Viser Technology Pte. Ltd.
Research and Application of Materials Science
DOI: 10.33142/rams.v4i1.8461

Research Article Open Access

Recent Progress of Catalytic Cathodes for Lithium-oxygen Batteries

Wei WANG [1], Simin WANG [1], Longhai ZHANG [1*], Sijiang HU [2], Xuyang XIONG [1, 3], Tengfei ZHOU [1], Chaofeng ZHANG [1*]

1.Institutes of Physical Science and Information Technology, Leibniz Joint Research Center of Materials Sciences, Anhui Graphene Engineering Laboratory, Anhui University, Hefei 230601, China
2.Guangxi Key Laboratory of Low Carbon Energy Material, Guangxi Normal University, Guilin 541004, China
3.Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

***Corresponding Author**: Longhai ZHANG, Chaofeng ZHANG*

Abstract:
Lithium-oxygen batteries are among the most promising electrochemical energy storage systems, which have attracted significant attention in the past few years duo to its far more energy density than lithium-ion batteries. Lithium oxygen battery energy storage is a reactive storage mechanism, and the discharge and charge processes are usually called oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Consequently, complex systems usually create complex problems, lithium oxygen batteries also face many problems, such as excessive accumulation of discharge products (Li_2O_2) in the cathode pores, resulting in reduced capacity, unstable cycling performance and so on. Cathode catalyst, which could influence the kinetics of OER and ORR in lithium oxygen (Li-O_2) battery, is one of the decisive factors to determine the electrochemical performance of the battery, so the design of cathode catalyst is vitally important. This review discusses the catalytic cathode materials, which are divided into four parts, carbon based materials, metals and metal oxides, composite materials and other materials.

Keywords: *lithium oxygen battery; cathode; catalyst; energy storage*

1 Introduction

With the continuous progress of science and technology, the demand for energy becomes higher and higher, which presents a huge challenge to energy storage technology. Electrochemical energy storage modes include fuel cells, supercapacitors, rechargeable batteries, etc [1-3]. At present, rechargeable lithium-ion batteries are widely used in human daily life (such as notebook computers and smart phones) [4-8]. However, lithium-ion battery (LIB) also face some serious problems, the most fatal problem of lithium-ion batteries is the low energy density, only 250 Wh kg-1, which hinders its application in some fields [5-9]. Other ion batteries (such as zinc ion batteries and sodium ion batteries) still need a lot of research to improve their performance [10-15]. This has led to an increasing requirement for electrochemical energy storage devices with high energy density. Lithium-oxygen batteries (LOB) as a promising energy storage form is widely studied, due to the ultra-high theoretical specific energy density (about 3500 Wh kg-1), which is much higher than lithium-ion battery [16-20].

Electrochemical storage of nonaqueous lithium oxygen batteries is reactive storage mechanism [21]. As shown in equation 1, during the discharge process of lithium oxygen battery, oxygen is reduced in the cathode and reacts with Li+ to form Li_2O_2, which stays in the pores of the cathode. This process is also called oxygen reduction reaction (ORR). In the charging reaction, Li_2O_2 decomposes to form Li+ and O_2 (equation 2). This process is also called oxygen evolution reaction (OER) [22]. However, in the ORR process, Li_2O_2 will be continuously generated and attached to the surface of the catalyst. Excessive deposition of Li_2O_2 will block the pores of the catalyst, resulting in the reduction of discharge capacity. In turn, in the OER process, the incomplete decomposition of Li_2O_2 will reduce the charging capacity [23-24]. Due to the insulation of Li_2O_2, it leads to sluggish kinetics in ORR and OER process [25-26]. In this case, LOB face issues such as large overpotential between charge and discharge process, low round-trip

Received on February 20, 2022; Accepted on April 10, 2022

efficiency, and poor cycle life, which hinder their commercial application [4, 27-31]. Using appropriate catalyst can enhance the cycle stability and diminish the overpotential [23, 29, 32]. Therefore, it is necessary to study suitable and porous cathode catalysts.

$$\mathrm{ORR:}\quad 2\mathrm{Li}^+ + \mathrm{O}_2 + 2\mathrm{e}^- \rightarrow \mathrm{Li}_2\mathrm{O}_2 \qquad (1)$$

$$\mathrm{OER:}\quad \mathrm{Li}_2\mathrm{O}_2 \rightarrow 2\mathrm{Li}^+ + \mathrm{O}_2 + 2\mathrm{e}^- \qquad (2)$$

In the past several decades, an army of scientists have been committed to solving the challenges which confronted with lithium oxygen batteries. Research shows that Li_2O_2 is only ideal discharge product, but it is not the only discharge product. LOB may also generate products such as LiOH during discharge, which cannot be completely changed back to Li ions and O_2 in charging [5]. This will lead to poor performance of lithium oxygen batteries. Recent studies have pointed out that cathode catalyst as an indispensable part of lithium oxygen battery. The structure, the surface pores and the type of catalyst will affect the formation of Li_2O_2, so the selection and design of catalyst is of great significance [33-36].

Figure 1 Classification of cathode materials for lithium oxygen batteries

This paper reviews the effects of cathode catalyst types on the performance of LOBs in recent years. In this review, catalysts are divided into four types as shown in figure 1. (1) Carbon materials [37-38]. Carbon materials are used in LOB cathode because of high conductivity and rich pores, which can accommodate more discharge product Li_2O_2 [39]. Moreover, carbon materials can also promote the ORR process. However, during the OER process, the catalytic activity of carbon materials is slightly low.[40] (2) Metals and metal oxides [41].They can enhance the decomposition of Li_2O_2, thereby accelerating the OER process [42-44]. (3) Composite materials [45-46]. Few single materials can promote both ORR and OER process in LOB at the same time. Scientists try to composite two or more materials to make up for their shortcomings, so as to obtain better electrochemical performance. For example, the combination of carbon materials and metals, on the one hand, the addition of metals can effectively improve the shortcomings of carbon materials in the OER process, on the other hand, it can also have the advantages of porous carbon materials. (4) Other materials [47-48]. In addition to the three types of materials mentioned above, sulfides and nitrides etc. Can also be used as cathode of lithium oxygen batteries and show good performance. In order to clearly understand the performance of various catalyst materials, we compared them in the form of radar chart (figure 2), where their pore size, catalytic activity, preparation complexity, cycle stability, overpotential and price are considered. In the following chapters, we will briefly introduce these types of catalyst materials.

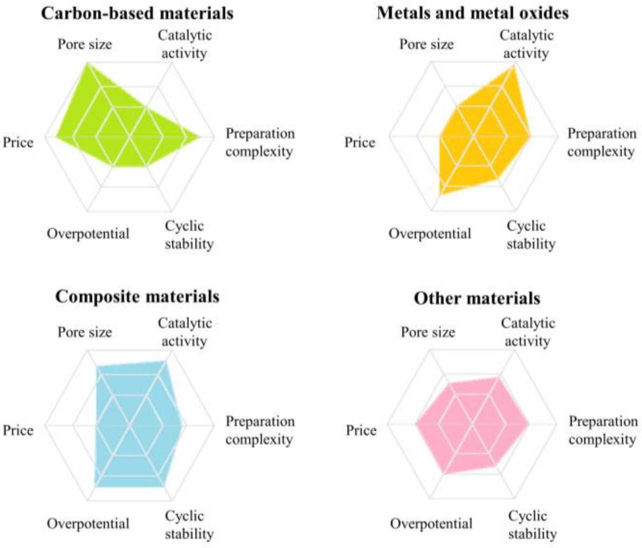

Figure 2 Overview of performance of different types of catalysts in lithium oxygen batteries

2 Carbon based materials

Carbon materials have been broadly used as conductive agents, cathode material and catalyst carrier in lithium oxygen batteries due to their high specific surface area, excellent electrical conductivity and low cost. Carbon material can show very good catalytic performance in ORR and OER processes and can be used as porous cathode catalyst in non-aqueous lithium oxygen batteries [3].

2.1 Carbon materials

General speaking, the properties of lithium oxygen cells may be influenced by the morphology, specific surface area and pore structure of carbon materials. To explore the link between carbon performance and battery capacity. Ding et al [49]. have compared the influence of eight different carbon materials on the capacity of lithium oxygen batteries: multi-walled carbon nanotubes (MWCNT), and ordered mesoporous carbon (OMC), and activated carbon and commercial carbon black (Ketjen black, Super P and acetylene black), and inverse opal carbon (IOC) and reduced graphene oxide (rGO).

Figure 3a shows the initial charge-discharge curves of different carbon materials as the cathode electrode of lithium oxygen batteries. MWCNT clearly delivers the lowest discharge capacity of only 1311 mA h g-1, while rGO delivers the highest discharge capacity of above 8400 mA h g-1. The OMC and activated carbon have a slightly higher discharge capacity than the MWCNT, with only 1812 mA h g-1 and 1897 mA h g-1 respectively. The capacities of three kinds of carbon black (Ketjen black, Super P and acetylene black) cathode are 2865, 3399 and 3512 mA h g-1. Both IOC and OMC are mesoporous carbon materials, but the discharge capacity of IOC is 4504 mA h g-1, which is more than twice that of OMC. The difference of the capacities between OMC and IOC can be attributed to different properties of carbon materials. As seen from the Table 1, the discharge capacity of battery exhibits proportionality to the pore sizes. When the pore size of the carbon material is larger, the capacity to store the product Li_2O_2 becomes better, so the discharge capacity is increased. However, MWCNT is an exception. The reason for this is the large length-to-diameter ratio of the MWCNT. The ultralong transport channel is not conducive to the diffusion of O_2. The open ends of MWCNT are small, which are easily to be blocked by the discharge products, resulting in little actual utilization rate of pore and low discharge capacity.

Table 1 Surface area and pore characteristics of various carbons and their influence on the capacity of Li－O_2 batteries

Carbon materials	Surface area (m2 g-1)	Pore volume (cm3 g-1)	Pore size (nm)	Discharge capacity (mA h g-1)
MWCNT	929	1.64	7.0	1311
OMC	863	1.14	5.2	1812
Activated carbon	1230	1.07	4.7	1897
Ketjen black	818	1.17	7.7	2865
Super P	62	0.32	11.9	3399
Acetylene black	56	0.16	11.4	3512
IOC	794	3.17	16.0	4504
rGO	361	1.58	17.5	8418

The disadvantage of single carbon material is that there are fewer active sites and the catalytic activity cannot meet the needs of batteries. At high voltage single carbon material will promote the conversion of discharge product Li_2O_2 to other lithium compounds, which will lead to the degradation of the cycle performance of the battery.

2.2 Doped carbon materials

Many studies have shown that the introduction of heteroatoms will change the morphology and electronegativity of carbon-based materials, resulting in the formation of pores and functional groups. Therefore, carbon materials with low doping level of non-metallic elements (such as N-element doping) can significantly enhance the electrochemical properties of carbon materials. N-doped carbon materials can obviously improve the electrochemical performance. As the concentration of N element doping in the carbon material increases, the band gap decreases, which benefit to improve the conductivity of the carbon material.

Shui *et al* [50]. used CVD (chemical vapor deposition) method to get vertically aligned nitrogen-doped coral-like carbon fiber (VA-NCCF). As shown in the figure 3b, the overpotential decreases obviously due to the doping of the N element. At 500 mA g-1 current density, the lithium oxygen battery which used VA-NCCF as cathode catalyst demonstrated a high discharge capacity more than 40000 mA h g-1 (figure 3c). At limit high specific capacities (1000 mA h g-1), the cell could cycle stably for 150 times. Because of low overpotential and minimal electrolyte decomposition. The doping of N elemental improved the catalytic activity, reduced the overpotential between charge and discharge, and reduced the decomposition of electrolyte. The unique structure provided space for the deposition of product Li_2O_2 and transport of reactants.

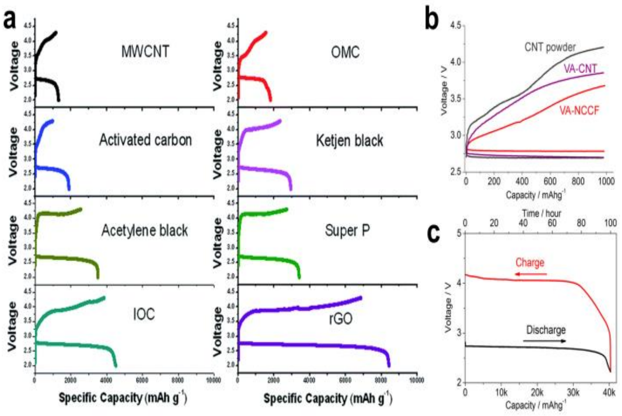

Figure 3 (a) Initial charge/discharge voltage profiles of various carbon materials cycled under 50 mA g-1. (b) Comparisons of VA-NCCF, VA-CNT and CNT powder. (c) Charge/discharge voltage profile of VA-NCCF at a current density of 500 mA g-1

Zhang *et al* [51]. controlled flow of H_2O (gas) to oxidize the reduced graphene into holey graphene (hG) with plenty of nanoholes. The as-prepared hG was heating under NH3/Ar and heating with H_3BO_3 under Ar atmosphere to prepared B,N-hG. B,N-hG shows the lowest overpotential at a current density of 100 mA g-1 and the highest discharge capacity (15340 mA h g-1) than bare hG, B-hG and N-hG. At limit high specific capacities (1000 mA h g-1) and a current density of 500 mA g-1, the battery with B,N-hG as cathode could cycle stably for 117 times which is better than the other three materials. These excellent properties are attributed to the nanopore enlargement in graphene induced by the doping of elements B and N and the synergy between the two elements. The enlargement of nanopore allows the cathode to accommodate more Li_2O_2, and the doping of B and N atoms increases the conductivity of the material itself. Combining these advantages, B,N-hG can obtain higher discharge capacity. Although doping non-metallic elements can improve the properties of carbon materials, large-scale production and control of uniform doping of elements still a challenge. This makes it more difficult to commercialize the method of doping non-metallic elements to improve the electrochemical performance of lithium oxygen batteries.

3 Metals and metal oxides

In oxygen reduction reaction (ORR), metal and metal oxides promote the formation of thin films or nanoparticles with low crystallinity Li_2O_2. Because of the low crystallinity, Li_2O_2 is more easily decomposed during charging (OER), and therefore has a lower decomposition potential during charging. Therefore, metal and metal oxides as catalyst can reduce the overpotential during charge and discharge process and improve the cycle stability of lithium oxygen batteries [52]. In this part, metals and metal oxides are introduced from the following three aspects: (1) noble metal and noble metal oxides, (2) transition metal and transition metal oxides, and (3) perovskite and their oxides.

3.1 Noble metal and noble metal oxides

Noble metal nanoparticles are considered to be excellent catalytic materials that can promote oxygen reduction reactions (ORR) in batteries and many oxidation reactions.

Bui *et al* [53]. prepared carbon nanofibers with platinum nanoparticles (CNF@Pt) by electrospinning. Compared with the traditional encapsulating method, the catalyst prepared by electrospinning can expose more active materials, thus improving the electrochemical performance of lithium oxygen battery. Pt nanoparticles are evenly distributed on CNF. At various current densities of 200 mA g-1, 500 mA g-1, and 1000 mA g-1, the charge-discharge curves of CNF@Pt and CNF are similar, but the capacity of CNF@Pt is much larger than that of CNF, and the overpotential of CNF@Pt is lower than that of CNF in the charge-discharge process. At a current density of 200 mA g-1, the capacity of CNF@Pt was 6938 mA h g-1. At a current density of 500 mA g-1 and limited high specific capacity of 1000 mA h g-1, the battery with CNF@Pt as cathode could cycle stably for 162 times which is better than the battery with CNF as cathode. Due to the catalytic activity of Pt in ORR and OER processes, lithium oxygen batteries with CNF@Pt exhibit higher specific capacity and better cycle stability.

Jeong *et al* [54]. systematically evaluated the catalytic performance of Pt, Pb and Ru nanoparticles by supported them on rGo as cathode catalysts for lithium oxygen batteries. At a current density of 200 mA g-1 and limited high specific capacity of 2000 mA h g-1, the introduction of noble metal can obviously reduce the overpotential between charge and discharge. Among them, Ru presents the best cyclic stability and the lowest overpotential during the charge and discharge process. In the charge discharge curve (figure 4a), it can be found that the introduction of ruthenium can significantly reduce the potential during charging. There are two advantages when Ru is used as a catalyst. First, Ru has obvious effect in reducing the size and induced morphology of the discharge product, and the formed discharge product is easier to be completely decomposed during charging. Second, ruthenium is mixed with Li_2O_2, the discharge product is catalysis decomposed by electron transfer, which reduces the decomposition voltage of the discharge product. Compared with Ru, the incorporation of Pt and Pd will promote the decomposition of electrolyte, resulting in slightly poor performance of lithium oxygen battery.

Compared to single noble metal system, it is difficult for a single metal to perform well in both ORR and OER processes. Therefore, the noble bimetal system can cooperate with the catalytic effect of the two noble metals, and the two metals show excellent catalytic performance in the ORR and OER processes respectively [52].

Lu *et al* [55]. introduced PtAu nanoparticles, which can significantly improve the kinetics of the ORR and OER processes of rechargeable lithium oxygen batteries. As catalysts, PtAu/C and carbon exhibit similar specific capacities (～1200 mA h g-1) in lithium oxygen batteries (figure 4b). It was obvious that PtAu/C overpotential is lower than pure carbon during ORR and OER. As shown in the figure 4c, the discharge curve of PtAu/C is similar to that of Pt in the OER process, and the charge curve of PtAu/C is similar to that of Au in the ORR process. Therefore, it is concluded that Pt nanoparticles have catalytic effect on OER, while Au nanoparticles have catalytic effect on ORR.

Choi *et al* [56]. synthesized PdCu noble bimetal nanoparticles with disordered face-centered cubic and ordered body-centered cubic mixed phase by polyol method for lithium oxygen battery cathode. The lithium oxygen battery with PdCu has a cycle efficiency of nearly 80% at a current density of 200 mA g-1. The discharge voltage without decay after 50 cycles at high current density 5000 mA g-1. The excellent performance of the battery could be attributed to the good catalytic activity of PdCu noble bimetal material during ORR and OER processes, thus greatly reducing the overpotential in the process of charge and discharge. Their theoretical calculations showed that the transfer of electrons from Cu atom to Pd atom weakens the adsorption strength of lithium oxide on the PdCu nanoparticles and ultimately reduces the overpotential.

Noble metal oxides can also be used as catalysts for lithium oxygen batteries. For example, Jung *et al* [57]. synthesized ruthenium (Ru) and hydrated ruthenium oxide ($RuO_2 \cdot 0.64H_2O$) uniformly distributed on rGo. At a current density of 500 mA g-1 and a limited specific capacity of 5000 mA h g-1, the battery cycling stably for 30 cycles (figure 4d). Noble metals and their oxides are used as cathode catalysts for lithium oxygen batteries, the performance of batteries has been greatly improved.

However, the shortcomings of limited reserves in nature and high cost greatly limit the practical application of noble metals and their oxides.

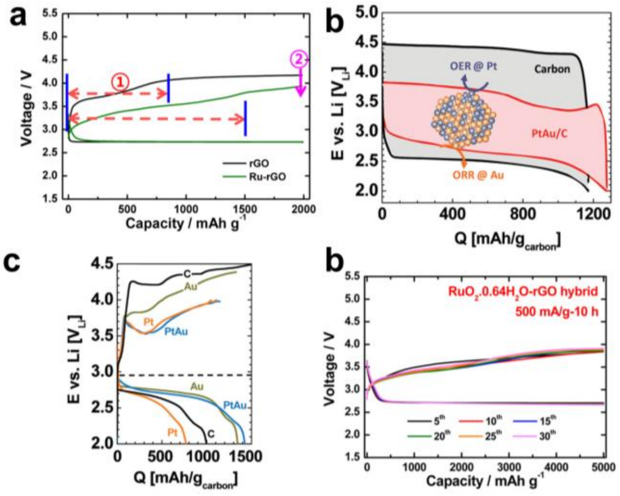

Figure 4 (a) The potential profiles of rGO and Ru-rGO at 200 mA g-1 for 10 h. (b) LOB charge/discharge profiles of carbon and PtAu/C in the third cycle. (c) LOB first charge/discharge profiles of carbon at 85 mA g-1 and of Au/C, Pt/C, and PtAu/C at 100 mA g-1. (d) Charge/discharge profiles of different cycles of $RuO_2 \cdot 0.64H_2O$-rGO hybrid

3.2 Transition metal and transition metal oxides

Transition metals (such as Mn, Fe, Co, Ni, Zn, etc.) and transition metal oxides (such as MnO_2, CoO, FeO, etc.) all show catalytic potential of ORR/OER. Compared with noble metals, they are abundant and cheap. Therefore, many studies have been conducted by using them as catalysts for lithium oxygen batteries.

Wang *et al* [58]. embedded Co single atoms in nitrogen-rich carbon (Co-SAs/N-C) as a catalyst for lithium-oxygen batteries. At a current density of 200 mA g-1, the battery with Co-SAs/N-C as cathode exhibited discharge capacity of 20105 mA h g-1 and charge capacity of 19765 mA h g-1 in the first cycle. The initial coulomb efficiency was close to 100%. At a current density of 400 mA g-1 and a limited specific capacity of 1000 mA h g-1, the battery could cycle stably for 260 times. As shown in the figure 5a, Li atom of the discharge product and N atom form effective coordination sites, and there is also strong binding between O atom and Co atom. In the figure 5b, the N-C material without Co-N4 has only the combination of Li atom and N atom. The overpotentials between charge and discharge is defined as: ΔU=UC-UDC, where UC and UDC represent charge and discharge potential respectively. It is obvious that the calculated overpotential of Co-SAs/N-C is significantly smaller than that of N-C, which indicates that doping Co atoms can reduce the overpotential. As shown in figure 5c that the exposed active sites are conducive to adsorbing more discharge products.

Gao *et al* [59]. reported a CoO/C composite with oxygen vacancy. Compared with commercial CoO, the lithium oxygen battery with CoO/C materials containing oxygen vacancies have higher initial capacity, better rate performance and cycle stability. They attributed the improved performance of CoO/C composites containing oxygen vacancies to the presence of oxygen vacancies. The existence of oxygen vacancies improves the migration capacity of electrons and Li+, and can be used as the active site for the reaction of oxygen and Li_2O_2. In addition, doped C not only has good ORR activity, but also improves the conductivity of CoO and stabilizes oxygen vacancy. Lin *et al* [60]. found that Co_3O_4/CNT had good catalytic activity when it was used as cathode of lithium oxygen battery, which significantly ameliorated the weak catalytic activity of CNT in OER process and reduced the overpotential. In situ EPR test showed that Co_3O_4 catalyst inhibited the formation of by-products.

As the catalyst of lithium oxygen battery, manganese-based material can not only improve the specific capacity, but also improve the coulombic efficiency of the battery.

Zhang *et al* [61]. prepared a tubular δ-MnO_2 material with microstructure by hydrothermal synthesis (as shown in figure 5d). SEM images (figure 5e and f) show that δ-MnO_2 tube is a nanorod with porous flower-like surface. This structure is conducive to the penetration of electrolyte, so as to speed up the transportation of Li+. The lithium oxygen battery with MnO_2/KB as catalyst exhibited a capacity of 6150 mA h g-1 at the current density of 25 mA g-1. Even at a high current density of 600 mA g-1, the battery exhibited a capacity of 2850 mA h g-1. Obviously, the rate properties and cycling properties of MnO_2/KB material are better than pure KB. They found that the discharge product Li_2O_2 of the lithium oxygen battery with MnO_2 forms a uniform nanosheet, which is more easily decomposed during charging. Therefore, the specific capacity and cycle performance of battery were improved, especially the OER reactivity were significantly improved. The improvement to unique microscopic tubular structure of δ-MnO_2 material, which promoted the generation of nanosheet Li_2O_2, thus improved the properties of lithium oxygen battery. In addition to pure manganese oxide, introducing other transition metals to replace a small amount of Mn element in manganese oxide to form doped catalysts is also a method to improve the properties of batteries.

Minowa *et al* [62]. found that the battery with Mn_2O_3 as cathode catalyst had better properties than both MnO and MnO_2. In order to improve the battery performance with Mn_2O_3, they used other transition metals to replace a small amount of Mn in Mn_2O_3 to form Mn_2-xMxO$_3$ (M = Fe, Mn, Ni and Co) catalyst. The experimental results show that when 0.2Mn is replaced by Fe, the battery exhibits the best property. For example, the capacity of the battery increased, and the overpotential decreased. So far, researchers have studied a variety of manganese oxides, such as α-MnO_2, β-MnO_2, MnOOH and so on.

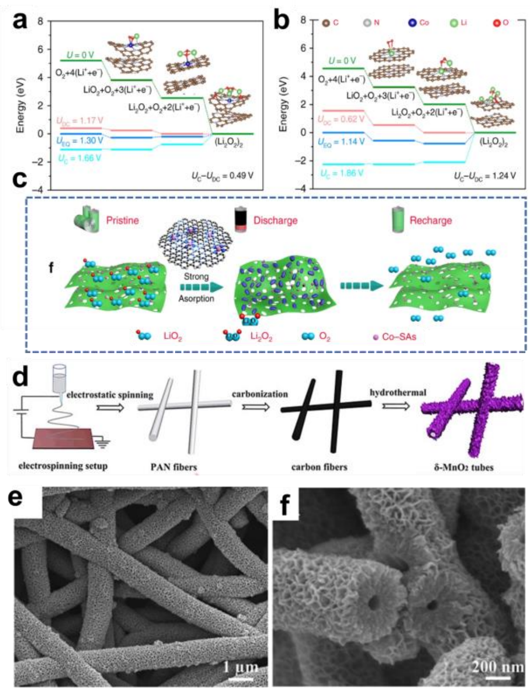

Figure 5 Calculated free energy diagrams for the charge/discharge reactions on the active surface of (a) Co-SAs/N-C and (b) N-C. (c) Schematic illustrations of the working mechanism for the Co-SAs/N-C electrodes. (d) Scheme of the preparation of δ-MnO$_2$ tubes. (e, f) SEM images of δ-MnO$_2$ tubes

3.3. Perovskite and their oxides

The molecular formula for perovskite oxide is ABO$_3$. Perovskite oxides are used in lithium oxygen batteries because of their excellent catalytic activity and electrical conductivity. Hedge *et al* [25]. prepared the oxygen vacant CaMnO$_3$ (H-CMO) with multiple oxygen vacancies by sol-gel method and low-temperature hydrogen reduction method. It is obvious from the figure 6a that H-CMO not only reduces the charging over potential, but also reduces the discharge over potential, which generally reduces the over potential between charging and discharging. In terms of circulation, the performance of H-CMO is also significantly better than that of CMO. At a current density of 500 mA g-1 and a limited specific capacity of 500 mA h g-1, the battery could cycle stably for 110 times. Li *et al* [63]. prepared one-dimensional porous La0.5Sr0.5CoO$_2$.91 nanotubes by electrostatic spinning technology. Electrochemical test showed that the initial discharge capacity is 7205 mA h g-1 at a current density of 100 mA g-1, which is close to the performance of noble metal CNT@Pt. At a current density of 200 mA g-1 and a limited specific capacity of 1000 mA h g-1, the battery could cycle stably for 85 times. The excellent performance of the battery is attributed to the structure of the nanotubes to transport electrons and the addition of active sites.

Compared with common perovskite oxides, double perovskite oxides have higher oxygen and electron transfer capacity. Ma *et al* [64]. synthesized SrCrMoO6-δ (SCM) which is a double perovskite structure oxide. SCM was used as catalyst for lithium oxygen battery. At a current density of 75 mA g-1, the discharge capacity of battery was 2306 mA h g-1, which is much higher than the Super P electrode capacity (1434 mA h g-1). In addition, the overpotential of SCM is lower than that of Super P (figure 6b). At a current density of 200 mA g-1 and a limited specific capacity of 600 mA h g-1, the terminal discharge voltage drops to 2.34 V after 30 cycles. Under the same conditions, the terminal discharge voltage of Super P drops below 1.5 V after 13 cycles. The experimental results showed that the oxides with double perovskite structure can promote the properties of lithium oxygen battery. Zhu *et al* [65]. reported a new cathode catalyst called PrBaCo$_2$O$_5$+δ (PBCO). The electrochemical performance of PBCO is much better than that of commercial BP2000. As shown in the figure 8c and d, it can be seen from the charge discharge curve under various current densities that the capacity of PBCO is much higher than that of BP2000. PBCO exceeds 8000 mA h g-1 when the current density is 0.02 mA cm-2. Moreover, the overpotential is also significantly lower than BP2000. When the current density is limited to 1000 mA h g-1, it can be stably maintained for more than 1000 cycles.

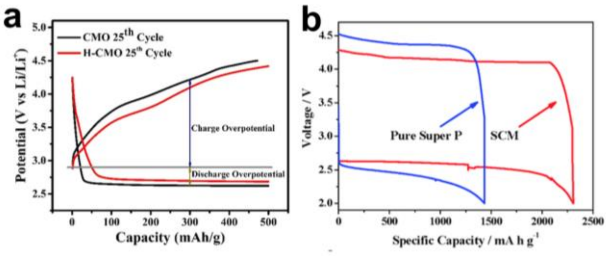

Figure 6 (a) Comparison of overpotentials for CMO and H-CMO. (b) Potential profiles of LOB with SCM based or pure Super P electrodes at 75 mA g-1

Although perovskite oxide can improve the performance of lithium oxygen battery, the battery performance degrades quickly and the cycle performance is at a low level (～ 100 times). Therefore, the research on these materials needs to be more in-depth and comprehensive.

4 Composite materials

The improvement of cathode catalyst can improve the properties of lithium oxygen batteries. Studies in recent years showed that catalysts with good properties usually need to meet the following two requirements, one of which is that catalysts have large specific surface area and more and large pores to store more discharge products (Li$_2$O$_2$) to achieve better properties. The other one is that the catalyst promotes both the ORR and OER processes to improve the energy efficiency of the battery. At present, there are few pure materials that can meet these two requirements, so scientists have come up with composite materials.

Functional carbon materials have more and large pores to store discharge product (Li_2O_2), and provide carriers for metal and metal oxides. Carbon materials have excellent catalytic activity for ORR process, but poor catalytic effect for OER process. The development of carbon-based nanocomposites solves this problem. Therefore, the composite materials of functional carbon materials with metal and metal oxides are ideal materials for cathode catalysts of lithium oxygen batteries.

Sun *et al* [66]. synthesized a mesoporous carbon nano-cubes (MCCs) by hard template method. At a current density of 200 mA g-1, the lithium oxygen battery with MCCs as the cathode catalyst showed the discharge capacity was 26100 mA h g-1 and the charge capacity was 16,090 mA h g-1, far higher than that of carbon black (CB) electrode (discharge capacity was 620 mA h g-1 and charge capacity was 3933 mA h g-1). Ru@MCCs was synthesized by wet impregnation method. And the TEM images of MCCs and Ru@MCCs (figure 7a and b) showed that the pore structures of them were similar, indicating that the introduction of Ru did not affect the pores of MCCs. It can be seen from the figure 7c that the charging voltage platform of Ru@MCCs is much lower than MCCs, so the overpotential of Ru@MCCs is much lower than MCCs, only 0.28 V. At a current density of 400 mA g-1 and a limited specific capacity of 1000 mA h g-1, the battery could cycle stably for 120 times. Such excellent performance can be attributed to the unique architecture of MCCs combined with the highly efficient Ru nanocrystal catalysts.

Guo *et al* [67]. prepared N-doped graphene with encapsulated RuO_2 nanoparticles. They compared the electrochemical properties of N-doped graphene, N-doped graphene with unencapsulated RuO_2 nanoparticles and N-doped graphene encapsulated RuO_2 nanoparticles. As exhibited in the figure 7d, it is obvious that the introduction of RuO_2 can reduce the overpotential between charge and discharge progresses. At a current density of 400 mA g-1 and a limited specific capacity of 2000 mA h g-1, the battery could cycle stably for 110 times. The author attributed the excellent performance of the battery to the high catalytic activity of RuO_2 nanoparticles, which reduced the overpotential of Li_2O_2 decomposition. In addition, RuO_2 nanoparticles were encapsulated in graphene, so the batteries showed excellent cycling performance.

In addition to carbon matrix composites, the composite of metals or metal oxides can also make up for defects, so as to obtain better electrochemical performance. Lian *et al* [68]. improved the electrochemical performance of lithium oxygen batteries by loading transition metal atoms on Co_3O_4 nanosheets (MSA-Co_3O_4/CC, M = Ti, V, Cr, Mn, Fe, Ni, Cu, Zn). Through comparison charge/discharge curves, it is found that the introduction of Ni reduces the over potential of the battery most significantly. When the current density is 300 mA g-1 and the limited capacity is 1500 mA h g-1, the overpotential of NiSA-Co_3O_4/CC is only 1.06 V. When the current density is 200 mA g-1 and the limited capacity is 1000 mA h g-1, the over potential is only 0.72 V, and it can circulate stably for 128 cycles. Li *et al* [69]. prepared three-dimensional open Co_3O_4@MnO_2 catalyst. Co_3O_4 has excellent OER catalysis, while MnO_2 is an efficient ORR catalyst. The combination of the two reflects the synergistic effect. Moreover, the three-dimensional open structure also facilitates the generation and decomposition of Li_2O_2. As a catalyst, the LOB shows ultra-high capacity (12980 mA h g-1) and good recyclability (331 cycles can be stably circulated when the capacity is limited to 500 mA h g-1).

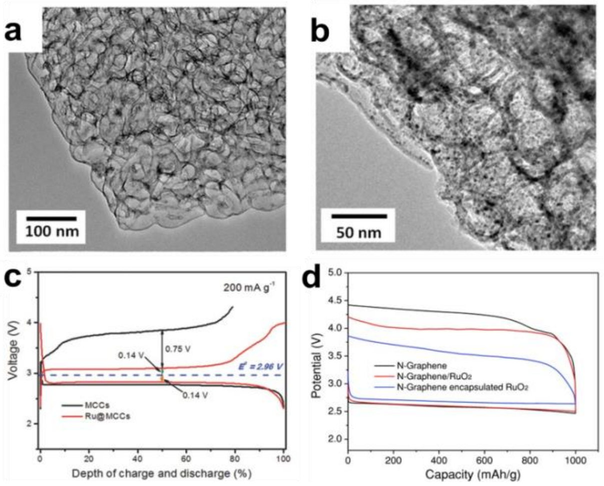

Figure 7 (a, b) High-magnification TEM images of MCCs and Ru@MCCs, and (c) charge/discharge profiles tested of Ru@MCC and MCC at 200 mA g-1. (d) The comparisons of charge/discharge profiles of LOB based on three different cathodes at the same current density and limited capacity

In addition, composite materials of organic compounds and carbon materials have been applied to lithium oxygen batteries, and their electrochemical performance has also been improved. Lin *et al.* [70] studied composite materials, which were composed by nitrogen-containing organic compounds with Ketjin black. The charge and discharge capacity increased significantly. The nitrogen element in the organic compound improves the solvent pathway of Li_2O_2 growth, so that the discharge product exists in an incompact nanosheet shape, which is benefit for decomposition during charging. The organic composite material can also alleviate the sensitivity to the electrolyte. Cui *et al.*[71] reported the influence of different polyaniline contents in three-dimensional porous polyaniline (PANI)/reduced graphene oxide foam (PPGFs) on lithium oxygen batteries. PPGFs-50 shows excellent electrochemical performance, with a high discharge capacity of 36010 mA h g-1 at 200 mA g-1, which can be comparable to noble metal catalysts. Too much polyaniline leads to pore clogging and reduces pore size, while a small amount of polyaniline leads to the reduction of catalytic activity. PPGFs-50 not only has sufficient catalytic activity to promote the generation and decomposition of discharge products, but also can provide sufficient transport channels for lithium ions and oxygen.

Composite materials are the main research direction of lithium oxygen battery. The prepared composites not only need to have sufficient catalytic activity to promote the generation and decomposition of discharge products, but also need to have transport channels for the rapid transport of lithium ions and oxygen. Metal carbon matrix composites have both the characteristics of porous carbon materials and the advantages of high catalytic activity of metals. At present, there are many researches. Nonmetallic composites, such as organic carbon matrix composites, have excellent properties, and the designability of organic structures makes them have great potential.

5 Other materials

In addition to the three kinds of materials mentioned above, there are other types of materials used in lithium oxygen batteries. Such as sulfides, nitrides and so on. Li *et al.* [72] reported the performance of TiN nanoparticles supported on VC as cathode catalysts for lithium oxygen batteries. By comparing the performance of nano TiN/VC (n-TiN/VC), micrometer TiN/VC (m-TiN/VC) and bare VC, it is found that n-TiN /VC overpotential was lower than the other two materials. At a current density of 500 mA g-1, the discharge capacity of N-Tin /VC reaches 6407 mA h g-1, which is much higher than n-TiN /VC and VC. The improvement of battery performance was mainly due to the excellent catalytic activity of TiN nanoparticles and the internal contact between TiN and VC.

Cao *et al.* [73] introduced nitrogen-doped MoS2 (N-MoS2) which was nanoflower-like and porous by hydrothermal method and ammonia-atmosphere calcination process. As cathode catalyst for lithium oxygen battery, N-MOS2 has good performance, such as excellent cycle stability and rate performance. For example, N-MOS2 has a higher specific capacity than MoS2, and the gap between charge and discharge potentials of N-MOS2 is smaller than MoS2 under a same current density. This was due to the rich porous structure of N-MOS2, which provides more catalytic active centers for catalytic reaction. And N doping increased the electrochemical activity. And at a current density of 200 mA g-1 and a limited specific capacity of 1000 mA h g-1, the battery could cycle stably for 100 times. The rate test shows With the increase of current density, the polarization of N-MOS_2 changes little. When the current density returns to 100, the charge discharge voltage of MoS2 also returns to the same as the initial one. As the current density of N-MOS_2 increases, the polarization increases. Even if the current density recovers, the charge discharge voltage does not recover. Sun *et al.* [74] embedded VOx in carbon paper, and then nitrogenize it at 850oC to obtain NV@C-850. The performance of the catalyst doped with nitrogen element is obviously improved at 100 mA g-1 current density, it can have an ultra-high capacity of 8269 mA h g-1, which is attributed to the internal channel of the catalyst, which is conducive to the transportation of Li_2O_2. The synergistic effect between NV and N-doped carbon reduces the overpotential between charge and discharge process (only 0.88 V) and improves the cycle stability (183 cycles at a cut-off capacity of 1000 mA h g-1).

6 Summary

Lithium oxygen battery is a promising form of energy storage. But some problems of LOB make it cannot be used commercially. For example, there are some side reactions in the charge and discharge process, which irreversibly produce other lithium compounds, greatly reducing the charge and discharge capacity of LOB. The cycle life of LOB is very short, and at least 1000 stable cycles are possible to be commercialized. The current research has not met such requirements. In this review, the effects of several types of cathode catalysts on the electrochemical performance of LOB were reviewed, including the formation mechanism and morphology of Li_2O_2. The growth morphology of the discharge product Li_2O_2 will directly affect the electrochemical performance of LOB. LOB with film-like Li_2O_2 has a lower charging potential and a smaller discharge capacity. Whereas LOB with toroidal-like Li_2O_2 shows the discharge capacity increases and the charging overpotential increases. In order to obtain the best electrochemical performance (high capacity and low potential), it can be adjusted by reducing the size of Li_2O_2 particles and increasing the thickness of Li_2O_2 film. There are many methods to adjust the morphology of Li_2O_2. Firstly, the reasonable design of catalyst structure. Porous and large specific surface area cathode materials can improve the structure of Li_2O_2. Secondly, it is favorable to form thin-film Li_2O_2 under high current density. Finally, the selection of electrolyte is also a method to adjust the morphology of discharge products.

In conclusion, the LOB with large capacity, low overpotential and long cycle stability needs to consider the following two factors: 1) forming Li_2O_2 film with increased thickness and 2) forming discharge products particles with decreased size. The following suggestions can be considered to meet the above requirements.

(1) Cathode design. Porous, high specific surface area and high conductivity cathode materials are conducive to the formation of Li_2O_2.

(2) Catalyst selection. Catalysts with advantages like oxygen vacancies and surface coatings can contain more discharge products. The catalyst has the ability to catalyze the formation and decomposition of Li_2O_2, which is helpful to improve the capacity and cycle life of the battery.

(3) Selection of electrolyte. Proper electrolyte is helpful to alleviate the solubility problem. Moreover, solid electrolyte can inhibit the growth of lithium negative dendrite and improve the safety performance of the battery. It is a potential research direction. In addition, electrolyte additive is also a new method to adjust battery life.

The research of LOB is very promising, but more experiments are still needed to study and overcome the shortcomings like the poor cycle performance. The future research and application of lob is very promising.

Acknowledgements

We thank the financial support from the National Natural Science Foundation of China (52172173, 51872071), Anhui Provincial Natural Science Foundation for Distinguished Young Scholar (2108085J25), Anhui Provincial Natural Science Foundation for Outstanding Young Scholar (2208085Y05), Anhui Province Key Laboratory of Environment-Friendly Polymer Materials, the Natural Science Research Projects of Universities in Anhui Province (KJ2020A0021), Guangxi Key Laboratory of Low Carbon Energy Materials (2021GXKLLCEM04).

Author contribution

Chaofeng Zhang and Longhai Zhang putted forward the review topics and gave suggestions. Xuyang Xiong conducted the literature review and classification. Sijiang Hu and Tengfei Zhou designed and drew the figures. Wei Wang and Simin Wang communicated, wrote, and corrected the manuscript.

Conflict of interest

The authors declare no conflict of interest.

References

[1] Wu, F Yu, Y., Toward True Lithium-Air Batteries, Joule 2018(2): 815-817.

[2] Li, J Ding, S Zhang, S et al., Catalytic redox mediators for non-aqueous Li-O2 battery, Energy Storage Mater. 2021(43): 97-119.

[3] Ma, Z.; Yuan, X.; Li, L., et al., A review of cathode materials and structures for rechargeable lithium–air batteries, Energy Environ. Sci. 2015(8): 2144-2198.

[4] Shen, S.; Wu, A.; Xia, G., et al., Facile preparation of unique three-dimensional (3D) α-MnO_2/MWCNTs macroporous hybrid as the high-performance cathode of rechargeable Li-O2 batteries, Nano Res. 2019(12): 69-75.

[5] Jung, J.-W.; Cho, S.-H.; Nam, J. S., et al., Current and future cathode materials for non-aqueous Li-air (O_2) battery technology – A focused review, Energy Storage Mater. 2020(24): 512-528.

[6] Zhang, X.; Mu, X.; Yang, S., et al., Research Progress for the Development of Li-Air Batteries: Addressing Parasitic Reactions Arising from Air Composition, Energy & Environmental Materials. 2018(1): 61-74.

[7] Sun, T.; Li, Z. J.; Zhi, Y. F., et al., Poly(2,5‐Dihydroxy‐1,4‐Benzoquinonyl Sulfide) As an Efficient Cathode for High‐Performance Aqueous Zinc–Organic Batteries, Adv. Funct. Mater. 2021(31): 1.

[8] Wang, X.-T.; Yang, Y.; Guo, J.-Z., et al., An advanced cathode composite for co-utilization of cations and anions in lithium batteries, Journal of Materials Science & Technology 2022(102): 72-79.

[9] Liu, K.; Liu, Y. Y.; Lin, D. C., et al., Materials for lithium-ion battery safety, Sci. Adv. 2018(4): eaas9820.

[10] Gu, Z.-Y.; Guo, J.-Z.; Sun, Z.-H., et al., Air/water/temperature-stable cathode for all-climate sodium-ion batteries, Cell Reports Physical Science. 2021(2): 2-3.

[11] Wu, K.; Ning, F.; Yi, J., et al., Host-guest supramolecular interaction behavior at the interface between anode and electrolyte for long life Zn anode, J. Energy Chem. 2022(69): 237-243.

[12] Cui, J.; Liu, X.; Xie, Y., et al., Improved electrochemical reversibility of Zn plating/stripping: a promising approach to suppress water-induced issues through the formation of H-bonding, Materials Today Energy. 2020(18): 5.

[13] Wu, K.; Yi, J.; Liu, X., et al., Regulating Zn Deposition via an Artificial Solid-Electrolyte Interface with Aligned Dipoles for Long Life Zn Anode, Nanomicro Lett. 2021(13): 79.

[14] Liu, X.; Fang, Y.; Liang, P., et al., Surface-tuned two-dimension MXene scaffold for highly reversible zinc metal anode, Chin. Chem. Lett. 2021(32): 2899-2903.

[15] Li, Q.; Han, L.; Luo, Q., et al., Towards Understanding the Corrosion Behavior of Zinc‐Metal Anode in Aqueous Systems: From Fundamentals to Strategies, Batteries & Supercaps. 2022(5): 3-5.

[16] Chen, K.; Yang, D. Y.; Huang, G., et al., Lithium-Air Batteries: Air-Electrochemistry and Anode Stabilization, Acc Chem Res. 2021(54): 632-641.

[17] Zhan, Y.; Luo, S.-h.; Feng, J., et al., Improved electrocatalytic activity of hexagonal prisms Fe3O4 derived from metal-organic framework by covering dendritic-shaped carbon layer in Li–O_2 battery, Composites Part B: Engineering. 2021(226): 128-134.

[18] Chen, K.; Huang, G.; Ma, J. L., et al., The Stabilization Effect of CO2 in Lithium-Oxygen/CO2 Batteries, Angew. Chem. Int. Ed. Engl. 2020(59): 16661-16667.

[19] Liu, Z.; Zhao, Z.; Zhang, W., et al., Toward high‐performance lithium‐oxygen batteries with cobalt‐based transition metal oxide catalysts: Advanced strategies and mechanical insights, InfoMat. 2021(4): 2.

[20] Guo, X.; Xiao, L.; Yan, P., et al., Synergistic tuning of electrochemical surface area and surface Co^{3+} by oxygen plasma enhances the capacities of Co3O4 lithium–oxygen battery cathodes, Chin. Chem. Lett. 2021(32): 3491-3495.

[21] Hou, C.; Han, J.; Liu, P., et al., Synergetic Effect of Liquid and Solid Catalysts on the Energy Efficiency of Li-O_2 Batteries: Cell Performances and Operando STEM Observations, Nano Lett. 2020(20): 2183-2190.

[22] Liu, Y.; He, P.; Zhou, H., Rechargeable Solid-State Li-Air and Li-S Batteries: Materials, Construction, and Challenges, Adv.

Energy Mater. 2018(8): 6-8.

[23] Liu, L.; Liu, Y.; Wang, C., et al., Li_2 O_2 Formation Electrochemistry and Its Influence on Oxygen Reduction/Evolution Reaction Kinetics in Aprotic Li-O_2 Batteries, Small Methods. 2022(6): e2101280.

[24] Liu, B.; Sun, Y.; Liu, L., et al., Advances in Manganese-Based Oxides Cathodic Electrocatalysts for Li-Air Batteries, Adv. Funct. Mater. 2018(28): 56-58.

[25] Hegde, G. S.; Ghosh, A.; Badam, R., et al., Role of Defects in Low-Cost Perovskite Catalysts toward ORR and OER in Lithium – Oxygen Batteries, ACS Applied Energy Materials. 2020(3): 1338-1348.

[26] Zhao, Y.; Chen, W.; Wu, J., et al., Recent advances in charge mechanism of noble metal-based cathodes for Li-O_2 batteries, Chin. Chem. Lett. 2022.

[27] Chen, Y.; Gao, X.; Johnson, L. R., et al., Kinetics of lithium peroxide oxidation by redox mediators and consequences for the lithium-oxygen cell, Nat. Commun. 2018(9): 767.

[28] Sun, G.; Zhao, Q.; Wu, T., et al., 3D Foam-Like Composites of Mo2C Nanorods Coated by N-Doped Carbon: A Novel Self-Standing and Binder-Free O_2 Electrode for Li-O_2 Batteries, ACS Appl Mater Interfaces. 2018(10): 6327-6335.

[29] Ju, B.; Song, H. J.; Lee, G.-H., et al., Nickel disulfide nanosheet as promising cathode electrocatalyst for long-life lithium – oxygen batteries, Energy Storage Mater. 2020(24): 594-601.

[30] Lim, H. D.; Lee, B.; Bae, Y., et al., Reaction chemistry in rechargeable Li-O_2 batteries, Chem. Soc. Rev. 2017(46): 2873-2888.

[31] Shu, C.; Wang, J.; Long, J., et al., Understanding the Reaction Chemistry during Charging in Aprotic Lithium-Oxygen Batteries: Existing Problems and Solutions, Adv Mater. 2019(31): e1804587.

[32] Li, F.; Chen, J., Mechanistic Evolution of Aprotic Lithium-Oxygen Batteries, Adv. Energy Mater. 2017(7):4-7.

[33] Song, L. N.; Zhang, W.; Wang, Y., et al., Tuning lithium-peroxide formation and decomposition routes with single-atom catalysts for lithium-oxygen batteries, Nat. Commun. 2020(11): 2191.

[34] Hou, Y.; Wang, J.; Hou, C., et al., Oxygen vacancies promoting the electrocatalytic performance of CeO_2 nanorods as cathode materials for Li – O_2 batteries, J. Mater. Chem. 2019(7): 6552-6561.

[35] Liang, R.; Shu, C.; Hu, A., et al., Interface engineering induced selenide lattice distortion boosting catalytic activity of heterogeneous CoSe2@NiSe2 for lithium-oxygen battery, Chem. Eng. J. 2020(393):1.

[36] Hou, Y.; Wang, J.; Liu, J., et al., Interfacial Super-Assembled Porous CeO_2/C Frameworks Featuring Efficient and Sensitive Decomposing Li2O2 for Smart Li-O-2 Batteries, Adv. Energy Mater. 2019(9):5.

[37] Jung, I.-S.; Kwon, H. J.; Kim, M., et al., Rapid oxygen diffusive lithium – oxygen batteries using a restacking-inhibited, free-standing graphene cathode film, J. Mater. Chem. 2029(7): 10397-10404.

[38] Li, M.; Xiao, L.; Wang, D., et al., Surface carboxyl groups enhance the capacities of carbonaceous oxygen electrodes for aprotic lithium–oxygen batteries: A direct observation on binder-free electrodes, Chin. Chem. Lett. 2019(30): 2328-2332.

[39] Xu, J.; Xu, F.; Qian, M., et al., Conductive Carbon Nitride for Excellent Energy Storage, Adv Mater. 2017(29): 87-99.

[40] Yao, L.; Lin, J.; Li, S., et al., Metal-organic frameworks-derived hollow dodecahedral carbon combined with FeNx moieties and ruthenium nanoparticles as cathode electrocatalyst for lithium oxygen batteries, J. Colloid Interface Sci. 2021(596): 1-11.

[41] Du, D.; Zheng, R.; He, M., et al., A-site cationic defects induced electronic structure regulation of $LaMnO_3$ perovskite boosts oxygen electrode reactions in aprotic lithium – oxygen batteries, Energy Storage Mater. 2021(43): 293-304.

[42] Shen, J.; Wu, H.; Sun, W., et al., In-situ nitrogen-doped hierarchical porous hollow carbon spheres anchored with iridium nanoparticles as efficient cathode catalysts for reversible lithium-oxygen batteries, Chem. Eng. J. 2019(358): 340-350.

[43] Zhang, Y.; Ma, J.; Yuan, M. W., et al., The design of hollow PdO-Co_3O_4 nano-dodecahedrons with moderate catalytic activity for Li-O_2 batteries, Chem. Commun. (Camb.). 2019(55): 12683-12686.

[44] Zheng, M.; Jiang, J.; Lin, Z., et al., Stable Voltage Cutoff Cycle Cathode with Tunable and Ordered Porous Structure for Li-O_2 Batteries, 2018(14): e1803607.

[45] Zhao, Z.; Liu, Y.; Wan, F., et al., Free-standing nitrogen doped graphene/$Co(OH)_2$ composite films with superior catalytic activity for aprotic lithium-oxygen batteries, Chin. Chem. Lett. 2021(32): 594-597.

[46] Wang, F.; Qiao, J.; Wang, J., et al., Multimetallic Core – Bishell Ni@Au@Pd nanoparticles with reduced graphene oxide as an efficient bifunctional electrocatalyst for oxygen reduction/evolution reactions, J. Alloys Compd. 2019(811): 3.

[47] Wen, C.; Zhu, T.; Li, X., et al., Nanostructured Ni/Ti_3C_2T MXene hybrid as cathode for lithium-oxygen battery, Chin. Chem. Lett. 2020(31): 1000-1003.

[48] Liu, X.; Huang, Q.; Wang, J., et al., In-situ deposition of Pd/Pd4S heterostructure on hollow carbon spheres as efficient electrocatalysts for rechargeable Li-O_2 batteries, Chin. Chem. Lett. 2021(32): 2086-2090.

[49] Ding, N.; Chien, S. W.; Hor, T. S. A., et al., Influence of carbon pore size on the discharge capacity of Li – O_2batteries, J. Mater. Chem. 2014(A 2): 12433-12441.

[50] Shui, J.; Du, F.; Xue, C., et al., Vertically Aligned N-Doped Coral-like Carbon Fiber Arrays as Efficient Air Electrodes for High-Performance Nonaqueous Li-O-2 Batteries, ACS Nano 2014(8): 3015-3022.

[51] Zhang, J.; Chen, X.; Lei, Y., et al., Highly rechargeable lithium oxygen batteries cathode based on boron and nitrogen co-doped holey graphene, Chem. Eng. J. 2022(428):7.

[52] Yi, L. C.; Ci, S. Q.; Sun, C. L., et al., Cathode Materials of Non-Aqueous Lithium-Oxygen Battery, Progress in Chemistry. 2016(28): 1251-1264.

[53] Bui, H. T.; Kim, D. Y.; Kim, D. W., et al., Carbon nanofiber@platinum by a coaxial electrospinning and their

improved electrochemical performance as a Li–O_2 battery cathode, Carbon. 2018(130): 94-104.

[54] Jeong, Y. S.; Park, J.-B.; Jung, H.-G., et al., Study on the Catalytic Activity of Noble Metal Nanoparticles on Reduced Graphene Oxide for Oxygen Evolution Reactions in Lithium-Air Batteries, Nano Lett. 2015(15): 4261-4268.

[55] Lu, Y.-C.; Xu, Z.; Gasteiger, H. A., et al., Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium-Air Batteries, J. Am. Chem. Soc. 2010(132): 12170-12171.

[56] Choi, R.; Jung, J.; Kim, G., et al., Ultra-low overpotential and high rate capability in Li – O2 batteries through surface atom arrangement of PdCu nanocatalysts, Energy Environ. Sci. 2014(7): 1362-1368.

[57] Jung, H.-G.; Jeong, Y. S.; Park, J.-B., et al., Ruthenium-Based Electrocatalysts Supported on Reduced Graphene Oxide for Lithium-Air Batteries, ACS Nano. 2013(7): 3532-3539.

[58] Wang, P.; Ren, Y.; Wang, R., et al., Atomically dispersed cobalt catalyst anchored on nitrogen-doped carbon nanosheets for lithium-oxygen batteries, Nat. Commun. 11(2020): 1576.

[59] Gao, R.; Li, Z.; Zhang, X., et al., Carbon-Dotted Defective CoO with Oxygen Vacancies: A Synergetic Design of Bifunctional Cathode Catalyst for Li – O_2 Batteries, ACS Catalysis 6(2015): 400-406.

[60] Lin, Y.; Yang, Q.; Geng, F., et al., Suppressing Singlet Oxygen Formation during the Charge Process of Li-O_2 Batteries with a Co3O4 Solid Catalyst Revealed by Operando Electron Paramagnetic Resonance, J. Phys. Chem. Lett. 2021(12): 10346-10352.

[61] Zhang, P.; Sun, D.; He, M., et al., Synthesis of Porous delta-MnO2 Submicron Tubes as Highly Efficient Electrocatalyst for Rechargeable Li-O_2 Batteries, ChemSusChem. 2015(8): 1972-1979.

[62] Minowa, H.; Hayashi, M.; Hayashi, K., et al., Mn – Fe-based oxide electrocatalysts for air electrodes of lithium – air batteries, J. Power Sources. 2013(244): 17-22.

[63] Li, P.; Zhang, J.; Yu, Q., et al., One-dimensional porous La0.5Sr0.5CoO2.91 nanotubes as a highly efficient electrocatalyst for rechargeable lithium-oxygen batteries, Electrochim. Acta. 2015(165): 78-84.

[64] Ma, Z.; Yuan, X.; Li, L., et al., The double perovskite oxide Sr2CrMoO(6-delta) as an efficient electrocatalyst for rechargeable lithium air batteries, Chem. Commun. (Camb.) 2014(50): 14855-14858.

[65] Zhu, X.; Pan, X.; Wu, Y., et al., Layered perovskite oxide PrBaCo2O5+δ as a potential cathode for lithium–oxygen batteries: High-performance bi-functional electrocatalysts, Mater. Lett. 2019(237): 200-203.

[66] Sun, B.; Chen, S.; Liu, H., et al., Mesoporous Carbon Nanocube Architecture for High-Performance Lithium-Oxygen Batteries, Adv. Funct. Mater. 2015(25): 4436-4444.

[67] Guo, X.; Liu, P.; Han, J., et al., 3D Nanoporous Nitrogen-Doped Graphene with Encapsulated RuO2 Nanoparticles for Li-O_2 Batteries, Adv Mater. 2015(27): 6137-6143.

[68] Lian, Z.; Lu, Y.; Ma, S., et al., Metal atom-doped Co3O4 nanosheets for Li-O_2 battery catalyst: Study on the difference of catalytic activity, Chem. Eng. J. 2022(445):98-109.

[69] Li, J.; Zhou, H.; Jian, Z., et al., Improved Electrocatalytic Activity of Three-Dimensional Open-Structured Co3O_4@MnO_2 Bifunctional Catalysts of Li-O2 Batteries by Inducing the Oriented Growth of Li2O_2, ACS Sustainable Chemistry & Engineering. 2021(9): 5334-5344.

[70] Lin, H.; Liu, Z.; Mao, Y., et al., Effect of nitrogen-doped carbon/Ketjenblack composite on the morphology of Li2O2 for high-energy-density Li – air batteries, Carbon. 2016(96): 965-971.

[71] Cui, R.; Xiao, Y.; Li, C., et al., Polyaniline/reduced graphene oxide foams as metal-free cathodes for stable lithium-oxygen batteries, Nanotechnology. 2020(31): 445402.

[72] Li, F.; Ohnishi, R.; Yamada, Y., et al., Carbon supported TiN nanoparticles: an efficient bifunctional catalyst for non-aqueous Li-O_2 batteries, Chem. Commun. (Camb.) 2013(49): 1175-1177.

[73] Cao, X.; Chen, Z.; Wang, N., et al., Defected molybdenum disulfide catalyst engineered by nitrogen doping for advanced lithium – oxygen battery, Electrochim. Acta 2021(383): 2.

[74] Sun, K.; Liu, M.; Yu, S., et al., In-situ grown vanadium nitride coated with thin layer of nitrogen-doped carbon as a highly durable binder-free cathode for Li – O_2 batteries, J. Power Sources. 2020(460):6.