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

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

Abstract: Rechargeable aprotic lithium-oxygen (Li-O_{2}) 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-O_{2} 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-O_{2} batteries. In this review, three main categories of catalyst for the positive electrode of Li-O_{2} 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-O_{2} batteries are discussed.

Keywords: Li-O_{2} 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-O_{2}, Na-O_{2}) batteries have attracted intensive interest in recent years. Among them, rechargeable aprotic Li-O_{2} 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-O_{2} battery was first proposed by Littauer and Tsai in 1976 [7]. With the hypothetical discharge product Li_{2}O, 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-O_{2} 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$_2$O$_2$ rather than Li$_2$O 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$_2$O$_2$ 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 a solidly evidenced discharge product of Li$_2$O$_2$ [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]:

$$\text{Li} \leftrightarrow \text{Li}^+ + e^- \quad \text{(negative electrode side)} \quad (1)$$

$$2\text{Li}^+ + 2e^- + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \quad \text{(positive electrode side)} \quad (2)$$

$$2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \quad \text{(overall)} \quad (3)$$

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$_2$O$_2$ discharge product. For the charging progress, Li$_2$O$_2$ 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$_2$O$_2$, 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$_2$O$_2$ [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-O\(_2\) 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 Li\(_2\)O\(_2\) [21]. As schematically shown in Figure 1b, in the first step, the solvated O\(_2\) molecule is reduced by one electron, forming a solvated O\(_2^-\) intermediate. While divergence occurs in the second step, if the adsorption toward the intermediate is strong enough, the solvated O\(_2^-\) 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 Li\(_2\)O\(_2\) in the surface pathway. Alternately, if the electrolyte shows a high enough donor number (DN) and the electrode adsorption toward O\(_2^-\) intermediate is weak enough [22], the solvated O\(_2^-\) intermediates keep accumulating in electrolyte, and disproportionate to generate a bulk or toroid Li\(_2\)O\(_2\) product through the solution pathway [23–25].

To verify the previously mentioned steps for Li\(_2\)O\(_2\) formation, efforts were made to detect the existence of O\(_2^-\)/LiO\(_2\) 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 LiO\(_2\) 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 LiO\(_2\). Such a result directly proved the formation of unstable LiO\(_2\) discharge intermediate which underwent a quick disproportionation to form the final discharge product Li\(_2\)O\(_2\). 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-O\(_2\) batteries, the reaction mechanism of OER remained quite elusive. Only a SAED ring of LiO\(_2\) 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-O\(_2\) batteries under real operation [33]. Later on, Lu et al. [34] proposed that the oxidation mechanism of Li\(_2\)O\(_2\) 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-O\(_2\) batteries using different solvent varied in DN as described in Figure 1d. In a high DN solvent, the oxidation of Li\(_2\)O\(_2\) followed a solution way with the formation of soluble LiO\(_2\) 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 Li\(_2\)O\(_2\) 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 LiO\(_2\) intermediate in the ORR progress with in-situ SERS, they detected no signal of LiO\(_2\) during charging, and proposed a direct two electron oxidation mechanism for charging in Li-O\(_2\) batteries. Note that the solvent of electrolyte they used is ACN (low DN solvent), it’s reasonable that no LiO\(_2\) 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 Li\(_2\)O\(_2\) oxidation but without further experimental proof [35]. Thus, we can conclude that the charging and discharging process shared a common intermediate, LiO\(_2\), whose solubility was greatly depended on the DN of solvents. Moreover, there are competition interactions between electrolyte and positive electrode surface toward LiO\(_2\) intermediate. Different degree of solubility and the attraction of positive electrode toward LiO\(_2\) 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-O$_2$ battery system. (b) Proposed mechanisms for Li$_2$O$_2$ growth in Li-O$_2$ batteries. (c) In situ SERS during O$_2$ reduction and re-oxidation on Au positive electrode. (d) Proposed solvent-controlled Li$_2$O$_2$ 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 Li$_2$O$_2$ also shows a great impact on the battery performance. According to previous conclusion, there are two pathways for Li$_2$O$_2$ 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 Li$_2$O$_2$ 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 Li$_2$O$_2$ 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-O$_2$ 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-O\textsubscript{2} 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-O\textsubscript{2} 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 Li\textsubscript{2}O\textsubscript{2} 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\textsuperscript{-2}. Li-O\textsubscript{2} batteries with the as-prepared ultra-thick electrodes exhibited unexpected areal capacity values (up to ~40 mAh·cm\textsuperscript{-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-O\textsubscript{2} 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 Li\textsubscript{2}O\textsubscript{2} 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 Li\textsubscript{2}O\textsubscript{2} (Figure 2b), was successfully employed as the positive electrode for Li-O\textsubscript{2} batteries [55]. In contrast to bulk Li\textsubscript{2}O\textsubscript{2}, the 1-D and amorphous Li\textsubscript{2}O\textsubscript{2} 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-O\textsubscript{2} 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 Li\textsubscript{2}O\textsubscript{2} 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-O\textsubscript{2} batteries.
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\textsubscript{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 Li\textsubscript{1.3}Al\textsubscript{0.3}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{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\textsubscript{2} battery was realized due to the reduced ceramic electrolyte layer (from several hundred micrometers to only 20 µm) and the expanded electrode/electrolyte interface area (330 times). For Li-O\textsubscript{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\textsubscript{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\textsubscript{2}O\textsubscript{2} discharge products. A Li-O\textsubscript{2} battery using this membrane as the positive electrode displayed exceptional performance under ambient conditions, including a high capacity.

Figure 2. (a) Schematic illustration of the high-density carbon paper. (b) Schematic illustration of the growth and decomposition of Li\textsubscript{2}O\textsubscript{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 mA·g\textsuperscript{-1}_\textsubscript{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.
(>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 CₓNᵧ 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⁻²geo, 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.
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-O₂ 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-O₂ batteries. Furthermore, for the sake of covering up the defects and preventing them from contacting with the reactive intermediates (e.g., O₂⁻), the researchers also fabricated a rather thin layer of FeOₓ 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 the decrease surface defects of carbon materials. Dong et al. [48] prepared ultra-long, highly ordered, and vertically arranged CNTs on permeable tantalum foil, thus significantly inhibiting the emergence of side reactions. The optimization of the synthesis methods can effectively the decrease surface defects of carbon materials.
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-O$_2$ batteries equipped with the N-CNTs@SS positive electrode displayed a high discharge capacity (9299 mAh·g$^{-1}$ at 500 mA·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-O$_2$ batteries by inducing the deposition of Li$_2$O$_2$ and controlling the morphology of Li$_2$O$_2$ into an amorphous, and in most cases, presenting a film-like morphology rather than a bulk crystalline Li$_2$O$_2$. 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 LiO$_2$

As mentioned above, the morphology and crystallinity of Li$_2$O$_2$ 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 Li$_2$O$_2$ product always surpass those with large Li$_2$O$_2$ particles. They found the formed Li$_2$O$_2$ 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 LiO$_2$ 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 LiO$_2$ adsorption energy could benefit the fast nucleation of newly formed discharging intermediate LiO$_2$, 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 Li$_2$O$_2$ 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 Li$_2$O$_2$ thanks to the stronger interaction
between the Pd electrode and LiO$_2$. In contrast, a nearly perfect crystalline Li$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$. With such a vision, Lu’s group [84] proposed a unique Li-O$_2$ 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-O$_2$ 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 mA 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$_3$Li sharing similar crystallographic lattice of LiO$_2$ (orthorhombic lattice). As shown in Figure 4e, the good lattice matches between the crystalline faces of Ir$_3$Li and LiO$_2$ demonstrated that the Ir$_3$Li 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-O$_2$ 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-O$_2$ 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 mA 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].
4.3. Utilisation of Bi-Metallic Catalysts

As the studies on noble metal catalysts for Li-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 $O_2^-/LiO_2$ in solution could be oxidized at the ring, while the oxidation current of the surface adsorbed $O_2^-/LiO_2$ 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 $O_2^-/LiO_2$ 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, $Li^{2+}$ 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 mAh·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 $Li_2O_2$ 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 LiO\(_2\) adsorption on the positive electrode surfaces of (i) Co\(_3\)O\(_4\) (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\(_2\)O\(_2\) 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$_2$O$_2$. 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 mA·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 mA·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$_2$O$_2$ 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 (~2 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$_2$O$_2$ 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].
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 Li$_2$O$_2$ enabled by Fe$_2$O$_3$ positive electrode [125], quite a similar concept to the Ir$_3$Li as the template for the epitaxially induced nucleation and growth LiO$_2$ in Lu’s work [84]. Additionally, an optimized sp$^2$/sp$^3$ carbon bond was proposed by introducing CuCeO$_3$ nanorods to graphene nanosheet, together with the stabilized Cu$^+/Cu^{2+}$ 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-O\textsubscript{2} batteries with different positive electrode materials.

| Positive Electrode | Cycle Number/Capacity (mAh g\textsuperscript{-1}/Rate (mA g\textsuperscript{-1}) | The First Charge Potential (V) \textsuperscript{1} | Maximal Capacity (mAh g\textsuperscript{-1}) | Maximal Rate (mA g\textsuperscript{-1})/Corresponding Charge Potential (V) \textsuperscript{2} | Electrolyte | Ref. |
|---------------------|-----------------------------------------------------------------|---------------------------------|---------------------------------|---------------------------------------------------------------------------------|----------------|------|
| **Carbon materials** | | | | | | |
| C-800 (nearly 96% microporous) | 120/1000/200 | 3.51 | 6003 | - | 1.0 M LiNO\textsubscript{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\textsubscript{3}SO\textsubscript{3} in TEGDME | [43] |
| Screen-printed cathode | 40/1000/- | 4.06 | 6840 | - | 1.0 M LiTFSI in TEGDME | [60] |
| PCNF/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 LiCF\textsubscript{3}SO\textsubscript{3} 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 P1MIMTFSI | [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\textsubscript{3} in DMac | [50] |
| CB-H (graphene hollow spheres) | 104/500/300 | 3.9 | 16805 | 1000/-4.05 | 1.0 M LiNO\textsubscript{3} in DMac | [67] |
| NPGAs (N-doped graphene aerogels) | 72/1000/300 | 4.12 | 10081 | 3200/- | 1.0 M LiTFSI in TEGDME | [51] |
| C\textsubscript{3}N\textsubscript{4}@NPG | 200/1000/1000 | 4.1 | 16705 | 1000/-4.25 | 1.0 M LiTFSI in TEGDME | [52] |
| S-doped graphene | 300/1000/500 | -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 | [54] |
| VA-G/NF | 10/280/-140 | 3.4 | - | - | 1.0 M LiTFSI in TEGDME | [55] |
| 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 DGM | [35] |
| MCCs (meso-porous carbon nanocubes) | 5/1000/400 | 3.75 | 26100 | 2000/- | 0.1 M LiClO\textsubscript{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] |
| CNFs/CNFs-LATP | 1174/-/141.5/-/94.3 | -3.9 | - | - | LATP (Li\textsubscript{1.3}Al\textsubscript{0.3}Ti\textsubscript{3}P\textsubscript{2}O\textsubscript{13}) | [65] |
| **Noble metals and their oxides** | | | | | | |
| Pt-HgNs | 10/1000/100 | 3.1 | -5600 | 50/3.35 | 1.0 M LiTFSI in TEGDME | [77] |
| Pt-Cu (2.5% Pt + 5% Cu) | 35/500/100 | 3.15 | 2376 | - | 1.0 M LiCF\textsubscript{3}SO\textsubscript{3} in TEGDME | [91] |
| PtCo Ncs | 65/1000/200 | 3.1 | 11000 | 2000/- | 1.0 M LiCF\textsubscript{3}SO\textsubscript{3} in DMSO | [86] |
| MnCo@Ru | 100/1000/400 | 3.4 | 12400 | 1000/3.55 | 0.5 M LiClO\textsubscript{4} in DMSO | [81] |
| VACNTs@RuO\textsubscript{2} | 100/-1613/-/806.5 | 3.6 | 9050 | -1613/-4 | 1.0 M LiTFSI in TEGDME | [83] |
| RuO\textsubscript{2}-CNp@In\textsubscript{2}O\textsubscript{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) | Maximal Capacity (mAh g⁻¹) | Maximal Rate (mA g⁻¹)/Corresponding Charge Potential (V) | Electrolyte | Ref. |
|-----------------------------|-----------------------------------------------|--------------------------------|----------------------------|--------------------------------------------------|--------------|------|
| Pd/UPC                      | 231/1000/300                                | 3.35                           | -                          | 500/3.95                                        | 1.0 M LiCF₃SO₃ in TEGDME | [82] |
| RuO₂/UPC                    | 150/1000/300                                | 3.6                            | -                          | 500/3.7                                         | 1.0 M LiCF₃SO₃ in TEGDME | [82] |
| MGP-20 (MnO₂–GeO₂–Pd)       | 163/1000/300                                | 3.1                            | 10900                      | 500/3.5                                         | 1.0 M LiF₃SO₃ in TEGDME | [76] |
| Pd–rGO                      | 100/500/1000                                | 3.25                           | 16867                      | 2000                                            | 1.0 M LiF₃SO₃ in TEGDME | [85] |
| Co₂O₃–NiAs/Pd NCs           | 258/500/100                                | 3.75                           | 5337                       | ~/                                            | 1.0 M LiO₃O₂ in DMSO | [75] |
| Ir–rGO                      | ~40/1000/1000                               | 3.62                           | ~9500                      | ~/                                            | 1.0 M LiF₃SO₃ in TEGDME | [84] |
| Au/rCST                     | 112/500/400                                | 3.8                            | 5488                       | 1000/4.4                                        | 1.0 M LiO₃O₂ in DMSO | [79] |
| Au–SnMnO₂                   | 165/500/400                                | 3.8                            | 10600                      | 1600/3.9                                        | 1.0 M LiO₃O₂ in TEGDME | [80] |

Transition metals and their oxides

| Positive Electrode                        | Cycle Number/Capacity (mAh g⁻¹)/Rate (mA g⁻¹) | The First Charge Potential (V) | Maximal Capacity (mAh g⁻¹) | Maximal Rate (mA g⁻¹)/Corresponding Charge Potential (V) | Electrolyte | Ref. |
|------------------------------------------|-----------------------------------------------|--------------------------------|----------------------------|--------------------------------------------------|--------------|------|
| Mixed-valent MnO₂ spheres                | 320/1000/100                                | 3.5                            | 9709                       | 800/3.6                                          | 1.0 M LiCF₃SO₃ in TEGDME | [119] |
| Li₀.5MnO₂                                 | 197/1000/200                                | 3.6                            | 10823                      | 2000/4                                           | 1.0 M LiF₃SO₃ in TEGDME | [121] |
| Co⁶⁺-salen/MCNTs/MnO₂                    | 300/1000/500                                | 3.7                            | 13050                      | 500/3.7                                          | 5 mM Co⁶⁺-salen/1.0 M LiF₃SO₃ in TEGDME | [113] |
| MnO₂/HPC                                  | 300/1000/350                                | 3.5                            | ~9200                      | 5000                                            | 1.0 M LiF₃SO₃ in TEGDME | [116] |
| Holey-2-D MnO₂ nanosheets                | 33/1000/200                                 | 4.0                            | 3600                       | ~                                             | 1.0 M LiF₃SO₃ in TEGDME | [120] |
| CMO-4 (CoMoO₄)                           | 41/500/200                                  | ~4                            | ~5860                      | 400/                                            | 0.5 M LiF₃SO₃ in TEGDME | [107] |
| Co-CoO/N-CNR                              | 88/1000/100                                 | 3.9                            | 10555                      | 1000/                                            | 1.0 M LiF₃SO₃ in TEGDME | [111] |
| CoO mesoporous spheres                   | 300/1000/40                                 | ~3.6                           | 4849                       | ~/                                             | 1.0 M LiF₃SO₃ in TEGDME | [97] |
| CoO/BH₂@CNNS                              | 40/715/150                                  | 3.8                            | 5403                       | ~/                                             | 1.0 M LiF₃SO₃ in TEGDME | [114] |
| CCO (Co₂O₃–yolk-shell nanospheres)        | 236/1000/200                                | 3.25                           | 8554                       | 500/3.85                                         | 1.0 M LiF₃SO₃ in TEGDME | [98] |
| p-CNT/Co₂O₃                            | 116/500/200                                 | 3.65                           | 4331                       | 1000/4.35                                       | 1.0 M LiF₃SO₃ in TEGDME | [93] |
| Co₂O₃–TiO₂(B)                            | 200/1000/100                                | 3.8                            | 11000                      | 500/                                            | 1.0 M LiF₃SO₃ in TEGDME | [101] |
| NCO8N–rGO (NiCo₂O₄ nanoparticles)         | 112/1000/200                                | 3.44                           | 6716                       | 1000/3.9                                         | 1.0 M LiF₃SO₃ in TEGDME | [110] |
| Ni-MOFs                                  | 170/600/1200                                | ~3.7                           | 9000                       | 1440/3.95                                        | 1.0 M LiF₃SO₃ in TEGDME | [96] |
| NiFe₂O₄–CNT                              | 126/1000/200                                | ~3.75                          | 16987                      | 2000/                                            | 0.5 M LiF₃SO₃ in TEGDME | [103] |
| Fe₃O₄–Fe nanobrids                      | 100/1000/500                                | ~3.87                          | 13890                      | 2000/4.3                                        | 1.0 M LiF₃SO₃ in TEGDME | [106] |
| 3DOM FePO₄                               | 300/1000/250                                | 3.95                           | 9923                       | 500/4.2                                         | 1.0 M LiF₃SO₃ in TEGDME | [124] |
| LFO-900 (ex-Fc₂O₃-LaFeO₃₋₋)             | 108/500/100                                 | ~3.6                           | 7183.3                     | 500/                                            | 1.0 M LiF₃SO₃ in TEGDME | [106] |
| LNO/N₄ (N-doped LaNiO₃)                  | 50/500/250                                  | 3.9                            | 5910                       | 400/                                            | 1.0 M LiF₃SO₃ in TEGDME | [108] |
| G/nanoscale-La3SrMnO₃                   | 50/500/125                                  | 3.4                            | 6515                       | 1000/4.1                                       | 1.0 M LiF₃SO₃ in TEGDME | [112] |
| Red-CuGeO₃–G (reduced CuGeO₃–G)          | 50/2000/1000                                | 4.2                            | 10300                      | ~/                                             | 1.0 M LiO₃O₂ in DMSO | [121] |
| ZnO/VCNTs                                | 112/1000/50                                 | 3.55                           | 4580                       | ~/                                             | 0.9 M LiF₃SO₃ in TEGDME | [104] |
| MoO₂/graphitic foam                     | >55/500/1000                                | ~4.18                          | 5500                       | 1000/4.18                                     | 1.0 M LiF₃SO₃ in TEGDME | [115] |
| MoO₂–N₃ NSs-2                            | 60/1000/100                                 | 3.45                           | 10825                      | ~/                                             | 1.0 M LiO₃O₂ 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.

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