maximal rate. ³ The electrochemical data of Ref. [50] were acquired under ambient air.

Author Contributions: Proposal of this review's topic, J.C.; literature search, Y.C.; table and figures design, Y.H.; manuscript writing, discussing and revising, J.C., Y.C., Y.H., and Y.L.

Funding: This research was funded by the National Programs for Nano-Key Project, grant number 2017YFA0206700, the National Natural Science Foundation of China, grant number 21835004, and 111 Project from the Ministry of Education of China grant number B12015.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sathiya, M.; Rousse, G.; Ramesha, K.; Laisa, C.P.; Vezin, H.; Sougrati, M.-T.; Doublet, M.L.; Foix, D.; Gonbeau, D.; Walker, W.; et al. Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. *Nat. Mater.* **2013**, *12*, 827–835. [[CrossRef](#)]
2. Darwiche, A.; Marino, C.; Sougrati, M.T.; Fraisse, B.; Stievano, L.; Monconduit, L. Better cycling performances of bulk Sb in Na-ion batteries compared to Li-ion systems: An unexpected electrochemical mechanism. *J. Am. Chem. Soc.* **2012**, *134*, 20805–20811. [[CrossRef](#)] [[PubMed](#)]
3. Chen, J. Na⁺/vacancy disordering promises high-rate Na-ion batteries. *Acta Phys. Chim. Sin.* **2019**, *35*, 347–348.
4. Zhao, Q.; Yan, Z.; Chen, C.; Chen, J. Spinel: Controlled preparation, oxygen reduction/evolution reaction application, and beyond. *Chem. Rev.* **2017**, *117*, 10121–10211. [[CrossRef](#)] [[PubMed](#)]
5. Li, R.; Lu, Y.; Lei, K.; Li, F.; Cheng, F.; Chen, J. Resumption of the discharged Li-AgVO₃ primary batteries for rechargeable Li-O₂ batteries. *Acta Chim. Sin.* **2017**, *75*, 199–205. [[CrossRef](#)]
6. Chen, J. Materials for advanced batteries—A driving force of the mobile information society. *Acta Chim. Sin.* **2017**, *75*, 127–128. [[CrossRef](#)]
7. Littauer, E.L.; Tssai, K.C. Anodic behavior of lithium in aqueous electrolytes. *J. Electrochem. Soc.* **1976**, *6*, 964–969. [[CrossRef](#)]
8. Abraham, K.M.; Jiang, Z. A polymer electrolyte-based rechargeable lithium/oxygen battery. *J. Electrochem. Soc.* **1996**, *143*, 1–5. [[CrossRef](#)]
9. Wang, H.; Xie, K. Investigation of oxygen reduction chemistry in ether and carbonate based electrolytes for Li-O₂ batteries. *Electrochim. Acta* **2012**, *64*, 29–34. [[CrossRef](#)]
10. Oh, D.; Qi, J.; Lu, Y.-C.; Zhang, Y.; Shao-Horn, Y.; Belcher, A.M. Biologically enhanced cathode design for improved capacity and cycle life for lithium-oxygen batteries. *Nat. Commun.* **2013**, *4*, 2756. [[CrossRef](#)]
11. Cheng, F.; Chen, J. Metal-air batteries: From oxygen reduction electrochemistry to cathode catalysts. *Chem. Soc. Rev.* **2012**, *41*, 2172–2192. [[CrossRef](#)] [[PubMed](#)]
12. Peng, Z.; Freunberger, S.A.; Chen, Y.; Bruce, P.G. A reversible and higher-rate Li-O₂ battery. *Science* **2012**, *337*, 563–566. [[CrossRef](#)] [[PubMed](#)]
13. Ma, L.; Yu, T.; Tzoganakis, E.; Amine, K.; Wu, T.; Chen, Z.; Lu, J. Fundamental understanding and material challenges in rechargeable nonaqueous Li-O₂ batteries: Recent progress and perspective. *Adv. Energy Mater.* **2018**, *8*, 1800348. [[CrossRef](#)]
14. Ottakam Thotiyil, M.M.; Freunberger, S.A.; Peng, Z.; Bruce, P.G. The carbon electrode in nonaqueous Li-O₂ cells. *J. Am. Chem. Soc.* **2013**, *135*, 494–500. [[CrossRef](#)] [[PubMed](#)]
15. Mahne, N.; Schafzahl, B.; Leypold, C.; Leypold, M.; Grumm, S.; Leitgeb, A.; Strohmeier, G.A.; Wilkening, M.; Fontaine, O.; Kramer, D.; et al. Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium-oxygen batteries. *Nat. Energy* **2017**, *2*, 17036. [[CrossRef](#)]
16. Wang, Y.; Liang, Z.; Zou, Q.; Cong, G.; Lu, Y.-C. Mechanistic insights into catalyst-assisted nonaqueous oxygen evolution reaction in lithium-oxygen batteries. *J. Phys. Chem. C* **2016**, *120*, 6459–6466. [[CrossRef](#)]
17. Wang, D.; Mu, X.; He, P.; Zhou, H. Materials for advanced Li-O₂ batteries: Explorations, challenges and prospects. *Mater. Today* **2019**. [[CrossRef](#)]
18. Shu, C.; Wang, J.; Long, J.; Liu, H.-K.; Dou, S.-X. Understanding the reaction chemistry during charging in aprotic lithium-oxygen batteries: Existing problems and solutions. *Adv. Mater.* **2019**, 1804587. [[CrossRef](#)] [[PubMed](#)]
19. Wang, K.-X.; Zhu, Q.-C.; Chen, J.-S. Strategies toward high-performance cathode materials for lithium-oxygen batteries. *Small* **2018**, *14*, 1800078. [[CrossRef](#)]

20. Zhang, P.; Zhao, Y.; Zhang, X. Functional and stability orientation synthesis of materials and structures in aprotic Li-O₂ batteries. *Chem. Soc. Rev.* **2018**, *47*, 2921–3004. [[CrossRef](#)] [[PubMed](#)]
21. Lyu, Z.; Zhou, Y.; Dai, W.; Cui, X.; Lai, M.; Wang, L.; Huo, F.; Huang, W.; Hu, Z.; Chen, W. Recent advances in understanding of the mechanism and control of Li₂O₂ formation in aprotic Li-O₂ batteries. *Chem. Soc. Rev.* **2017**, *46*, 6046–6072. [[CrossRef](#)] [[PubMed](#)]
22. Johnson, L.; Li, C.; Liu, Z.; Chen, Y.; Freunberger, S.A.; Ashok, P.C.; Praveen, B.B.; Dholakia, K.; Tarascon, J.-M.; Bruce, P.G. The role of LiO₂ solubility in O₂ reduction in aprotic solvents and its consequences for Li-O₂ batteries. *Nat. Chem.* **2014**, *6*, 1091–1099. [[CrossRef](#)] [[PubMed](#)]
23. Gao, X.; Chen, Y.; Johnson, L.; Bruce, P.G. Promoting solution phase discharge in Li-O₂ batteries containing weakly solvating electrolyte solutions. *Nat. Mater.* **2016**, *15*, 882–889. [[CrossRef](#)] [[PubMed](#)]
24. Aetukuri, N.B.; McCloskey, B.D.; Garcia, J.M.; Krupp, L.E.; Viswanathan, V.; Luntz, A.C. Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li-O₂ batteries. *Nat. Chem.* **2015**, *7*, 50–56. [[CrossRef](#)] [[PubMed](#)]
25. Aurbach, D.; McCloskey, B.D.; Nazar, L.F.; Bruce, P.G. Advances in understanding mechanisms underpinning lithium-air batteries. *Nat. Energy* **2016**, *1*, 16128. [[CrossRef](#)]
26. Peng, Z.; Freunberger, S.A.; Hardwick, L.J.; Chen, Y.; Giordani, V.; Barde, F.; Novak, P.; Graham, D.; Tarascon, J.-M.; Bruce, P.G. Oxygen reactions in a non-aqueous Li⁺ electrolyte. *Angew. Chem. Int. Ed.* **2011**, *50*, 6351–6355. [[CrossRef](#)] [[PubMed](#)]
27. Yu, Q.; Ye, S. In situ study of oxygen reduction in dimethyl sulfoxide (DMSO) solution: A fundamental study for development of the lithium-oxygen battery. *J. Phys. Chem. C* **2015**, *119*, 12236–12250. [[CrossRef](#)]
28. Frith, J.T.; Russell, A.E.; Garcia-Araez, N.; Owen, J.R. An in-situ Raman study of the oxygen reduction reaction in ionic liquids. *Electrochem. Commun.* **2014**, *46*, 33–35. [[CrossRef](#)]
29. Galloway, T.A.; Hardwick, L.J. Utilizing in situ electrochemical SHINERS for oxygen reduction reaction studies in aprotic electrolytes. *J. Phys. Chem. Lett.* **2016**, *7*, 2119–2124. [[CrossRef](#)]
30. Zhai, D.; Wang, H.-H.; Lau, K.C.; Gao, J.; Redfern, P.C.; Kang, F.; Li, B.; Indacochea, E.; Das, U.; Sun, H.-H.; et al. Raman evidence for late stage disproportionation in a Li-O₂ battery. *J. Phys. Chem. Lett.* **2014**, *5*, 2705–2710. [[CrossRef](#)]
31. Olivares-Marin, M.; Sorrentino, A.; Lee, R.-C.; Pereiro, E.; Wu, N.-L.; Tonti, D. Spatial distributions of discharged products of lithium-oxygen batteries revealed by synchrotron X-ray transmission microscopy. *Nano Lett.* **2015**, *15*, 6932–6938. [[CrossRef](#)] [[PubMed](#)]
32. Cao, R.; Walter, E.D.; Xu, W.; Nasybulin, E.N.; Bhattacharya, P.; Bowden, M.E.; Engelhard, M.H.; Zhang, J.-G. The mechanisms of oxygen reduction and evolution reactions in nonaqueous lithium-oxygen batteries. *ChemSusChem* **2014**, *7*, 2436–2440. [[CrossRef](#)] [[PubMed](#)]
33. Luo, L.; Liu, B.; Song, S.; Xu, W.; Zhang, J.-G.; Wang, C. Revealing the reaction mechanisms of Li-O₂ batteries using environmental transmission electron microscopy. *Nat. Nanotechnol.* **2017**, *12*, 535–540. [[CrossRef](#)] [[PubMed](#)]
34. Wang, Y.; Lai, N.-C.; Lu, Y.-R.; Zhou, Y.; Dong, C.-L.; Lu, Y.-C. A solvent-controlled oxidation mechanism of Li₂O₂ in lithium-oxygen batteries. *Joule* **2018**, *2*, 2364–2380. [[CrossRef](#)]
35. Lu, Y.-C.; Shao-Horn, Y. Probing the reaction kinetics of the charge reactions of nonaqueous Li-O₂ batteries. *J. Phys. Chem. Lett.* **2013**, *4*, 93–99. [[CrossRef](#)]
36. Zhai, D.; Wang, H.-H.; Yang, J.; Lau, K.C.; Li, K.; Amine, K.; Curtiss, L.A. Disproportionation in Li-O₂ batteries based on a large surface area carbon cathode. *J. Am. Chem. Soc.* **2013**, *135*, 15364–15372. [[CrossRef](#)]
37. Gallant, B.M.; Kwabi, D.G.; Mitchell, R.R.; Zhou, J.; Thompson, C.V.; Shao-Horn, Y. Influence of Li₂O₂ morphology on oxygen reduction and evolution kinetics in Li-O₂ batteries. *Energy Environ. Sci.* **2013**, *6*, 2518–2528. [[CrossRef](#)]
38. Zhang, Y.; Cui, Q.; Zhang, X.; McKee, W.C.; Xu, Y.; Ling, S.; Li, H.; Zhong, G.; Yang, Y.; Peng, Z. Amorphous Li₂O₂: Chemical synthesis and electrochemical properties. *Angew. Chem. Int. Ed.* **2016**, *55*, 10717–10721. [[CrossRef](#)]
39. Tian, F.; Radin, M.D.; Siegel, D.J. Enhanced charge transport in amorphous Li₂O₂. *Chem. Mater.* **2014**, *26*, 2952–2959. [[CrossRef](#)]
40. Rinaldi, A.; Wijaya, O.; Hoster, H.E. Lithium-oxygen cells: An analytical model to explain key features in the discharge voltage profiles. *ChemElectroChem* **2016**, *3*, 1944–1950. [[CrossRef](#)]

41. Frackowiak, E.; Beguin, F. Carbon materials for the electrochemical storage of energy in capacitors. *Carbon* **2001**, *39*, 937–950. [[CrossRef](#)]
42. Lin, Y.; Moitoso, B.; Martinez-Martinez, C.; Walsh, E.D.; Lacey, S.D.; Kim, J.-W.; Dai, L.; Hu, L.; Connell, J.W. Ultrahigh-capacity lithium-oxygen batteries enabled by dry-pressed holey graphene air cathodes. *Nano Lett.* **2017**, *17*, 3252–3260. [[CrossRef](#)] [[PubMed](#)]
43. Wang, M.; Yao, Y.; Tang, Z.; Zhao, T.; Wu, F.; Yang, Y.; Huang, Q. Self-nitrogen-doped carbon from plant waste as an oxygen electrode material with exceptional capacity and cycling stability for lithium-oxygen batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32212–32219. [[CrossRef](#)] [[PubMed](#)]
44. Kim, M.-C.; So, J.-Y.; Moon, S.-H.; Han, S.-B.; Choi, S.; Kim, E.-S.; Shin, Y.-K.; Lee, J.-E.; Kwak, D.-H.; Lee, C.; et al. Nature inspired cathodes using high-density carbon papers with an eddy current effect for high-rate performance lithium-air batteries. *J. Mater. Chem. A* **2018**, *6*, 9550–9560. [[CrossRef](#)]
45. Liu, J.; Wang, Z.; Zhu, J. Binder-free nitrogen-doped carbon paper electrodes derived from polypyrrole/cellulose composite for Li-O₂ batteries. *J. Power Sources* **2016**, *306*, 559–566. [[CrossRef](#)]
46. Zhu, Q.-C.; Du, F.-H.; Xu, S.-M.; Wang, Z.-K.; Wang, K.-X.; Chen, J.-S. Hydroquinone resin induced carbon nanotubes on Ni foam as binder-free cathode for Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3868–3873. [[CrossRef](#)] [[PubMed](#)]
47. Lou, P.; Li, C.; Cui, Z.; Guo, X. Job-sharing cathode design for Li-O₂ batteries with high energy efficiency enabled by in situ ionic liquid bonding to cover carbon surface defects. *J. Mater. Chem. A* **2016**, *4*, 241–249. [[CrossRef](#)]
48. Yu, R.; Fan, W.; Guo, X.; Dong, S. Highly ordered and ultra-long carbon nanotube arrays as air cathodes for high-energy-efficiency Li-oxygen batteries. *J. Power Sources* **2016**, *306*, 402–407. [[CrossRef](#)]
49. Yang, X.-Y.; Xu, J.-J.; Chang, Z.-W.; Bao, D.; Yin, Y.-B.; Liu, T.; Yan, J.-M.; Liu, D.-P.; Zhang, Y.; Zhang, X.-B. Blood-capillary-inspired, free-standing, flexible, and low-cost super-hydrophobic N-CNTs@SS cathodes for high-capacity, high-rate, and stable Li-air batteries. *Adv. Energy Mater.* **2018**, *8*, 1702242. [[CrossRef](#)]
50. Zhong, X.; Papandrea, B.; Xu, Y.; Lin, Z.; Zhang, H.; Liu, Y.; Huang, Y.; Duan, X. Three-dimensional graphene membrane cathode for high energy density rechargeable lithium-air batteries in ambient conditions. *Nano Res.* **2017**, *10*, 472–482. [[CrossRef](#)]
51. Zhao, C.; Yu, C.; Liu, S.; Yang, J.; Fan, X.; Huang, H.; Qiu, J. 3D porous N-doped graphene frameworks made of interconnected nanocages for ultrahigh-rate and long-life Li-O₂ batteries. *Adv. Funct. Mater.* **2015**, *25*, 6913–6920. [[CrossRef](#)]
52. Wu, A.; Shen, S.; Yan, X.; Xia, G.; Zhang, Y.; Zhu, F.; Zhang, J. C_xN_y particles@N-doped porous graphene: A novel cathode catalyst with a remarkable cyclability for Li-O₂ batteries. *Nanoscale* **2018**, *10*, 12763–12770. [[CrossRef](#)] [[PubMed](#)]
53. Han, J.; Guo, X.; Ito, Y.; Liu, P.; Hojo, D.; Aida, T.; Hirata, A.; Fujita, T.; Adschiri, T.; Zhou, H.; et al. Effect of chemical doping on cathodic performance of bicontinuous nanoporous graphene for Li-O₂ batteries. *Adv. Energy Mater.* **2016**, *6*, 1501870. [[CrossRef](#)]
54. Han, C.-P.; Veeramani, V.; Hsu, C.-C.; Jena, A.; Chang, H.; Yeh, N.-C.; Hu, S.-F.; Liu, R.-S. Vertically-aligned graphene nanowalls grown via plasma-enhanced chemical vapor deposition as a binder-free cathode in Li-O₂ batteries. *Nanotechnology* **2018**, *29*, 505401. [[CrossRef](#)] [[PubMed](#)]
55. Dutta, A.; Wong, R.A.; Park, W.; Yamanaka, K.; Ohta, T.; Jung, Y.; Byon, H.R. Nanostructuring one-dimensional and amorphous lithium peroxide for high round-trip efficiency in lithium-oxygen batteries. *Nat. Commun.* **2018**, *9*, 680. [[CrossRef](#)] [[PubMed](#)]
56. Sun, B.; Chen, S.; Liu, H.; Wang, G. Mesoporous carbon nanocube architecture for high-performance lithium-oxygen batteries. *Adv. Funct. Mater.* **2015**, *25*, 4436–4444. [[CrossRef](#)]
57. Shu, C.; Lin, Y.; Su, D. N-doped onion-like carbon as an efficient oxygen electrode for long-life Li-O₂ battery. *J. Mater. Chem. A* **2016**, *4*, 2128–2136. [[CrossRef](#)]
58. Xie, J.; Yao, X.; Cheng, Q.; Madden, I.P.; Dornath, P.; Chang, C.-C.; Fan, W.; Wang, D. Three dimensionally ordered mesoporous carbon as a stable, high-performance Li-O₂ battery cathode. *Angew. Chem. Int. Ed.* **2015**, *54*, 4299–4303. [[CrossRef](#)]
59. Kim, M.; Yoo, E.; Ahn, W.-S.; Shim, S.E. Controlling porosity of porous carbon cathode for lithium oxygen batteries: Influence of micro and meso porosity. *J. Power Sources* **2018**, *389*, 20–27. [[CrossRef](#)]
60. Jung, C.Y.; Zhao, T.S.; An, L.; Zeng, L.; Wei, Z.H. Screen printed cathode for non-aqueous lithium-oxygen batteries. *J. Power Sources* **2015**, *297*, 174–180. [[CrossRef](#)]

61. Balaish, M.; Ein-Eli, Y. Meso-pores carbon nano-tubes (CNTs) tissues-perfluorocarbons (PFCs) hybrid air-electrodes for Li-O₂ battery. *J. Power Sources* **2018**, *379*, 219–227. [[CrossRef](#)]
62. Luo, J.; Yao, X.; Yang, L.; Han, Y.; Chen, L.; Geng, X.; Vattipalli, V.; Dong, Q.; Fan, W.; Wang, D.; et al. Free-standing porous carbon electrodes derived from wood for high-performance Li-O₂ battery applications. *Nano Res.* **2017**, *10*, 4318–4326. [[CrossRef](#)]
63. Sun, Y. Lithium ion conducting membranes for lithium-air batteries. *Nano Energy* **2013**, *2*, 801–816. [[CrossRef](#)]
64. Shao, Y.; Ding, F.; Xiao, J.; Zhang, J.; Xu, W.; Park, S.; Zhang, J.-G.; Wang, Y.; Liu, J. Making Li-air batteries rechargeable: Material challenges. *Adv. Funct. Mater.* **2013**, *23*, 987–1004. [[CrossRef](#)]
65. Zhu, X.; Zhao, T.; Tan, P.; Wei, Z.; Wu, M. A high-performance solid-state lithium-oxygen battery with a ceramic-carbon nanostructured electrode. *Nano Energy* **2016**, *26*, 565–576. [[CrossRef](#)]
66. Li, D.; Wang, Q.; Yao, Y.; Wu, F.; Yu, Y.; Zhang, C. New application of waste citrus maxima peel-derived carbon as an oxygen electrode material for lithium oxygen batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32058–32066. [[CrossRef](#)] [[PubMed](#)]
67. Lim, K.H.; Kim, S.; Kweon, H.; Moon, S.; Lee, C.-H.; Kim, H. Preparation of graphene hollow spheres from vacuum residue of ultra-heavy oil as an effective oxygen electrode for Li-O₂ batteries. *J. Mater. Chem. A* **2018**, *6*, 4040–4047. [[CrossRef](#)]
68. Lin, X.; Yuan, R.; Cai, S.; Jiang, Y.; Lei, J.; Liu, S.-G.; Wu, Q.-H.; Liao, H.-G.; Zheng, M.; Dong, Q. An open-structured matrix as oxygen cathode with high catalytic activity and large Li₂O₂ accommodations for lithium-oxygen batteries. *Adv. Energy Mater.* **2018**, *8*, 1800089. [[CrossRef](#)]
69. Woo, H.; Kang, J.; Kim, J.; Kim, C.; Nam, S.; Park, B. Development of carbon-based cathodes for Li-air batteries: Present and future. *Electron. Mater. Lett.* **2016**, *12*, 551–567. [[CrossRef](#)]
70. Jing, Y.; Zhou, Z. Computational insights into oxygen reduction reaction and initial Li₂O₂ nucleation on pristine and N-doped graphene in Li-O₂ batteries. *ACS Catal.* **2015**, *5*, 4309–4317. [[CrossRef](#)]
71. Wu, F.; Xing, Y.; Li, L.; Qian, J.; Qu, W.; Wen, J.; Miller, D.; Ye, Y.; Chen, R.; Amine, K.; et al. Facile synthesis of boron-doped rGO as cathode material for high energy Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 23635–23645. [[CrossRef](#)] [[PubMed](#)]
72. Yang, Y.; Liu, W.; Wu, N.; Wang, X.; Zhang, T.; Chen, L.; Zeng, R.; Wang, Y.; Lu, J.; Fu, L.; et al. Tuning the morphology of Li₂O₂ by noble and 3d metals: A planar model electrode study for Li-O₂ battery. *ACS Appl. Mater. Interfaces* **2017**, *9*, 19800–19806. [[CrossRef](#)]
73. Yang, Y.; Zhang, T.; Wang, X.; Chen, L.; Wu, N.; Liu, W.; Lu, H.; Xiao, L.; Fu, L.; Zhuang, L. Tuning the morphology and crystal structure of Li₂O₂: A graphene model electrode study for Li-O₂ battery. *ACS Appl. Mater. Interfaces* **2016**, *8*, 21350–21357. [[CrossRef](#)]
74. Cho, S.M.; Yom, J.H.; Hwang, S.W.; Seong, I.W.; Kim, J.; Cho, S.H.; Yoon, W.Y. Morphology control of lithium peroxide using Pd₃Co as an additive in aprotic Li-O₂ batteries. *J. Power Sources* **2017**, *342*, 427–434. [[CrossRef](#)]
75. Cao, C.; Yan, Y.; Zhang, H.; Xie, J.; Zhang, S.; Pan, B.; Cao, G.; Zhao, X. Controlled growth of Li₂O₂ by cocatalysis of mobile Pd and Co₃O₄ nanowire arrays for high-performance Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31653–31660. [[CrossRef](#)] [[PubMed](#)]
76. Lu, X.; Si, W.; Sun, X.; Liu, B.; Zhang, L.; Yan, C.; Schmidt, O.G. Pd-functionalized MnO_x-GeO_y nanomembranes as highly efficient cathode materials for Li-O₂ batteries. *Nano Energy* **2016**, *19*, 428–436. [[CrossRef](#)]
77. Wu, F.; Xing, Y.; Zeng, X.; Yuan, Y.; Zhang, X.; Shahbazian-Yassar, R.; Wen, J.; Miller, D.J.; Li, L.; Chen, R.; et al. Platinum-coated hollow graphene nanocages as cathode used in lithium-oxygen batteries. *Adv. Funct. Mater.* **2016**, *26*, 7626–7633. [[CrossRef](#)]
78. Ryu, W.-H.; Gittleston, F.S.; Li, J.; Tong, X.; Taylor, A.D. A new design strategy for observing lithium oxide growth-evolution interactions using geometric catalyst positioning. *Nano Lett.* **2016**, *16*, 4799–4806. [[CrossRef](#)] [[PubMed](#)]
79. Tu, F.; Hu, J.; Xie, J.; Cao, G.; Zhang, S.; Yang, S.A.; Zhao, X.; Yang, H.Y. Au-decorated cracked carbon tube arrays as binder-free catalytic cathode enabling guided Li₂O₂ inner growth for high-performance Li-O₂ batteries. *Adv. Funct. Mater.* **2016**, *26*, 7725–7732. [[CrossRef](#)]
80. Liu, S.; Wang, G.; Tu, F.; Xie, J.; Yang, H.Y.; Zhang, S.; Zhu, T.; Cao, G.; Zhao, X. Au-nanocrystals-decorated δ-MnO₂ as an efficient catalytic cathode for high-performance Li-O₂ batteries. *Nanoscale* **2015**, *7*, 9589–9596. [[CrossRef](#)] [[PubMed](#)]

81. Guo, X.; Sun, B.; Zhang, J.; Liu, H.; Wang, G. Ruthenium decorated hierarchically ordered macro-mesoporous carbon for lithium oxygen batteries. *J. Mater. Chem. A* **2016**, *4*, 9774–9780. [[CrossRef](#)]
82. Lu, X.; Hao, G.-P.; Sun, X.; Kaskel, S.; Schmidt, O.G. Highly dispersed metal and oxide nanoparticles on ultra-polar carbon as efficient cathode materials for Li-O₂ batteries. *J. Mater. Chem. A* **2017**, *5*, 6284–6291. [[CrossRef](#)]
83. Jung, C.Y.; Zhao, T.S.; Zeng, L.; Tan, P. Vertically aligned carbon nanotube-ruthenium dioxide core-shell cathode for non-aqueous lithium-oxygen batteries. *J. Power Sources* **2016**, *331*, 82–90. [[CrossRef](#)]
84. Lu, J.; Lee, Y.J.; Luo, X.; Lau, K.C.; Asadi, M.; Wang, H.-H.; Brombosz, S.; Wen, J.; Zhai, D.; Chen, Z.; et al. A lithium-oxygen battery based on lithium superoxide. *Nature* **2016**, *529*, 377–382. [[CrossRef](#)] [[PubMed](#)]
85. Gao, R.; Liang, X.; Yin, P.; Wang, J.; Lee, Y.L.; Hu, Z.; Liu, X. An amorphous LiO₂-based Li-O₂ battery with low overpotential and high rate capability. *Nano Energy* **2017**, *41*, 535–542. [[CrossRef](#)]
86. Jung, J.; Song, K.; Bae, Y.; Choi, S.-I.; Park, M.; Cho, E.; Kang, K.; Kang, Y.-M. Achieving outstanding Li⁺-ORR and -OER activities via edge- and corner-embedded bimetallic nanocubes for rechargeable Li-O₂ batteries. *Nano Energy* **2015**, *18*, 71–80. [[CrossRef](#)]
87. Choi, S.-I.; Xie, S.; Shao, M.; Odell, J.H.; Lu, N.; Peng, H.-C.; Protsailo, L.; Guerrero, S.; Park, J.; Xia, X.; et al. Synthesis and characterization of 9 nm Pt-Ni octahedra with a record high activity of 3.3 A/mg(Pt) for the oxygen reduction reaction. *Nano Lett.* **2013**, *13*, 3420–3425. [[CrossRef](#)] [[PubMed](#)]
88. Yang, H.; Zhang, J.; Sun, K.; Zou, S.; Fang, J. Enhancing by weakening: Electrooxidation of methanol on Pt₃Co and Pt nanocubes. *Angew. Chem. Int. Ed.* **2010**, *49*, 6848–6851. [[CrossRef](#)] [[PubMed](#)]
89. Kang, Y.-J.; Jung, S.C.; Kim, H.-J.; Han, Y.-K.; Oh, S.H. Maximum catalytic activity of Pt₃M in Li-O₂ batteries: M=Group V transition metals. *Nano Energy* **2016**, *27*, 1–7. [[CrossRef](#)]
90. Kim, H.-J.; Jung, S.C.; Han, Y.-K.; Oh, S.H. An atomic-level strategy for the design of a low overpotential catalyst for Li-O₂ batteries. *Nano Energy* **2015**, *13*, 679–686. [[CrossRef](#)]
91. Luo, X.; Ge, L.; Ma, L.; Kropf, A.J.; Wen, J.; Zuo, X.; Ren, Y.; Wu, T.; Lu, J.; Amine, K. Effect of componential proportion in bimetallic electrocatalysts on the aprotic lithium-oxygen battery performance. *Adv. Energy Mater.* **2018**, *8*, 1703230. [[CrossRef](#)]
92. Ma, L.; Luo, X.; Kropf, A.J.; Wen, J.; Wang, X.; Lee, S.; Myers, D.J.; Miller, D.; Wu, T.; Lu, J.; et al. Insight into the catalytic mechanism of bimetallic platinum-copper core-shell nanostructures for nonaqueous oxygen evolution reactions. *Nano Lett.* **2016**, *16*, 781–785. [[CrossRef](#)] [[PubMed](#)]
93. Zhou, Y.; Lyu, Z.; Wang, L.; Dong, W.; Dai, W.; Cui, X.; Hao, Z.; Lai, M.; Chen, W. Co₃O₄ functionalized porous carbon nanotube oxygen-cathodes to promote Li₂O₂ surface growth for improved cycling stability of Li-O₂ batteries. *J. Mater. Chem. A* **2017**, *5*, 25501–25508. [[CrossRef](#)]
94. Liu, Q.; Jiang, Y.; Xu, J.; Xu, D.; Chang, Z.; Yin, Y.; Liu, W.; Zhang, X. Hierarchical Co₃O₄ porous nanowires as an efficient bifunctional cathode catalyst for long life Li-O₂ batteries. *Nano Res.* **2015**, *8*, 576–583. [[CrossRef](#)]
95. Lee, S.; Lee, G.-H.; Lee, H.J.; Dar, M.A.; Kim, D.-W. Fe-based hybrid electrocatalysts for nonaqueous lithium-oxygen batteries. *Sci. Rep.* **2017**, *7*, 9495. [[CrossRef](#)] [[PubMed](#)]
96. Hu, X.; Zhu, Z.; Cheng, F.; Tao, Z.; Chen, J. Micro-nano structured Ni-MOFs as high-performance cathode catalyst for rechargeable Li-O₂ batteries. *Nanoscale* **2015**, *7*, 11833–11840. [[CrossRef](#)]
97. Shang, C.; Dong, S.; Hu, P.; Guan, J.; Xiao, D.; Chen, X.; Zhang, L.; Gu, L.; Cui, G.; Chen, L. Compatible interface design of CoO-based Li-O₂ battery cathodes with long-cycling stability. *Sci. Rep.* **2015**, *5*, 8335. [[CrossRef](#)]
98. Zhao, Q.; Wu, C.; Cong, L.; Zhang, Y.; Sun, G.; Xie, H.; Sun, L.; Liu, J. Yolk-shell Co₂CrO₄ nanospheres as highly active catalysts for Li-O₂ batteries: Understanding the electrocatalytic mechanism. *J. Mater. Chem. A* **2017**, *5*, 544–553. [[CrossRef](#)]
99. Lyu, Z.; Yang, L.; Luan, Y.; Wang, X.R.; Wang, L.; Hu, Z.; Lu, J.; Xiao, S.; Zhang, F.; Wang, X.; et al. Effect of oxygen adsorbability on the control of Li₂O₂ growth in Li-O₂ batteries: Implications for cathode catalyst design. *Nano Energy* **2017**, *36*, 68–75. [[CrossRef](#)]
100. Yang, C.; Wong, R.A.; Hong, M.; Yamanaka, K.; Ohta, T.; Byon, H.R. Unexpected Li₂O₂ film growth on carbon nanotube electrodes with CeO₂ nanoparticles in Li-O₂ batteries. *Nano Lett.* **2016**, *16*, 2969–2974. [[CrossRef](#)]
101. Wang, G.; Zhang, S.; Qian, R.; Wen, Z. Atomic-Thick TiO₂(B) nanosheets decorated with ultrafine Co₃O₄ nanocrystals as a highly efficient catalyst for lithium-oxygen battery. *ACS Appl. Mater. Interfaces* **2018**, *10*, 41398–41406. [[CrossRef](#)] [[PubMed](#)]

102. Zhang, S.; Wang, G.; Jin, J.; Zhang, L.; Wen, Z.; Yang, J. Self-catalyzed decomposition of discharge products on the oxygen vacancy sites of MoO₃ nanosheets for low-overpotential Li-O₂ batteries. *Nano Energy* **2017**, *36*, 186–196. [[CrossRef](#)]
103. Huang, J.; Zhang, B.; Bai, Z.; Guo, R.; Xu, Z.-L.; Sadighi, Z.; Qin, L.; Zhang, T.-Y.; Chen, G.; Huang, B.; et al. Anomalous enhancement of Li-O₂ battery performance with Li₂O₂ films assisted by NiFeO_x nanofiber catalysts: Insights into morphology control. *Adv. Funct. Mater.* **2016**, *26*, 8290–8299. [[CrossRef](#)]
104. Fan, W.; Wang, B.; Guo, X.; Kong, X.; Liu, J. Nanosize stabilized Li-deficient Li_{2-x}O₂ through cathode architecture for high performance Li-O₂ batteries. *Nano Energy* **2016**, *27*, 577–586. [[CrossRef](#)]
105. Hou, Y.; Wang, J.; Liu, L.; Liu, Y.; Chou, S.; Shi, D.; Liu, H.; Wu, Y.; Zhang, W.; Chen, J. Mo₂C/CNT: An efficient catalyst for rechargeable Li-CO₂ batteries. *Adv. Funct. Mater.* **2017**, *27*, 1700564. [[CrossRef](#)]
106. Cong, Y.; Geng, Z.; Sun, Y.; Yuan, L.; Wang, X.; Zhang, X.; Wang, L.; Zhang, W.; Huang, K.; Feng, S. Cation segregation of A-site deficiency perovskite La_{0.85}FeO_{3-δ} nanoparticles toward high-performance cathode catalysts for rechargeable Li-O₂ battery. *ACS Appl. Mater. Interfaces* **2018**, *10*, 25465–25472. [[CrossRef](#)] [[PubMed](#)]
107. Sadighi, Z.; Huang, J.; Qin, L.; Yao, S.; Cui, J.; Kim, J.-K. Positive role of oxygen vacancy in electrochemical performance of CoMn₂O₄ cathodes for Li-O₂ batteries. *J. Power Sources* **2017**, *365*, 134–147. [[CrossRef](#)]
108. Zhang, J.; Zhang, C.; Li, W.; Guo, Q.; Gao, H.; You, Y.; Li, Y.; Cui, Z.; Jiang, K.-C.; Long, H.; et al. Nitrogen-doped perovskite as a bifunctional cathode catalyst for rechargeable lithium oxygen batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5543–5550. [[CrossRef](#)]
109. Bae, Y.; Ko, D.-H.; Lee, S.; Lim, H.-D.; Kim, Y.-J.; Shim, H.-S.; Park, H.; Ko, Y.; Park, S.K.; Kwon, H.J.; et al. Enhanced stability of coated carbon electrode for Li-O₂ batteries and its limitations. *Adv. Energy Mater.* **2018**, *8*, 1702661. [[CrossRef](#)]
110. Gong, H.; Xue, H.; Wang, T.; Guo, H.; Fan, X.; Song, L.; Xia, W.; He, J. High-loading nickel cobaltate nanoparticles anchored on three-dimensional N-doped graphene as an efficient bifunctional catalyst for lithium-oxygen batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 18060–18068. [[CrossRef](#)]
111. Hyun, S.; Shanmugam, S. Mesoporous Co-CoO/N-CNR nanostructures as high-performance air cathode for lithium-oxygen batteries. *J. Power Sources* **2017**, *354*, 48–56. [[CrossRef](#)]
112. Yang, Y.; Yin, W.; Wu, S.; Yang, X.; Xia, W.; Shen, Y.; Huang, Y.; Cao, A.; Yuan, Q. Perovskite-type LaSrMnO electrocatalyst with uniform porous structure for an efficient Li-O₂ battery cathode. *ACS Nano* **2016**, *10*, 1240–1248. [[CrossRef](#)] [[PubMed](#)]
113. Hu, X.; Wang, J.; Li, T.; Wang, J.; Gregory, D.H.; Chen, J. MCNTs@MnO₂ nanocomposite Cathode Integrated with Soluble O₂-Carrier Co-salen in Electrolyte for High-Performance Li-air batteries. *Nano Lett.* **2017**, *17*, 2073–2078. [[CrossRef](#)] [[PubMed](#)]
114. Jung, J.-W.; Choi, D.-W.; Lee, C.K.; Yoon, K.R.; Yu, S.; Cheong, J.Y.; Kim, C.; Cho, S.-H.; Park, J.-S.; Park, Y.J.; et al. Rational design of protective In₂O₃ layer-coated carbon nanopaper membrane: Toward stable cathode for long-cycle Li-O₂ batteries. *Nano Energy* **2018**, *46*, 193–202. [[CrossRef](#)]
115. Zhao, G.; Zhang, L.; Lv, J.; Li, C.; Sun, K. A graphitic foam framework with hierarchical pore structure as self-supported electrodes of Li-O₂ batteries and Li ion batteries. *J. Mater. Chem. A* **2016**, *4*, 1399–1407. [[CrossRef](#)]
116. Zhu, J.; Metzger, M.; Antonietti, M.; Feller, T.-P. Vertically aligned two-dimensional graphene-metal hydroxide hybrid arrays for Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 26041–26050. [[CrossRef](#)] [[PubMed](#)]
117. Lin, Q.; Cui, Z.; Sun, J.; Huo, H.; Chen, C.; Guo, X. Formation of nanosized defective lithium peroxides through Si-coated carbon nanotube cathodes for high energy efficiency Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 18754–18760. [[CrossRef](#)] [[PubMed](#)]
118. Han, X.; Cheng, F.; Chen, C.; Hu, Y.; Chen, J. Uniform MnO₂ nanostructures supported on hierarchically porous carbon as efficient electrocatalysts for rechargeable Li-O₂ batteries. *Nano Res.* **2015**, *8*, 156–164. [[CrossRef](#)]
119. Zhang, S.; Wen, Z.; Lu, Y.; Wu, X.; Yang, J. Highly active mixed-valent MnO_x spheres constructed by nanocrystals as efficient catalysts for long-cycle Li-O₂ batteries. *J. Mater. Chem. A* **2016**, *4*, 17129–17137. [[CrossRef](#)]

120. Adpakpang, K.; Oh, S.M.; Agyeman, D.A.; Jin, X.; Jarulertwathana, N.; Kim, I.Y.; Sarakonsri, T.; Kang, Y.-M.; Hwang, S.-J. Holey 2D nanosheets of low-valent manganese oxides with an excellent oxygen catalytic activity and a high functionality as a catalyst for Li-O₂ batteries. *Adv. Funct. Mater.* **2018**, *28*, 1707106. [[CrossRef](#)]
121. Hu, Y.; Zhang, T.; Cheng, F.; Zhao, Q.; Han, X.; Chen, J. Recycling application of Li-MnO₂ batteries as rechargeable lithium-air batteries. *Angew. Chem. Int. Ed.* **2015**, *54*, 4338–4343. [[CrossRef](#)] [[PubMed](#)]
122. Guo, Y.; Dai, Z.; Lu, J.; Zeng, X.; Yuan, Y.; Bi, X.; Ma, L.; Wu, T.; Yan, Q.; Amine, K. Lithiation-induced non-noble metal nanoparticles for Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 811–818. [[CrossRef](#)] [[PubMed](#)]
123. Liu, B.; Yan, P.; Xu, W.; Zheng, J.; He, Y.; Luo, L.; Bowden, M.E.; Wang, C.-M.; Zhang, J.-G. Electrochemically formed ultrafine metal oxide nanocatalysts for high-performance lithium-oxygen batteries. *Nano Lett.* **2016**, *16*, 4932–4939. [[CrossRef](#)] [[PubMed](#)]
124. Li, C.; Guo, Z.; Pang, Y.; Sun, Y.; Su, X.; Wang, Y.; Xia, Y. Three-dimensional ordered macroporous FePO₄ as high-efficiency catalyst for rechargeable Li-O₂ batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31638–31645. [[CrossRef](#)] [[PubMed](#)]
125. Li, Z.; Ganapathy, S.; Xu, Y.; Zhu, Q.; Chen, W.; Kochetkov, I.; George, C.; Nazar, L.F.; Wagemaker, M. Fe₂O₃ nanoparticle seed catalysts enhance cyclability on deep (dis)charge in aprotic Li-O₂ batteries. *Adv. Energy Mater.* **2018**, *8*, 1703513. [[CrossRef](#)]
126. Lee, G.-H.; Sung, M.-C.; Kim, J.-C.; Song, H.J.; Kim, D.-W. Synergistic effect of CuGeO₃/graphene composites for efficient oxygen-electrode electrocatalysts in Li-O₂ batteries. *Adv. Energy Mater.* **2018**, *8*, 1801930. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).