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Recent Progress on Stability Enhancement for Cathode in Rechargeable Non-Aqueous Lithium-Oxygen Battery

*Zhi-wen Chang, Ji-jing Xu, Qing-chao Liu, Lin Li, and Xin-bo Zhang**

The pressing demand on the electronic vehicles with long driving range on a single charge has necessitated the development of next-generation high-energy-density batteries. Non-aqueous Li-O_2 batteries have received rapidly growing attention due to their higher theoretical energy densities compared to those of state-of-the-art Li-ion batteries.To make them practical for commercial applications, many critical issues must be overcome, including low round-trip efficiency and poor cycling stability, which are intimately connected to the problems resulting from cathode degradation during cycling. Encouragingly, during the past years, much effort has been devoted to enhancing the stability of the cathode using a variety of strategies and these have effectively surmounted the challenges derived from cathode deteriorations,thus endowing Li-O_2 batteries with significantly improved electrochemical performances. Here, a brief overview of the general development of Li-O_2 battery is presented. Then, critical issues relevant to the cathode instability are discussed and remarkable achievements in enhancing the cathode stability are highlighted. Finally, perspectives towards the development of next generation highly stable cathode are also discussed.

1. Introduction

The emergence of Li-O_2 technology, which has captured worldwide attention,[1–17] is viewed as a revolutionary event in the electrical energy storage field. Benefiting from the extremely high theoretical energy density that far outperforms that of other available battery systems (**Figure 1**), particularly the prevailing Li-ion battery, the Li-O_2 battery is generally recognized as a promising candidate for both mobile (electrical vehicles) and stationary (smart grids) applications. Specifically, as shown in Figure 1, the driving range of an electrical vehicle with a Li-O_2 battery is expected to be more than 500 km, far exceeding that with a Li-ion battery. Undisputedly, the development of Li-O_2 batteries could benefit transportation electrification and large scale renewable energy storage.

The exceptionally high energy density of Li-O_2 battery mainly originates from two aspects.[18] First, oxygen, the cathode material, is sourced outside environment rather than being stored within the battery, thus helping to reduce the weight of the assembled cell; Second, during the discharge process, the lithium anode (lithium metal) can deliver an extremely high specific capacity (3860 mAh g^{-1}) and rather low electrochemical potential (−3.04 V vs. standard hydrogen electrode, SHE),[19] ensuring a desirable discharge capacity and a high operation voltage, respectively. There are currently four types of Li-O_2 battery being investigated based on the employed electrolyte solvents: a) non-aqueous aprotic solvents, b) aqueous solvents, c) hybrid non-aqueous and aqueous solvents, and d) all solid-state solvents.[20–29] The focus of this article is exclusively on Li-O_2 batteries with non-aqueous solvents because these have dominated research efforts on Li-O_2 batteries for the past decade. For brevity, all of the Li-O_2 batteries discussed are operated with non-aqueous electrolytes. A typical rechargeable Li-O_2 battery consists of a metallic Li anode, a separator saturated with Li^+ conducting electrolyte, and a porous gas diffusion cathode. Upon discharge, the O_2 breathed outside is reduced on the active sites of cathode and combines with Li^+ to produce Li_2O_2; while the direction is reversed with the peroxide oxidized to O_2 and Li^+ during charge.[2,30–33] The electrochemical pathways described are: $2Li + O_2 \leftrightarrow Li_2O_2$.[32,33] As witnessed over the past decade, impressive progress has been made toward the commercialization of Li-O_2 batteries.[34–42] For example, as a media to transfer Li^+ ions and O_2 molecules during the cycling of a Li-O_2 battery, the properties of the electrolyte used are demonstrated to exert a prominent effect on the performances of Li-O_2 battery. Numerous researches have been conducted in the electrolyte field followed with encouraging results.[34] Simultaneously, various in situ and ex situ analysis techniques have been developed to address chemical species of reduction intermediate and final products, which has aided in gaining mechanistic insights into oxygen-based electrochemistry, thus allowing for breakthroughs to be achieved for efficient energy storage.[35] However, it should be noted that the development of this promising Li-O_2 technology is still in its infancy and to make the Li-O_2 battery suitable for practical

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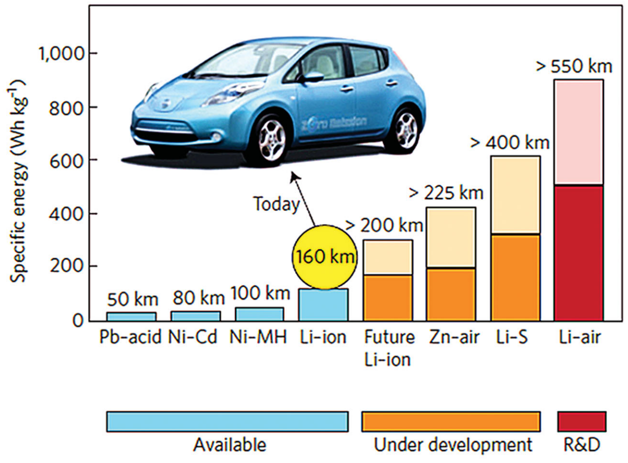

Figure 1. The energy densities of various rechargeable batteries along with the estimated driving range of vehicle with corresponding rechargeable batteries. Reprinted with permission.[7] Copyright 2012, Nature Publishing Group.

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application, significant efforts in a variety of fields to unlock its full potential are required. Among these fields, the construction of a stable cathode is a topic of strategic importance.

It is worth noting that, accompanied with the introduction of the prototype Li-O_2 battery by Abraham, the rechargeability of cathode in Li-O_2 battery demonstrated by Bruce's group has ignited a surging interest in the Li-O_2 field.[1,2] Simultaneously, tremendous efforts have been invested into the cathode construction for Li-O_2 battery since then.[43–49] Because of the high conductivity, low cost, and ease of fabrication, various carbon materials, such as carbon nanotubes (CNTs) and graphene,[50–55] are widely applied as the basis of oxygen cathodes for Li-O_2 cells. By providing triple phase (solid–electrolyte–gas) to sustain the Li-O_2 reactions and void space to house the generated Li_2O_2, the properties such as surface area and porosity of carbon cathode are seen to exert a prominent effect on the performances of Li-O_2 cells.[56–59] Central to these properties, the stability, which can be classified into the mechanical stability and chemical stability according to established results, of carbon cathode is a factor of particular importance. Principally, the architecture of carbon cathode should be well-maintained and the components of carbon cathode should be stable towards the oxidative species generated during the oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) processes, so as to provide a stable chemistry for the Li-O_2 reactions to occur.[60] However, in practice, the degradation of the carbon cathode upon application in Li-O_2 cells has presented many daunting challenges, which have hindered the advancement of Li-O_2 batteries. In general, the evolution of reaction products during cycling can lead to structural deterioration of the carbon cathode, which has restrained the cycle life of Li-O_2 batteries.[51,61] Additionally, when the carbon cathode is subjected to the harshly aggressive environment of a Li-O_2 battery, oxidation of the carbon cathode components to undesirable products such as Li_2CO_3 can occur,[62–64] which may result in severe cathode passivation and increase the charge voltage inexorably. As a consequence, the round-trip efficiency of the Li-O_2 battery is lowered and the cycling performances are decayed.[65–67] Together, the enhancement of carbon cathode stability will undoubtedly increase the performance of Li-O_2 batteries. Encouragingly, many protective strategies adopted in the past several years have endowed the carbon cathode with increased stability, thus improving the Li-O_2 performances remarkably; this should be a benefit for the applications of Li-O_2 batteries.

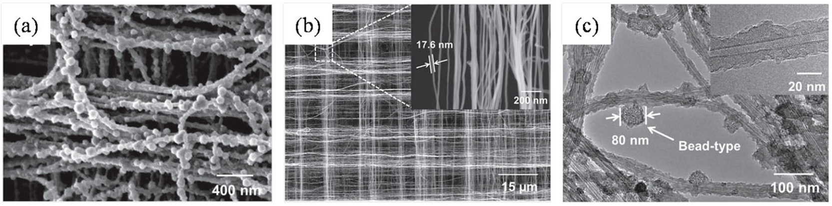

Figure 2. Scanning electron microscope (SEM) images of a) CNT fibrils cathode after 100 cycles, b) pristine CNT fibrils cathode and c) transmission electron microscope (TEM) image of the CNT fibrils cathodes after the first discharge. Reproduced with permission.[87]

It should be noted that, benefiting from the stability of carbon-alternative materials against the oxygen radical, the construction of carbon-alternative cathode is also an effective strategy in enhancing the cathode chemical stability, which has captured worldwide attention already.

To date, many insightful reviews on Li-O_2 batteries have been published from various perspectives,[68–82] which is an excellent starting point for any researchers with the desire to explore the Li-O_2 technology. However, there are few focused on the construction of cathode for Li-O_2 batteries, not to mention one that insightfully covers the recent progress on the enhancement of cathode stability, which holds strategic significance for the practical application of Li-O_2 batteries. Therefore, with an effort to reflect the recent achievements in augmenting the cathode stability and providing insight for further cathode stability optimization, this article concentrates exclusively on the cathode stability enhancement. This article is divided into three sections. In the first section, the critical issues of high relevance to structural destruction and chemical degradation of carbon cathode are presented separately, followed by a summary of the advances in enhancing the mechanical and chemical stability of carbon cathodes with novel strategies. Then, the development of non-carbon cathodes is summarized as a promising remedy to construct a cathode with robust chemical stability in the first section. Next, a body of insights on further fabricating a stable cathode is provided along with detailed comments regarding different cathode improvement methods. Finally, a brief discussion on the importance of stability of other battery components is also conducted.

2. Mechanical Stability Strengthening of Carbon Cathodes

In a typical Li-O_2 cell, the porous cathode is constructed from carbonaceous materials, which serve as electronically conductive pathways for the ORR/OER reactions and accommodate the deposited Li_2O_2.[83–85] However, it should be noted that the irregular deposition of thick film-like or large toroid-like Li_2O_2, which is insoluble in the organic electrolyte, can cause serious volume expansion of the carbon cathode, thus resulting in a serious structure degradation and a subsequent decayed cycling of the Li-O_2 battery.[51,61] To correct this deficiency, the construction of a carbon cathode with sufficient void space to prevent the damage caused by Li_2O_2 deposition on the cathode architecture is a choice of primary importance.

Recently, highly porous graphene cathodes with different pore sizes constructed via a hard template method were developed by Sun et al.[86] Simultaneously, the nonporous graphene cathode was also used for comparison. Notably, all the porous graphene cathodes have displayed a better capacity retention compared to the nonporous graphene during the first three cycles with the voltage ranging from 2.0 to 4.6 V at 500 mA g^{-1}. The capacity decay during cycling can be caused by the volume change of the cathode resulting from the build-up of excessive Li_2O_2 during depth-of-discharge, which may lead to collapse of the cathode architecture. Furthermore, as pointed out by Sun, the porous graphene with large pore size can provide ample space to house the generated Li_2O_2, thus effectively reducing the volume change during cycling. Clearly, the discoveries have unveiled the significance of ample space for Li_2O_2 deposition in alleviating the volume change of constructed cathode, which has necessitated the advanced cathode design with controlled porosity in maintaining the structural integrity of the carbonaceous cathode. By orthogonally plying sheets of well-aligned multiwalled nanotubes (MWNTs) on the Ni-mesh current collector as a whole part, a hierarchical porous electrode with controlled porous framework is constructed.[87] Upon application in the Li-O_2 battery, the woven fibrils electrode has exhibited a notable structural stability with a well-preserved overall framework after 100 cycles (**Figure 2**a,b). The origin of the impressive structural durability is the hierarchical porous architecture design as well as the uniform coating of deposited Li_2O_2 around the individual CNTs and CNT bundles (Figure 2c), which is supposed to cause much less volume change and less destruction of the architectural integrity of the fabricated cathode compared to the conventionally generated toroidal.[88] Additionally, other mechanically stable cathodes constructed with different precursors have been obtained. In this regard, a carbonized bacterial cellulose (CBC) cathode with a network structure was demonstrated.[89] Because of the abundant space provided by the network structure for Li_2O_2 deposition, the volume effect during the cycling of discharge and charge is effectively suppressed, thus contributing to the stable cycling of Li-O_2 battery. In another report from Guo et al,[90] a cathode based on ordered mesporous carbon nanofiber arrays (MCNAs) through a natural crab shell template was obtained. Notably, efficient buffer space for Li_2O_2/O_2 conversion was provided by the sufficient macrosized void spaces within MCNAs, which is believed to be one of the significant factors contributing to the excellent cycling stability of Li-O_2 battery. It is noteworthy that towards the construction of mechanically robust carbonaceous cathode, the application of carbon-supported cathode with non-carbon materials such as metal oxide also makes sense. As a typical example, via an efficient and facile electrodeposition method, a hierarchical porous cathode with cobalt oxide nanosheets (Co_3O_4 NSs) grown on carbon paper (CP) is developed.[91] Notably, the unique bimodal design, which is featured with the open macropores between the Co_3O_4 NSs as well as the mesoporous nature of Co_3O_4 NSs, has endowed the carbon cathode with a sustained structural stability, as evidenced by the recovered Co_3O_4 NSs even after the 40th cycle compared with the pristine cathode architecture (**Figure 3**a,b). The robust structure of the Co_3O_4 NSs/CP is suggested to be responsible

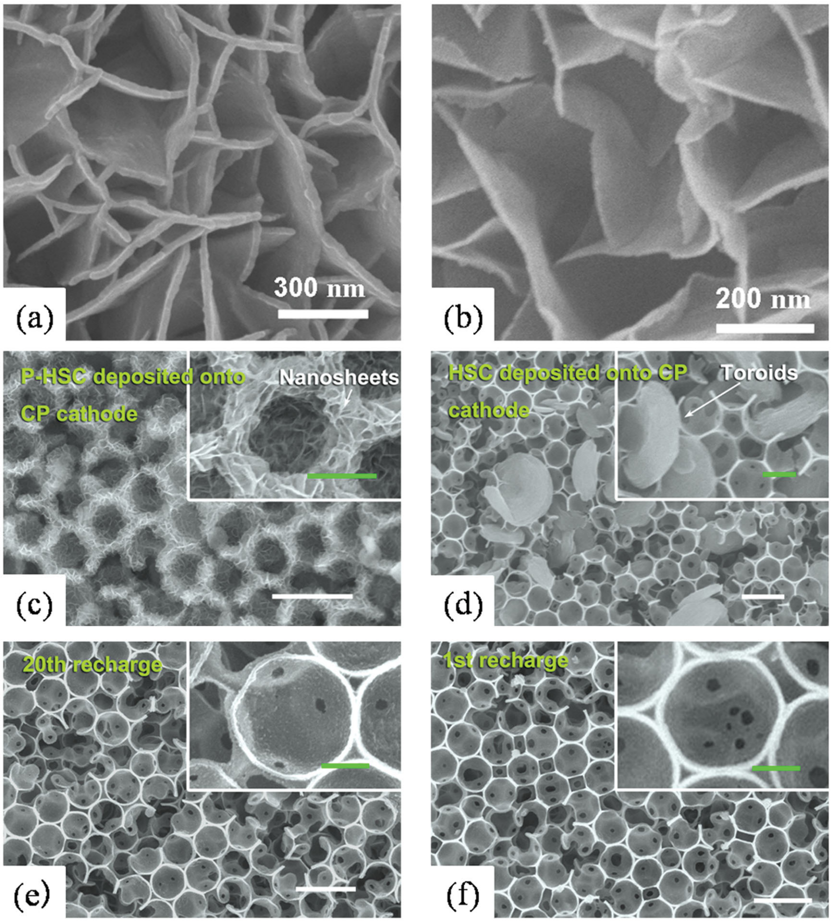

Figure 3. SEM images of a) Co_3O_4 NSs/CP cathode charged after the 40 cycles and b) pristine Co_3O_4 NSs/CP cathode. Reproduced with permission.[91] Copyright 2014, Royal Society of Chemistry. SEM images of c) the discharged P-HSC deposited onto CP cathode, d) the discharged HSC deposited onto CP cathode. SEM images of the recharged P-HSC deposited onto CP cathode after the e) 20th cycles and f) 1st cycles. These insets are corresponding enlarged SEM image, white scale bars, 1 mm, green scale bars, 400 nm. Reproduced with permission.[88] Copyright 2013, Nature Publishing Group.

for the enhanced cycling stability. One more point is that the formation of nanosheet-like Li_2O_2 rather than the toroidal one, which is supposed to be another important contributor to the well-maintained structural integrity of the fabricated cathode.[88] Encouragingly, the unique structures described here may provide some insight into the fabrication of efficient air electrodes that are mechanically robust for high-performance Li-O_2 batteries.

In addition to the tailored cathode architecture on enhancing the structural stability, the cathode component has proven to be another significant factor. For example, Liu reported a CNT film cathode with good structural stability by avoiding the use of auxiliary binders and related side reactions.[92] The structural defects in the graphene foam have proven to be detrimental to the structure stability of the fabricated cathode.[93] As a representative example, a mechanically robust carbon cathode modified with Pd NPs as developed by our group.[88] Benefiting from the unique nanosheets of the generated Li_2O_2 and its uniform distribution, the architecture of palladium (Pd)-modified hollow spherical carbon (P-HSC) deposited onto carbon paper (CP) cathode is well preserved, contrasting sharply with the fractured architecture of HSC deposited onto the CP cathode with the toroidal and irregularly dispersed Li_2O_2 (Figure 3c,d). Furthermore, the morphology of the P-HSC deposited onto CP cathode after 20th cycle is almost fully recovered, which is as integrated as that after the 1st cycle (Figure 3e,f). Undisputedly, the demonstrated mechanical stability of the P-HSC deposited onto CP cathode is believed to contribute to one of the best Li-O_2 electrochemical performances ever reported.

By providing sufficient void space with efficient architectural modification, the volume expansion caused by the cycling of Li_2O_2 is effectively alleviated, thus contributing to a carbonaceous cathode with improved mechanical stability. For the construction of stable carbon cathode for Li-O_2 battery, the reactivity of carbonaceous cathode component in the harshly oxidative environment is another critical issue that needs to be resolved.

3. Improving the Chemical Stability of Carbon Cathodes

Towards the construction of a stable carbonaceous cathode, the chemical stability of carbon cathode is another critical aspect in the Li-O_2 field that cannot be neglected. On ground of established results, the employed carbon cathode components are susceptible to decomposition under the harshly aggressive environment of the Li-O_2 battery, thus creating unintended products, which can lead to an increased charge polarization and a terminated battery life.[94,95] For this consideration, the reactivity exhibited by the carbon cathode is a critical topic that needs to be specifically cared. Fortunately, because of recent progress in unraveling the fundamentals associated with carbon cathode decomposition, the chemical stability of the carbon cathode is enhanced with various protective strategies, which will be specifically discussed in the following sections.

3.1. Binder-Free Cathode

Typically, a porous carbon matrix integrated with a polymeric binder and active materials is employed as the cathode in Li-O_2 battery.[96–100] However, it should be noted that the problems deriving from binder reactivity have inhibited the smooth operation of Li-O_2 battery to a large extent.[92] Due to the extreme nucleophilicity of the O^{2-} radical that is generated during discharge, unwanted products from binder degradation can be produced.[101–103] Moreover, these side products tend to form a film on the cathode matrix, suppressing its catalytic activity, thus causing serious capacity fading in the Li-O_2 cells.[101] By constructing a carbon cathode without any polymer binder, the challenges from binder degradation can be effectively eliminated, subsequently helping to achieve desirable Li-O_2 battery performances. Recently, by growing well-aligned carbon nanofibers (CNFs) on a porous ceramic substrate using a chemical vapor deposition (CVD) method, a new type of binder-free cathode was demonstrated.[104] The constructed cathode was capable of delivering gravimetric energy densities as high as 2500 Wh $kg_{discharged}^{-1}$. In another case, a binder-free cathode with porous CNT film was developed by Qiu's group.[92] Benefiting from the absence of auxiliary binder, the fabricated cathode exhibits good electrochemical performance. By virtue of the large surface area and good electronic conductivity that is comparable to other carbonaceous materials such as CNTs,[105–107] the graphene has also been widely used in Li-O_2 batteries, together with polymer binders.[108–110] However, the challenges from binder deterioration can retard the electrochemical performances of these cathodes. For this consideration, the nanotechnologies of cathode fabrication have opened up a new avenue in constructing a graphene cathode without any binder. By electrochemically leavening the graphite papers, Zhang et al. demonstrated the binder-free graphene foam as an O_2 cathode and evaluated its performance in a Li-O_2 battery.[93] With the help of template-assisted CVD, the binder-free graphene foam synthesized may exhibit an excellent Li-O_2 performance, which deserves investigation.[111] Wang reported a binder-free carbon cathode consisting of porous carbon (FHPC) derived from graphene oxide (GO) gel and Ni-foam conductive current collector.[112] By coating the as-synthesized mixture onto the Ni foam matrix followed with subsequent annealing treatment, the cathode is fabricated as a whole part. When tested in a Li-O_2 battery, this cathode demonstrated excellent electrochemical performances.

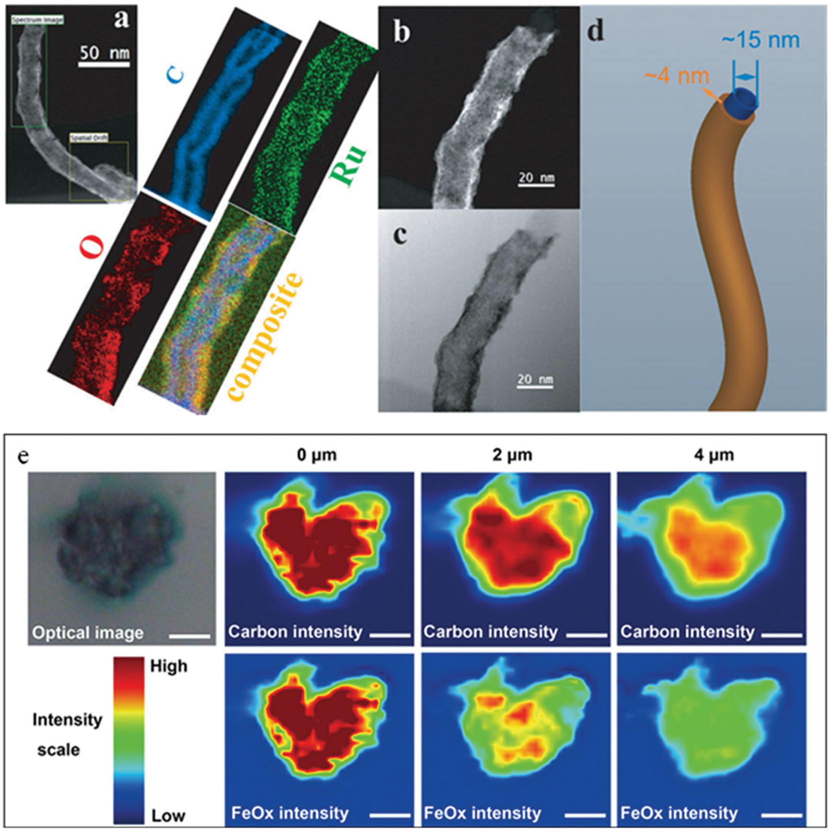

Figure 4. a) The dark field (HAADF)-scanning transmission electron microscopy (STEM) image and corresponding energy-dispersive X-ray (EDX) maps of the cathode. b) HAADF-STEM and c) bright-field (BF) STEM images of an individual CNT@RuO_2 architecture. d) Schematic illustration of the core/shell CNT@RuO_2 configuration. Reproduced with permission.[115] Copyright 2013, Wiley-VCH. e) Raman mapping of FeOx coated 3DOm carbon. Top left, photographical image of the researched carbon particle. Top right panels, carbon signal mapping with different focal depth; bottom right panels: FeOx signal mapping with the same focal depths. Scale bars: 5μm. Reproduced with permission.[116]

3.2. Carbon Surface Protection

In addition to the problems arising from binder deterioration, challenges from carbon instability caused by parasitic reactions inherent to carbonaceous materials still exist. Theoretically, oxidation of the carbon by Li_2O_2 or other reactions intermediates to Li_2CO_3-like species can occur.[63,113] To make the matters worse, the build-up of these species depletes the active sites on the carbon cathode and impedes charge transfer essential for oxygen evolution,[63,114] therefore leading to an increase in the overpotential during subsequent charge operation. Consequently, the rechargeability of the cell can be detrimentally affected, which has made the protection on C-Li_2O_2 interface from oxidation an issue of critical importance.

Recently, by effectively preventing the direct contact between the CNT and the deposited Li_2O_2 with a core-shell structure, Jian et al. reported a new cathode with high resistance to degradation by the generated Li_2O_2.[115] As evidenced in (**Figure** 4a–c), the protective layer of RuO_2 uniformly surrounds the CNTs, thereby endowing the CNTs@RuO_2 cathode with remarkably enhanced chemical stability. Eventually, the Li-O_2 cell with this protected cathode realizes a constant specific capacity for over 100 cycles at a high current of 500 mA g_{total}^{-1}. Most recently, to alleviate the negative influences from the reactivity exhibited by carbonaceous material under cell operation condition,[116] a protective layer of FeOx was uniformly coated on the carbon cathode surface by atomic layer deposition (ALD) that successfully concealed the carbon surface from the oxidative species (Figure 4e). As a benefit, the protected carbon cathode demonstrated an extended cycling life compared to the bare carbon cathode, which once again illustrates the significance of stabilizing the carbon cathode by physically separating the carbon surface away from Li_2O_2 and any reaction intermediates. In this regard, restricting the binding of the strong nucleophilic species to the surface, which is stable against oxygen radicals, instead of the carbon surface to protect the carbon material from preferential oxidization also makes sense. Recently, by improving the compatibility of cathode/Li_2O_2 interface with incorporated $CoSe_2$/CoO (CSCO) nanoparticles, the amount of interfacial Li_2CO_3 parasitically formed on the carbon surface was effectively reduced, which contributed to a notable enhancement in the cycling performance of $CoSe_2$/CoO/SP cathode over that of pristine SP cathode.[117] Additionally, benefitting from the modified valence state of surface Co ions by the "core" of $CoSe_2$ materials, the CSCO-based cathode was capable of delivering a more stable interface and a superior cycle performance compared to simply CoO materials. As indicated by Dong, the optimized electronic structure of the surface transition-metal ions can help to improve the interface stability of the chalcogenide-based cathode, of which the strategy may be extended to construct other stable carbon-based cathodes.

In addition to the reactivity exhibited by carbon materials in the presence of oxidative species, the defects sites on the carbonaceous materials are also active with superoxide radical to generate undesirable products such as carbonates,[118] thus undermining the round-trip efficiency and cycling stability of Li-O_2 battery. On this account, the surface chemistry of the carbonaceous materials should be optimized so as to minimize the associated defects density. In response, the annealing treatment on the carbonaceous materials makes sense. According to Zhang et al,[93] the graphene foam annealed in inert gas was less defective than the as-prepared one and the population of structural defects on the graphene foam was further reduced with a rise in the annealing temperature. When tested in the Li-O_2 battery, the graphene foam cathode with the least defective sites exhibited an impressive round-trip efficiency up to 80% and delivered a stable discharge voltage of approximately 2.8 V for 20 cycles, which far exceeds those of defective cathodes. In a similar case,[119] a strategy of heat treatment under argon atmosphere was carried out to reduce the amount of surface oxygen and selectively eliminate some unstable oxygen groups on graphene cathode. Consequently, the amount of Li_2CO_3 formed on the heated graphene cathode was much smaller than that on the pristine cathode, which was evident from the drop in the area ratio of Li_2O_2/Li_2CO_3 from 3.9 to 1.6, according to the XPS results of the discharged cathodes shown in **Figure 5**. As a benefit, the graphene cathode with improved surface chemistry exhibited a much extended cycling stability.

Clearly, the construction of chemically stable carbon cathode necessitates the existence of a stabilized surface around the carbonaceous cathode, which can resist the attack of oxygen radicals. In addition to the protection on the C-Li_2O_2 interface and the defect site passivation, the application of carbonaceous materials with a stable surface chemistry also holds promise. For this, the selection of carbon sources makes sense. According to Ryu et al.,[120] the graphene nanoflakes (GNFs) obtained from reduction of graphene oxides are rich in defects. For the fabrication of a stable carbonaceous cathode, the less defective nonoxidized GNFs is chosen as the supporting matrix to immobilize the Co_3O_4 nanofibers (NFs), based on which excellent Li-O_2 properties is demonstrated. Simultaneously, as pointed out by Muhammed et al,[64] the stability of carbon cathode also depends on the hydrophobicity/hydrophilicity of the carbon surface, and compared with the hydrophilic carbon, the hydrophobic is more stable against the corrosion during the charge process.

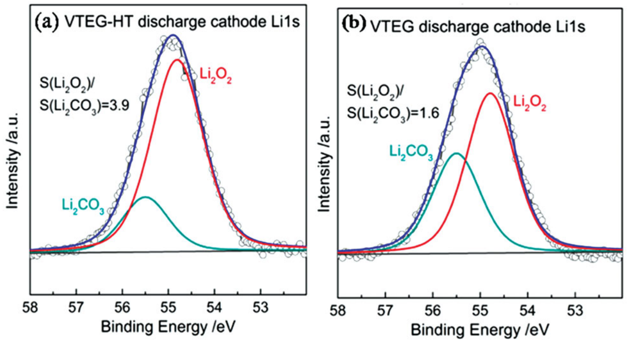

Figure 5. XPS spectra of discharged cathode: a) VTEG-HT cathode and b) VTEG cathode. Reproduced with permission.[119] Copyright 2015, American Chemical Society.

3.3. Lowered Charge Voltage

Recently, Muhammed et al. reported that the carbon material is relatively stable below 3.5 V, but is susceptible to decomposition upon charging above 3.5 V in the presence of Li_2O_2, which is exacerbated with the rise of charge voltage. As a result, the reactivity exhibited by carbon material can not only lead to carbon erosion over repeated cycling, but also give rise to undesirable Li_2CO_3, which are detrimental to the processes of ORR/OER in Li-O_2 batteries.[64] To alleviate the corrosion of carbon, the development of efficient catalysts that can reduce the charge overpotential is necessary.[121] For this, the incorporation of OER effective electrocatalyst has demonstrated feasibility in stabilizing the carbonaceous materials by aiding the smooth decomposition of Li_2O_2 at a lower recharge potential, despite the absence of obvious ideas on enhancing the chemical stability of carbon cathode with electrocatalyst in all the research discussed below.

To date, a tremendous amount of effort has been devoted to exploring effective catalysts to promote the OER kinetics in Li-O_2 batteries. Various types of materials including metals,[122–124] metal oxides,[125–128] and transition bimetallic nitrides,[129,130] have been investigated. The charge voltage of the Li-O_2 battery with these catalysts is lowered to some extent, which can benefit the chemical stability enhancement of carbon cathode. As a typical example, Oh reported the utilization of metallic pyrochlore as a catalyst, that exhibits a lower charge potential for Li_2O_2 oxidation than pure carbon.[131] The enhanced Li-O_2 charging efficiency was ascribed to the increased mass transport of reaction intermediate species that is promoted by both the high oxygen vacancies and porosity of the pyrochlore, thereby paving the way to new cathode architectures with lowered charge voltage for the Li-O_2 cell. In another case, perovskite-based porous $La_{0.75}Sr_{0.25}MnO_3$ nanotubes (PNT-LSM) electrocatalyst via an electrospinning technique and subsequent heating treatment was developed.[132] The Li-O_2 performances of the cathodes with

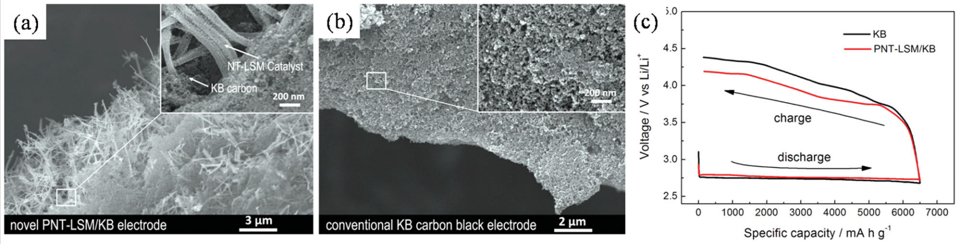

Figure 6. SEM images of the Ketjenblack (KB) cathode a) with and b) without a PNT-LSM catalyst. c) First cycle performance of the PNT/KB cathode and KB cathode. Reproduced with permission.[61]

and without the electrocatalyst are evaluated (**Figure 6**a,b).[61] With this novel electrocatalyst, the charge voltage of the Li-O_2 cells was found to be much lower than that of KB, by around 200 mV (Figure 6c). Consequently, the generation of Li_2CO_3 from carbon corrosion can be effectively minimized, which should contribute to the excellent cycle stabilities of the Li-O_2 cells. Other effective electrocatalysts were also reported,[133–137] including the reported multiwalled CNT paper (MWCNTP) embedded with Ru nanoparticles (NPs) (Ru@MWCNTP),[134] the Co_3O_4/RGO/KB cathode catalyst constructed by Nazar,[135] the increased OER activity after heteroatom doping,[136,137] etc.

4. Non-Carbon Cathode

As discussed, a chemically robust carbon cathode with the help of various protective strategies is constructed, however, it should be noted that the challenges from the chemically instability of carbon cathode are only partially resolved. Taking the strategy of catalyst incorporation as an example, in most cases, the carbon surface is always dominated in cathode due to its much higher surface area than that of catalyst. As a result, a majority of carbonaceous material is still exposed to the oxidative radical, of which the oxidation to parasitic products can occur. To get rid of the oxidation relevant to carbonaceous materials altogether, the development of carbon-alternative materials with inertness under the harshly oxidative environment is emerging with strong interests.[138–142]

By replacing the widely used carbon cathode with a nanoporous gold (NPG) cathode, the first truly rechargeable Li-O_2 battery with an overwhelmingly reversible formation/decomposition of Li_2O_2 for 100 cycles was constructed (**Figure 7**a).[138] This report provided clear insight into the benefit of carbon-alternative cathode in circumventing all the challenges associated with carbon oxidation, which has attracted worldwide attention in developing a stable cathode with non-carbonaceous materials for Li-O_2 battery.[143–148] Riaz reported a carbon-free cobalt oxide cathode via an electrodeposition-conversion process that is capable of delivering a long cycling stability.[140] Meanwhile, an efficient electrode based on cobalt oxide and manganese

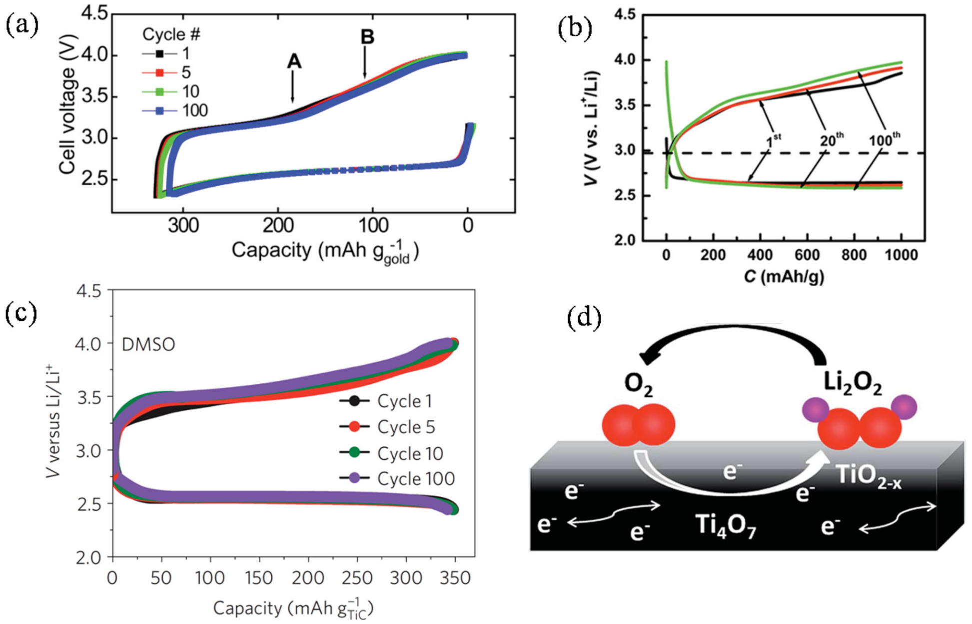

Figure 7. Cycling performances of a) NPG cathode. Reproduced with permission.[138] Copyright 2012, Science. b) Ru/$TiSi_2$ cathode Reproduced with permission.[150] Copyright 2014, American Chemical Society. c) TiC cathode. Reproduced with permission.[151] Copyright 2013, Nature Publishing Group. d) Schematic illustration for the reaction mechanism of Ti_4O_7 during the cycling of Li_2O_2. Reproduced with permission.[152] Copyright 2015, Royal Society of Chemistry.

oxide developed by Lin et al. demonstrated stable cycling performance accompanied with a high coulombic efficiency for up to 100 cycles.[141] A ε-MnO_2 nanostructure directly grown on Ni foam through a facile electrodeposition route was reported,[142] and exhibited a considerable high-rate capability and an enhanced cyclability (up to 120 cycles) without controlling the discharge depth. As a representative example of this research, an indium tin oxide (ITO) supported Ru NP cathode developed by Li et al. exhibited an excellent capacity retention for up to 50 cycles with charging voltages below 4 V,[145] accompanied with the dominantly reversible cycling of Li_2O_2.This superior capacity retention contrasted extremely favorably with the common Super P carbon cathode evaluated in this research, further highlighting the advantages of the carbon-alternative cathode over the carbon cathode in terms of stability towards aggressive radicals. Of note in this study is that the strategy for constructing Ru/ITO cathode can be extended to construct other carbon-alternative cathodes with excellent reversibility. Similarly, an efficient non-carbon cathode based on Ru/STO is also fabricated with a good cycling stability that is comparable to the Ru/ITO cathode.[147]

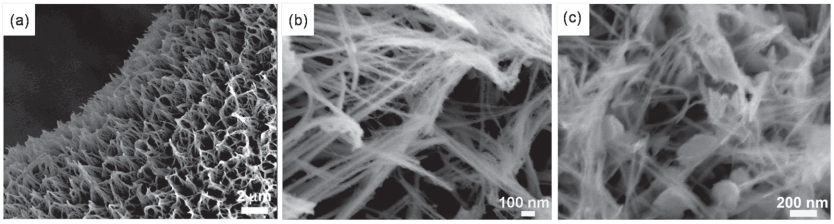

Figure 8. SEM image of a) the Ni foam supported Pt/Co_3O_4 cathode after the 5th discharge to 500 mAhg^{-1}. SEM images of b) the Ni foam supported Pt/Co_3O_4 cathode and c) the Ni foam supported Co_3O_4 cathode after the first discharge to 500 mAh g^{-1}. Reproduced with permission.[154] Copyright 2015, American Chemical Society.

Recently, to alleviate the challenges brought by carbon corrosion, a stable carbon-alternative catalyst support based on TiO_2 nanotube arrays grown on Ti foam is developed.[149] After the deposition of Pt NPs with a cool sputtering approach, an efficient Pt modified TiO_2 nanotube arrays (Pt/TNT) cathode was constructed, realizing a long-term rechargeability at high discharge/charge current densities (for example, up to 140 cycles at 1 or 5 Ag^{-1}). The superior stability of catalyst-support TiO_2, which is verified by the unchanged crystal structure and cathode surface state of the cathodes before and after cycling, has contributed to the exhibited long-term cycling performance. Undoubtedly, the reversible cycling of Li_2O_2 holds the key to the successful operation of a rechargeable Li-O_2 cell. As a major step towards this goal, a Ru NP-decorated $TiSi_2$ nanonet was constructed as a carbon-alternative cathode.[150] Compared with the popularly used carbon support, the $TiSi_2$ nanonet is advantageous in that it shows little reactivity towards reaction intermediates such as superoxide ions. As a consequent, an extensive cyclability (>100 cycles) with confirmed Li_2O_2 formation and decomposition was obtained (Figure 7b), of which the result is supposed to offer a guidance to develop other new catalyst supports stable to superoxide radical for the construction of suitable carbon-alternative cathode with desirable rechargeability.

With an effort to identify a suitable alternative cathode to carbon, a chemically robust carbon-free cathode based on TiC is reported,[151] which exhibited an even higher reversibility than the NPG cathode (Figure 7c). Notably, the surface chemistry of the TiC cathode was also probed in this research, which unveiled the origin for its superior chemical stability. Along with some TiOC, the presence of TiO_2 formed on the TiC is suggested to be responsible for the superior stability of the TiC cathode, which indicated the prime importance of a stable interface to the reversibility of the carbon-alternative cathode. More recently, the Nazar group reported a cathode based on metallic Magnéli phase Ti_4O_7,[152] which is capable of greatly reducing the overpotential compared to carbon. The conductive, self-passivating substoichiometric metal oxide layer formed at the surface is suggested to be responsible for the reversible cycling of Li_2O_2 (Figure 7d). Taken together, this research has confirmed the strategic importance of establishing a stable cathode interface for a chemically robust carbon-alternative cathode of the use of carbon-alternative materials has eliminated the challenges arising from the reactivity of carbonaceous materials in the Li-O_2 field, thus boosting the chemical stability of the cathode applied. However, towards the construction of a stable cathode, the mechanical stability of the carbon-alternative cathode is another aspect that cannot be neglected. As reported, the non-carbon cathode can suffer from volume expansion during the cycling of Li_2O_2, thus the contact between active materials and the conductive substrate can be loosened, degrading the performance of a Li-O_2 battery.[153] The solution to this challenge necessitates the improvement of the cathode fabrication. With the help of in situ chemical deposition, a free-standing carbon-alternative cathode consisting of aligned Co_3O_4 nanorod grown directly on the Ni foam substrate was proposed by Cui et al.[153] In contrast to the conventional carbon-supported cathode constructed by a simple mechanical mixing method, the Co_3O_4 nanorod on the Ni substrate exhibits a much improved adhesion, thus effectively suppressing the cathode expansion that occurred during cycling. By accommodating active sites to promote the Li-O_2 reactions and void spaces to store the generated Li_2O_2, the carbon-free cathode should be rigid enough to tolerate the effect from the cycling of Li_2O_2 particles on its conducting network. To this end, an improvement in the cathode architecture is proven to be a reliable approach. According to Cao et al.,[154] by bundling the tips of the Co_3O_4 nanowires together with the help of Pt NPs, the obtained Pt/Co_3O_4 cathode is more mechanically strong than the Co_3O_4 cathode to support the discharge product. As displayed in **Figure 8**a, the well-kept morphology of the cathode after the fifth discharge has evidenced the excellent mechanical stability of the Pt/Co_3O_4 cathode that is believed to contribute to the better cycling stability of the Li-O_2 battery with Pt/Co_3O_4 cathode than that with Co_3O_4 cathode. It is worth noting that the uniform deposition of a fluffy, thin Li_2O_2 layer only on the periphery of Pt/Co_3O_4 has caused much less damage on the cathode architecture compared with the large crystal of Li_2O_2 on the pure Co_3O_4 cathode (Figure 8b,c). As reported by Lee et al,[155] the Li_2O_2 generated at a low discharge rate is concentrated on the top region of a Co_3O_4 nanowire (NW) and this

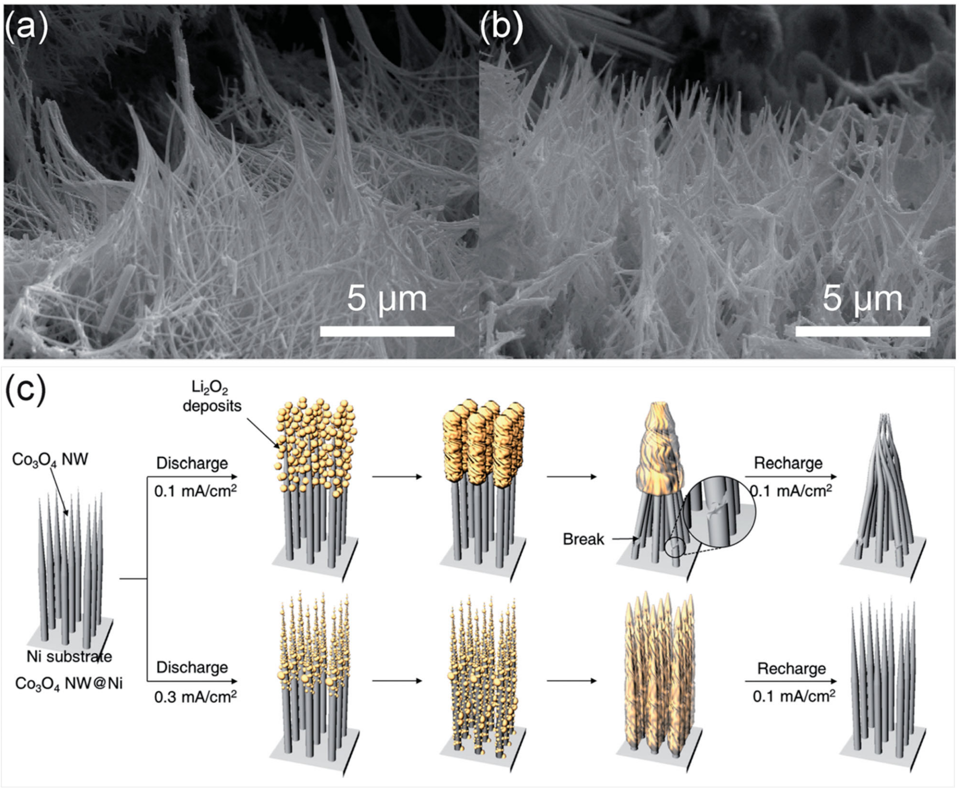

Figure 9. SEM images of Co_3O_4 NW@Ni-foam cathode after charging at discharge-charge rates of a) 0.1/0.1 mA cm^{-2} and b) 0.3/0.1 mA cm^{-2}. c) Schematic illustration of the structural evolution of the Co_3O_4 NWs with low and high discharge rates. Reproduced with permission.[155] Copyright 2014, Royal Society of Chemistry.

inhomogeneous distribution of Li_2O_2 has lead to a pointed-tip-brush-like aggregation of NWs, causing deformation and breakage of the NW. In contrast, the NWs are well-separated and maintained during the cycling with a more uniform distribution of the generated Li_2O_2 along the NW (**Figure 9**). Even though the idea of enhancing the mechanical stability of carbon-alternative cathode is not clearly proposed in the work that has already been published, it should be noted that the improvement on the mechanical stability of carbon-alternative cathode is a topic of equal significance to that of carbonaceous cathode, which deserves much attention.

5. Conclusion and Outlook

So far, the Li-O_2 technology has enjoyed worldwide attention because of its ultrahigh theoretical energy density. Much effort has been devoted to the Li-O_2 field to push forward its commercialization. However, the development of Li-O_2 technology is still at its infancy regardless of the significant achievements already made, which include the deepened understanding on the Li-O_2 electrochemistry, the application of efficient ORR/OER electrocatalyst, etc. Prior to its practical application, numerous urgent problems including low round-trip efficiency, poor cycling performances, etc. need to be resolved. It should be noted that these problems are closely associated with the structural destruction and/or chemical deterioration of cathode applied in Li-O_2 battery. Encouragingly, various creative strategies have been adopted based on which the mechanical or chemical stability of the cathode are boosted, thus creating Li-O_2 batteries with excellent performances. As for the construction of a mechanically robust carbonaceous cathode, the strategy of architectural modification has been proven to be a choice of primary importance. By providing sufficient void space with rational cathode architecture, the structural destruction caused by the formation/decomposition of Li_2O_2 is effectively alleviated, thus enhancing the cathode mechanical stability effectively. However, the components of carbonaceous cathode exposed in the harshly environment of Li-O_2 battery can be easily oxidized, thus generating the parasitic products that can degrade the performances of Li-O_2 batteries. To this end, various protective strategies including binder-free design, carbon surface protection, and catalyst incorporation are applied and have boosted the chemical stability of carbonaceous cathodes to varying degrees. However, in most cases, restricted by the limit of these strategies that a significant part of carbonaceous materials is exposed to the oxidative species even after protection, the challenges regarding the chemical instability of carbon cathode still exist. In response, the development of a non-carbon cathode that is stable against the superoxide attack holds great promise. With the help of effective strategies, such as electrodeposition,[142] template methods,[148] and ALD,[150] various robust carbon-alternative cathodes have been obtained. Unfortunately, the high mass of these carbon-free cathodes has

Table 1. Summary of cathode modification methods in Li-O_2 batteries.

Cathode modification method	Advantages	Limits
Architectural modification	Suppressed volume expansion caused by cycling of Li_2O_2	Carbon oxidation
Binder-free design	Problems form binder decomposition are addressed	Carbon oxidation
Carbon surface protection	Enhanced chemical stability of C-Li_2O_2 interface	Reduced ORR/OER activity
Catalyst incorporation	Alleviated carbon corrosion by lowering the charge voltage	Increased cathode weight
Carbon-alternative cathode design	Robust chemical stability	Huge cathode weight

destroyed the specific capacities of Li-O_2 battery. For this consideration, the application of carbon-alternative materials with low mass density is a choice of great potential. In summary, all the cathode modification methods have their own advantages and limits in terms of stability enhancement and practical application and these are summarized in **Table 1**.

Encouragingly, the chances for improving the stability of cathode are still great.

Towards the construction of mechanically robust carbonaceous or carbon-alternative cathode, the challenges regarding the volume expansion caused by the formation/decomposition of Li_2O_2 need to be addressed. In response, rational design of the cathode structure with sufficient void space constitutes a choice of primary importance. To this end, concepts and techniques for cathode design and fabrication adapted in the fuel cells could be possibly applied to the Li-O_2 field. Simultaneously, the rigidity of cathode architecture should be high enough to withstand the possible stress evolution resulting from continuous build-up of Li_2O_2 with the depth of discharge and the gradual decomposition of Li_2O_2 during charge, which necessitates the arrival of structure design and cathode composition optimization. Finally, when talking about the cathode mechanical stability, the physical appearance of Li_2O_2 is another factor of a great significance. It can be expected that a tailored morphology and uniform distribution of Li_2O_2 rather than the toroidal and discrete one can favor a preserved architectural integrity of the constructed cathode. For this consideration, the cathode composition and the testing conditions such as the discharge rate contributes significantly. Clearly, a mechanically robust cathode can be obtained if all three aspects can be realized. It should be also noted that a stable cathode for Li-O_2 battery can be obtained based on the construction of mechanically robust carbon-alternative cathode. The challenges from the reactivity of carbonaceous materials in the harshly aggressive Li-O_2 environment call for creative strategies for enhancing the chemical stability of carbon cathodes.

To enhance the chemical stability of carbonaceous cathode, the protection on the easily corroded C-Li_2O_2 interface is necessary and can be achieved by minimizing the contact area of the C-Li_2O_2 interface. As a solution, the deposition sites of Li_2O_2 could be restricted to a non-carbon surface, which is stable against the oxidation of generated Li_2O_2. To this end, the incorporation of non-carbon material such as metal/metal oxide, which might be more thermodynamically favorable for Li_2O_2 deposition than the carbon materials, should be a promising strategy. In addition, the optimization on ORR reactions routes is also promising in preventing the chemical corrosion of carbonaceous cathode, which can be achieved by reducing the contact area between the cathode surface and the oxidative reaction intermediates as much as possible. In this aspect, the application of high-donor-number electrolytes should make sense.[5] To completely address the problems brought by the corrosion of C-Li_2O_2 interface, it is essential to coat a layer of composites that is stable against the attack of oxygen radicals while insoluble in the applied electrolyte. To this end, the exploration and application of new materials is a task of urgent importance.

The carbon corrosion caused by charge voltage can be effectively suppressed with the incorporation of catalyst, which has necessitated the development of powerful electrocatalysts. To achieve this, the computational quantum chemistry can be a useful tool in design of catalyst materials that deserves attention.

Clearly, the performances of Li-O_2 battery based on a stable cathode can be effectively improved. It should be noted that in addition to cathode stability, the stability of the anode and electrolyte can also affect the performances of Li-O_2 battery and this is deserving of attention and should be addressed gradually.

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