Recent Advances on Ruthenium-Based Electrocatalysts for Lithium-Oxygen Batteries

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Abstract: Rechargeable lithium-oxygen (Li-O₂) batteries have attracted wide attention due to their high energy density. However, the sluggish cathode kinetics results in high overvoltages and poor cycling performance. Ruthenium (Ru)-based electrocatalysts have been demonstrated to be promising cathode catalysts to promote oxygen evolution reaction (OER). It facilitates lithium peroxide (Li₂O₂) decomposition by adjusting Li₂O₂ morphologies, which is due to the strong interaction between Ru-based catalyst and superoxide anion (O₂⁻) intermediate. In this review, the design strategies of Ru-based electrocatalysts are introduced to enhance their OER catalytic kinetics in Li-O₂ batteries. Different configurations of Ru-based catalysts, including metal particles (Ru metal and alloys), single-atom catalysts, and Ru-loaded compounds with various substrates (carbon materials, metal oxides/sulfides), have been summarized to regulate the electronic structure and the matrix architecture of the Ru-based electrocatalysts. The Ru-based catalyst structure-property relationship is discussed for a better understanding of the Li₂O₂ decomposition mechanism at the cathode interface. Finally, the challenges of Ru-based electrocatalysts are proposed for the future development of Li-O₂ batteries.

1. Introduction

Rechargeable lithium-oxygen (Li-O₂) batteries have an ultrahigh theoretical energy density of 3500 Wh·kg⁻¹, which is based on the reduction of O₂ and formation/decomposition of Li₂O₂[1-3]. During the discharge, Li₂O₂ can be generated via solution-mediated model or surface-adsorption model. Toroid-shaped Li₂O₂ will be formed via disproportionation or a second one-electron electrochemical reduction of soluble LiO₂ intermediate in the solution-mediated model. Film-like Li₂O₂ will be formed via a surface-adsorption model due to the strong affinity between LiO₂ and cathode materials. During the charge, Li₂O₂ decomposes to produce O₂. However, the heterogeneity of three-phase interfaces hinders the mass and electronic transportation, resulting in the sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics. The discharge product of Li₂O₂ is characterized by a low electronic conductivity and this leads to increased interfacial impedance. The incomplete Li₂O₂ decomposition gradually blocks the cathode surface and induces capacity decay[4-6]. Moreover, the insulated Li₂O₂ causes high charging overvoltages and low round-trip efficiency, which promotes the formation of reactive oxygen species such as singlet oxygen (¹O₂). The generated reactive species can easily attack the electrolytes and electrode materials, leading to by-product accumulation on the cathode surface. The catalytic activity of cathode materials is therefore suppressed due to the blocked reaction sites[5,6]. It is essential to design novel catalysts with superior OER kinetics to decrease the charging overpotential for stable Li-O₂ batteries.

Various materials have been employed as cathode catalysts to reduce discharge/charge overpotentials in Li-O₂ batteries, such as: carbon materials, noble metals and transition metal oxides[7-9]. Carbon materials have gained much attention due to their high surface area and low production cost. However, they are prone to react with electrolyte, and generate byproduct like lithium carbonate (Li₂CO₃). The side reactions quickly lead to capacity degradation and a low round-trip efficiency[10-12]. Ru-based materials are considered as a more efficient catalyst owing to their strong interaction with oxygen species intermediate[13-19]. This leads to adjustment of reaction routes and enhance the OER kinetics, decreasing the charge overpotential to less than 0.5 V. The intensive adsorption between superoxide anion (O₂⁻) and Ru active sites can significantly affect the Li₂O₂ growth and change its morphologies (toroid/film). Different Li₂O₂ morphologies are endowed with varied electronic transport and interfacial impedance, which finally leads to different charge overvoltages. The adsorption energy and charge transfer barrier are closely related to mass diffusion and electrophilicity of the catalytic sites[16-20]. Therefore, the matrix architecture is usually designed to increase the catalyst surface area for enhanced electron and reactant diffusion, while electronic structure is tuned to increase the interaction between catalyst and intermediates[22-24]. Unfortunately, the excessive catalytic effect of Ru-based materials may decompose organic electrolyte and high production cost of novel metal limits its practical application. It is essential to construct suitable structures to regulate Ru catalytic property and increase the utilization efficiency of Ru sites.

Although the Ru-based catalysts exhibit great potential to enhance the OER kinetics, the Li-O₂ battery still has poor cycling stability and Ru catalytic efficiency should be further improved. Understanding reaction mechanism of Li₂O₂ decomposition on the cathode is necessary to fully taking advantage of Ru-based catalysts for reducing the charging overpotential. This review has summarized various configurations of Ru-based catalysts, including metal particles, single atom catalyst, and Ru-based compounds with different substrates, in boosting OER kinetics of Li₂O₂ battery. Regulation of intermediate adsorption and catalyst electronic structure is introduced to control the Li₂O₂ morphology and decrease the interfacial impedance. Some perspectives are presented for the further development of reliable Ru-based catalysts to realize long-term stable Li-O₂ battery.

2. Design and modulation of Ru-based electrocatalysts

2.1 Ru metal and alloys

Precious metals and their alloys exhibit excellent oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) performances, and therefore they have been widely utilized as
cathode catalysts in the preliminary research of Li-O2 batteries[13]. Su et al. designed hierarchical Ru nanospheres as cathode catalysts for Li-O2 batteries by a simple hydrothermal method[26]. The hierarchical Ru nanospheres with large surface area increase catalytic active sites, promoting the reversible generation and decomposition of the leaf-like Li2O2. The Li2O2 batteries based on the hierarchical Ru nanospheres cathode display a low overpotential (0.3 V) at 200 mA·g−1. However, precious metal damages the reversibility of the battery. Peng and his collaborators loaded Ru metal onto carbon nanotubes as the cathode catalyst for Li-O2 batteries[26]. As illustrated in the transmission electron microscopy (TEM) image in Fig. 1a, carbon nanotubes are fully covered by Ru nanoparticles. This endows the Li2O2 battery with a low charge overpotential of 0.53 V and a long lifespan of 100 cycles (Fig. 1b). They then further investigate the reversibility of Li2O2 batteries with differential electrochemical mass spectrometry (DEMS). They find the charge to O2 ratio (e/O2) equals 2.08 during discharge, which is very close to theoretical 2e/O2 (Fig. 1c). However, the e/O2 value increases to 3.14 during charge, with a massive amount of CO2 generated (Fig. 1d). This phenomenon suggests strong catalytic activity and poor selectivity of Ru catalyst can result in the decomposition of electrolyte during charge, posing a threat to the stability of Li2O2 battery. An available strategy is to design suitable Ru-based compounds catalysts to boost ORR/OER performance for Li2O2 batteries.

2.2 Carbon materials

Carbon materials with high conductivity, low cost and light weight have been extensively used as cathode catalysts for Li-O2 batteries[27-29]. However, the limited catalytic activity of carbon materials constrains the capacity of Li-O2 batteries. Ru-based compounds with superior catalytic activity are often combined with carbon materials to form hybrid catalysts. In this hybrid system, Ru-based compounds serve as active sites, carbon-containing materials act as conductive medium. The synergistic effect of the two components ultimately reduces overpotential and improves cycle stability. Sun et al. synthesized carbon black-supported Ru nanocrystalline (Ru-CB) to improve the performance of Li-O2 batteries. The Li2O2 batteries based on Ru-CB cathode boost the ORR and OER reaction kinetics and reduce discharge/charge overpotential (0.37 V)[30].

The irregular accumulation of Li2O2 on the cathode covers the active sites of Ru, thereby restricting its catalytic performance. Porous carbon materials with a large surface area offer ample space for the growth of Li2O2. This makes Ru active sites are fully utilized to promote the decomposition of Li2O2, enhancing the reversibility of Li2O2 batteries. The mesoporous carbon nanocubes after loading Ru nanocrystals were designed as cathode catalysts for Li2O2 batteries, yielding higher discharge capacity than commercial carbon black catalysts[31]. Song et al. prepared a “breathable” wood-based cathode by anchoring Ru nanoparticles on the open porous microchannels of carbonized and activated wood (CA-wood)[32]. Numerous aligned microchannels in the three-dimensional wood-based material facilitate the fast lithium ions transport, oxygen diffusion and full electrolyte infiltration. Besides, the uniformly dispersed Ru particles form numerous reactive sites to promote the formation and decomposition of Li2O2 (Fig. 2a). During discharge, Li2O2 is generated on the wall of the microchannels and covers the surface of Ru nanoparticles, as revealed in Fig. 2b and 2c. After charging, the formed Li2O2 completely decomposes (Fig. 2d and 2e), showing good reversibility in the discharge/charge process. Therefore, Li2O2 batteries based on “breathable” CA-wood/Ru-based cathode exhibits a high specific area capacity of 8.58 mA·h·cm−2 at a current density of 0.1 mA·cm−2.

Figure 1. (a) TEM images of Ru-CNT. (b) Multiple cycles from 1 to 100 of the catalyzed Li2O2 cells based on Ru-CNT. (c) DEMS results of O2 gas consumption during discharge of Li2O2 batteries based on Ru-CNT. (d) DEMS results of O2 and CO2 evolution during the charging process of Li2O2 batteries based on Ru-CNT. Reprinted with permission of Ref. [26], copyright 2015 American Chemical Society.

Figure 2. (a) Schematic diagram of the Li2O2 batteries with the CA-wood/Ru cathode. (b) Schematic diagrams showing Li2O2 growth during discharging. (c) SEM images showing the microchannels after first discharge. (d) Schematic diagrams showing Li2O2 vanishing during charging. (e) SEM images showing the microchannels after first charge. Reprinted with permission of Ref. [32], copyright 2018 Wiley-VCH. (f) SEM images of Ru3D-NrGO. (g) HAADF-STEM image of Ru nanoclusters anchored on 3D-NrGO. (h) The cycling performance depending on cycle number of cathodes at a cut-off capacity of 1000 mA·h·g−1 and a charge-discharge rate of 200 mA·g−1. Reprinted with permission of Ref. [33], copyright 2020 American Chemical Society.

Previous literatures have reported that the majority of hybrid catalysts exhibit high Ru mass loading of 20-40 wt%, leading to the aggregation of Ru clusters and incomplete catalytic activity. For example, Sun et al. prepared a reduced graphene cathode with 20.34 wt% Ru nanoparticles. Wang et al. applied Ru-functionalized (43 wt%) vertical graphene nanosheets supported on a Ni-foam cathode (VGNS@NiFM) as cathode catalysts for Li-O2 batteries. Besides, the FeCo-doped NRGO mounted with
Ru nanoparticles (20 wt% loading) was synthesized as cathode catalysts for Li-O₂ batteries. Liu et al. fixed highly dispersed Ru nanoparticles on the nitrogen-doped three-dimensional graphene (3D-NrGO), achieving a reduced Ru loading of 9.37 wt% (Fig. 2f and 2g)[33]. The 3D architecture of graphene and highly dispersed Ru greatly improve the performance of Li-O₂ batteries, resulting in large discharge capacity of 23992 mAh g⁻¹ at 100 mA g⁻¹ and long lifespan of 200 cycles (Fig. 2h).

Figure 3. (a) Deconvoluted X-ray photoelectron spectra for the N 1s spectra of RuN-rGO. (b) Schematic of the discharge mechanism for RuN-rGO. Reprinted with permission of Ref. [34], copyright 2021 American Chemical Society. (c) The SEM image of Ru-chimera-CMT. (d) Schematic of contact electronizations for Ru-chimera-CMT. DFT calculations and proposed mechanisms. The optimized structures of (e) LiO₂ adsorbed on (101) plane of Ru configuration in Ru-on-graphene model and f) LiO₂ adsorbed on the Ru configuration of Ru-chimera-graphene. Discharge mechanisms of (g) Ru-on-CMT and h) Ru-chimera CMT. Reprinted with permission of Ref. [35], copyright 2021 Wiley-VCH.

In addition to the physical effects of carbon materials, carbon materials can interact with Ru to modulate the local electronic structure of Ru, inducing the adsorption of LiO₂ intermediates. The suitable adsorption between Ru and LiO₂ intermediates ensures a feasible LiO₂ formation and decomposition route. Dai et al. adopted nitrogen-doped reduced GO anchored the well-dispersed Ru nanoparticles (RuN-rGO) as an efficient bifunctional catalyst for Li-O₂ batteries[34]. The N dopants within rGO boost stronger electron transfer from Ru to carbon materials (Fig. 3a). The electron-deficient Ru increases LiO₂ adsorption, leading to the generation of Li₂O₂ film during initial discharge, followed by the generation of Li₂O₂ particles after subsequent deep discharge. The change of Li₂O₂ morphology is ascribed to altered reaction interface. During charge Li₂O₂ is easily decomposed due to their good electrical contact with RuN-rGO. As a result, the Li₂O₂ batteries show the reversible formation and decomposition of Li₂O₂ (Fig. 3b). However, Ru anchored on the carbon materials surface as conventional support-metal interaction is very easy to cause limit contact area, restricting the catalytic effect of Ru. A novel chimeric structure material was proposed by Sun et al[36]. The Ru nanoparticles partially confined in the microtubular walls of carbon fabrics (Ru-chimera-CMT) expose partial surface, increasing the electron density of Ru nanoparticles and inducing the LiO₂ gradient adsorption (Fig. 3c and 3d). The DFT calculation describes the adsorption energy of LiO₂ on the cathode, as shown in Fig. 3e-3h. The adsorption energy (ΔE_ads) of LiO₂ is -0.82 eV when Ru nanoparticles are anchored on graphene (Fig. 3e). On the contrary, the ΔE_ads of LiO₂ is -2.41 eV at Ru/graphene interface when Ru nanoparticles are partially embedded into the graphene. Different from the Ru/graphene interface, the ΔE_ads of LiO₂ is only -0.33 eV on the Ru center of the material (Fig. 3f). The gradient adsorption from Ru/graphene interface to Ru center induce the formation of Li₂O₂ nanosheets and particles. Such LiO₂ morphology greatly utilizes the Ru active site upon charging, expediting Li₂O₂ decomposition (Fig. 3g and 3h). As a result, the Ru-chimera-CMT cathode can exhibit excellent cycling performance for Li-O₂ batteries.

2.3 Metal oxides

Although hybrid catalysts composed of Ru-based compounds and carbon materials improve the ORR/OER reaction kinetics and reversibility of the Li-O₂ batteries, the parasitic reactions between the electrolyte and the carbon material still need to be carefully considered[36]. The occurrence of side reactions in Li-O₂ batteries is primarily attributed to the higher charging voltage. Metal or metal oxides combined with Ru-based compounds as carbon-free cathode can reduce the charge voltage, inhibiting the side reactions caused by high voltage. A conductive indium tin oxide (ITO) electrode embedded with Ru nanoparticles (Ru/ITO) was first introduced as a carbon-free cathode in Li-O₂ batteries by Zhou's group[37]. The Ru/ITO electrodes effectively decrease the generation of by-product, improving the cycling stability of Li-O₂ batteries. However, the Ru/ITO electrodes have the relative low specific capacity owing to the large weight of ITO. Li et al. further prepared Sb-doped tin oxide (STO) supported Ru nanoparticles (Ru/STO) as a carbon-free cathode for Li-O₂ batteries[38]. Compared with ITO, the Ru/STO cathode exhibit a large specific capacity of 750 mAh g⁻¹ and low overpotentials.

Various metal oxides with excellent ORR activity, including: manganese-based oxides[39], CeO₂[40], spinel[41,42] and perovskite oxides[43], can induce the formation of discharge products with different morphologies, and Ru-based compounds are more conducive to the decomposition of discharge products with different morphologies. Therefore, metal oxides with ORR activity can combine with Ru-based compounds as bifunctional catalysts to further enhance the ORR/OER activity of Li-O₂ batteries. Manganese-based oxides have been extensively studied as excellent ORR catalysts in Li-O₂ batteries. Yoon et al. fabricated RuO₂/Mn₂O₃ fiber-in-tube (RM-FIT) and RuO₂/MnO₂ tube-in-tube (RM-TIT) as bifunctional catalysts for Li-O₂ batteries, and manipulated the structures of catalysts to change the growth location of discharge products[43]. RM-FIT is composed of MnO₂ as the outer tube and most RuO₂ as the inner core. During discharge, Li₂O₂ are mainly generated on the surface of the outer tubes due to the high ORR activity of MnO₂. During charge, the relatively low OER catalytic activity of MnO₂ lead to the incomplete decomposition of Li₂O₂, which causes the reduction of round-trip efficiency and performance (Fig. 4a and 4b). On the contrary, RuO₂/MnO₂ tube-in-tube (RM-TIT) consists of distributed MnO₂ and RuO₂ nanocomposites in the double-walled fibers, resulting in the deposition of Li₂O₂ in the inner and outer tubes of MnO₂ components. The formation of Li₂O₂ can be decomposed by adjacent RuO₂ components, enhancing the cycling and rate performance of Li-O₂ batteries (Fig. 4c and 4d).
Similarly, Wu et al. synthesized the hybrid nanosheets composed of sub-5nm CeO$_2$ and Ru@RuO$_2$ nanoparticles attached to a low percentage (1.2%) antioxidant carbon as bifunctional catalysts for Li-O$_2$ batteries[46]. A number of Li$_2$O$_2$ nanoflakes form on the CeO$_2$/Ru@RuO$_2$ surface during discharge (Fig. 4e), which can be completely decomposed during charge. The phenomenon strongly suggests that the active sites of CeO$_2$ and Ru@RuO$_2$ play a significant role in adjusting the nucleation of Li$_2$O$_2$ to form nanoflakes. These nanoflakes are helpful to O$_2$ diffusion and electrolyte immersion, enhancing the reversibility of Li-O$_2$ batteries. In contrast, large island-like Li$_2$O$_2$ forms on the CeO$_2$/C surface after discharge (Fig. 4f), and a few particles cannot be completely decomposed on the surface after charging due to the lack of Ru-based compounds. Therefore, Li$_2$O$_2$ batteries based on CeO$_2$/Ru@RuO$_2$ cathode catalysts exhibit a very small ORR (0.17 V) and OER (0.45 V) overpotential, a reversible capacity of over 9700 mAh·g$^{-1}$ and good cycling performance of 79 cycles at the limited capacity test of 1000 mAh·g$^{-1}$ (Fig. 4g).

In order to improve the catalytic activity and durability of Ru-based compounds catalysts, the electronic metal-support interaction (EMSI) criterion has been used to rational design Ru-based compounds catalysts for Li-O$_2$ batteries. Lian et al. synthesized the hierarchical porous carbon shells loaded atomically distributed Fe modified RuO$_2$ nanoparticles (Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS) as shown in Fig. 5a and 5b. X-ray absorption spectroscopy (XAS) reveals the Ru-O-Fe$_{x}$ structure forms in the Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS by the electron interaction between Fe atoms and Ru sites (Fig. 5c). During discharge, the Ru-O-Fe$_{x}$ structure leads to the negative shift of the d-band center of the Fe$_{69}$Ru$_{8}$O$_{52}$, weakening the adsorption of O$_2$ and Li$_2$O$_2$ on the Fe$_{69}$Ru$_{8}$O$_{52}$ (Fig. 5d-5f). The suitable adsorption between Ru-O-Fe$_{x}$ structure and Li$_2$O$_2$ optimizes the growth Li$_2$O$_2$, improving the ORR reaction kinetics. During charge, Li$_2$O$_2$ is effectively decomposed by favor electron transfer between the Ru-O-Fe$_{x}$ sites and Li$_2$O$_2$, boosting the OER reaction kinetics. As a result, The Li$_2$O$_2$ batteries based on the Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS catalysts illustrate very low overpotential (0.34 V) and excellent cycling performance (232 cycles) (Figure. 5g).

**Figure 4.** (a) Proposed reaction mechanism of RM-FIT. (b) Discharged states in RM-FIT electrode during the operation of Li-O$_2$ cells. (c) Proposed reaction mechanism of RM-TIT. (d) Discharged states in RM-FIT electrode during the operation of Li-O$_2$ cells. Reprinted with permission of Ref. [44], copyright 2016 American Chemical Society. SEM images of (e) CeO$_2$/Ru@RuO$_2$ and (f) CeO$_2$/C after the first discharge at a limited capacity of 1000 mAh·g$^{-1}$; (g) Limited capacity (1000 mAh·g$^{-1}$) tested at 200 mA·g$^{-1}$: discharge/charge profiles of CeO$_2$/Ru@RuO$_2$. Reprinted with permission of Ref. [40], copyright 2022 Elsevier.

**Figure 5.** (a) Schematic illustration of the synthesis process of the Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS. (b) HAADF-STEM images of Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS. (c) Ru K-edge normalized XANES spectra. (d) Adsorption energy of reaction intermediate Li$_2$O$_2$ on Ru-O-Fe$_{x}$ active sites. (e) Charge density differences for Li$_2$O$_2$ adsorption states and corresponding charge transfer on the Ru-O-Fe$_{x}$ active sites. (f) The total density of states (DOS) and partial density of states (PDOS) of Ru-O-Fe$_{x}$ models. (g) Discharge-charge profiles of Fe$_{69}$Ru$_{8}$O$_{52}$/HPCS cathodes with different cycles at 200 mA·g$^{-1}$ and 1000 mAh·g$^{-1}$. Reprinted with permission of Ref. [45], copyright 2023 Wiley-VCH.

### 2.4 Metal sulfides

Metal sulfides exhibit better electric conductivity, thermal and mechanical stability compared to metal oxides[46]. The ternary chalcogenides (AB$_2$S$_x$) possess the unique surface electronic properties because the metal cations of A$^{2+}$/B$^{3+}$ take up the octahedral and tetrahedral sites of the tightly packed S anionic lattice, respectively[47]. The interaction between transition metal atoms and heteroatoms results in the generation of unsaturated coordination centers (M$^+$-M$^-$) by introducing S vacancy in AB$_2$S$_x$ and allowing heteroatoms to occupy S vacancy. M$^+$-M$^-$ acts as the active site to accelerate charge transfer, leading to the formation and decomposition of Li$_2$O$_2$ in Li-O$_2$ batteries[48].
Single-atom catalysts (SACs) with metal atoms occupying single active sites upon solid supports have been applied in various catalytic domains due to their high reactivity and selectivity, unsaturated coordination structure and maximum atomic utilization. The Ru SACs possessed the maximum atomic utilization rate are expected to absorb the discharge product Li₂O₂ and improve the reaction kinetics of ORR and OER. Therefore, it is crucial to design and explore Ru SACs to boost the electrochemical performance of Li₂O₂ batteries and understand the reaction mechanism of SACs applied in their application.

Hu et al. synthesized zeolitic imidazolate frameworks (ZIF-8) and partially replaced Zn²⁺ with Ru³⁺ as precursors, then they calcined Ru-doped precursors at 900 °C to obtain Ru single atoms distributed in nitrogen-doped porous carbon (Ru SAS-NC) (Fig. 7a)53. The Ru atoms disperse within the Ru₄₃ SAS-NC (Fig. 7b and 7c) and can coordinate with N atoms to form Ru-Nₓ bonds compare to the Ru nanoparticles on nitrogen-doped carbon (Ru NPs-NC) (Fig. 7d and 7g). DFT calculations reveal that the Ru-Nₓ moiety, serving as the active center, significantly influences the electron density distribution, modulating the affinity with Li₂O₂. That is beneficial for the growth of the flower-like Li₂O₂ on the surface of the Ru₄₃ SAS-NC (Fig. 7e). The flower-like Li₂O₂ can be readily decomposed to accelerate the OER kinetics of the Li₂O₂ batteries, resulting in the lower discharge/charge overpotential (0.38 V) and improved cycle life (60 cycles) (Fig. 7f). Compared with Ru₄₃ SAS-NC, typical toroidal Li₂O₂ grown on the pyrolyzed ZIF-8 leads to larger discharge/charge overpotential (1.22 V) and inferior cycling performance (21 cycles) in Li₂O₂ batteries (Fig. 7h and 7i). These results indicate Ru-Nₓ structure as active sites facilities the reversible formation and decomposition of Li₂O₂, thereby enhancing the ORR and OER kinetics of Li₂O₂ batteries. However, isolated atoms are prone to aggregation due to their
high surface energy [64]. Two-dimensional layered graphene materials have garnered extensive study owing to their high electrical conductivity and large surface area [65]. The structural defects caused by doping heteroatoms at the edges of graphene are considered to be one of the promising candidates for anchoring single atoms [66]. Xu’s group employed an impregnation method onto anchor Ru single atoms on N-doped reduced graphene oxide nanosheets (Ru-N/rGO) [67]. The N atoms provide efficient sites for anchoring single-atom Ru. Li2O2 nanosheets are formed on the surface of Ru-Ni/rGO after discharge, and these nanosheets disappear after charging. The DFT simulations indicate the combination of Ru single atoms and N heteroatoms defects creates efficient catalytic active sites for formation and decomposition of Li2O2. This accelerates the reaction kinetics of ORR and OER in Li2O2 battery.

2.6 Ru-based MOF and its derivatives

Metal-organic frameworks (MOFs) formed through the coordinated interaction between inorganic centers (metal ions or metal-containing clusters) and organic linkers have been widely applied in electrocatalytic field [68, 69]. They possess open metal sites to capture O2 as well as open channels for O2 diffusion [60]. However, the intrinsic insulation of traditional MOFs restricts their electrocatalytic performance and leads to high charge overvoltages. Over the past decade, a novel class of conductive MOFs assembled with electron-donating ligands have been progressing rapidly. They are constructed via “through-space”, “through-bond”, and “extended conjugation” approaches, and the third approach guarantees best electric conductivity [61]. These conductive MOFs can accelerate the charge transfer between metal nodes and oxygen, and then regulate the adsorption of superoxide species [62]. This significantly enhances cathode kinetics in Li2O2 batteries.

![Figure 8](Image)

Figure 8. (a) Simulated structure along c axis, (b) SEM, (c) Powder XRD and Pawley refinement patterns of NiRu-HTP. (d) The proposed reaction mechanism of NiRu-HTP. (e) SEM images of discharge NiRu-HTP cathode. (f) The rate performance of NiRu-HTP cathode. (g) The proposed reaction mechanism of Ni-HTP. (h) SEM images of discharge Ni-HTP cathode. (i) The rate performance of Ni-HTP cathode. Reprinted with permission of Ref. [63]. Copyright 2022 American Chemical Society.

Recently, Li’s group directly grew Ni-HTP nanowire arrays on carbon paper as electrodes by the coordination of Ni2+ with 2,3,6,7,10,11-hexaiminotriphenylene (HTP) in a hydrothermal reaction, and then partially replaced Ni sites with Ru via an ion-exchange method for NiRu-HTP [68]. The NiRu-HTP with layered graphene-like honeycomb structure show nanoarrays grown on the carbon paper and exhibits high crystalline features, as displayed in Fig. 8a-8c. This conductive MOF ensures a unique reaction mechanism for Li2O2 battery, as proposed in Fig. 8d and 8g. During discharge, Ru-Ni on the NiRu-HTP strongly absorbs O2 and accept electrons for Li2O2 facilitated by its tunable d-band center. The strong absorption between Li2O2 and Ru-Ni causes high local concentration around NiRu-HTP, fostering the production of film-like Li2O2 (Fig. 8e). This film-like Li2O2 is beneficial for electron transfer and ion diffusion on the cathode electrolyte interface, promoting its decomposition during charge. Conversely, Li2O2 tends to be dissolved in electrolytes and disproportionate for large charged Li2O2 due to the weak adsorption capability of Li2O2 on Ni-HTP. (Fig. 8h) The large toroidal Li2O2 can be oxidized by suffering from high charge overvoltages because the toroidal particles are remote from the catalytic active surface (Fig. 8i). Therefore, the NiRu-HTP-based Li2O2 batteries demonstrate the superior rate capability compared to the Ni-HTP-based Li2O2 batteries, indicating the ORR and OER performance of Li2O2 batteries are boosted (Fig. 8f).

![Figure 9](Image)

Figure 9. (a) Scheme illustration of preparation of Co@CoN-C and RuCo@CoN-C composite. (b) SEM images of RuCo@CoN-C. (c) The optimized configuration of Li2O2 adsorbed on the Co-Ru site with or without the presence of Ru. (d) First discharged RuCo@CoN-C electrode. (e) Schematic illustrations to compare the formation and decomposition of discharge products on RuCo@CoN-C and Co@CoN-C electrodes. (f) Discharge-charge profiles of RuCo@CoN-C based electrode with different cycles at 300 mA g-1. Reprinted with permission of Ref. [67], copyright 2022 Wiley-VCH.

MOF derivatives has been utilized as ORR electrocatalysts in the fuel batteries and aqueous Zn-air batteries, which effectively promote the formation and decomposition of products at solid-liquid interface [64, 65]. Different from solid-liquid interface, insulative Li2O2 as solid product deposits on the cathode surface of the Li2O2 batteries, leading to the formation of solid-solid interface between catalysts and Li2O2. Therefore, the design of electrocatalyst in the Li2O2 batteries should not only focus on the ORR, but also consider the spatial dispersion of Li2O2 on...
3. Conclusions and outlook

Aprotic Li-O₂ batteries have attracted significant attention due to their high theoretical energy density, but the sluggish cathode kinetics hinders their practical application. Ru-based compounds have been introduced as cathode catalysts due to their controllable morphology and electronic structure. These characteristics enable the adjustment of intermediate adsorption and modification of discharge product morphology. This review provides a comprehensive overview of the design and modulation of Ru-based compounds catalysts to enhance electrochemical performance in Li-O₂ batteries, such as: Ru metal or alloys, the incorporation Ru-based compounds into carbon materials, metal or metal oxides, metal sulfides, Ru single atoms and Ru-based MOF and its derivatives. These Ru-based compounds catalysts enhance ORR/OER activity, inhibit the formation of undesirable by-products, regulate the adsorption for LiO₂ by surface/interface engineering and establish favorable interfacial contact with LiO₂, respectively. The reversibility and cycling stability performance of Li-O₂ batteries are greatly improved due to these benefits of Ru-based compounds. However, Li-O₂ batteries still face numerous challenges, like the lithium metal anodes, electrolyte, cathode (i.e., solid catalyst), and additive (i.e., redox mediators)⁶⁸.

1) Most current literatures suggest that the active sites of catalyst can regulate the affinity of LiO₂ and facilitate charge transfer between the electrode and the discharge products. However, further research is necessary to fully understand the catalytic mechanism of the catalyst and the process of formation and decomposition of LiO₂. Technologies have been used to understand the catalytic mechanism of Ru-based electrocatalysts. For example, in-situ differential electrochemical mass spectrometry (DEM) can monitor the O₂ consumption and release in the discharge and charge processes. The affinity of the catalyst to LiO₂ can be revealed by electron paramagnetic resonance (EPR). Electrospray ionization mass spectrometry (ESI-MS) can identify the intermediate in the catalysts-mediated reaction process. This deeper understanding is paramount for designing more efficient cathode catalysts.

2) The stability of Li-O₂ batteries heavily relies on the performance of lithium metal anodes. The growth of Li dendrites and side reactions triggered by O₂, H₂O and intermediates have hindered the reversibility of lithium metal anodes. It is very significant to develop an effective strategy to protect Li metal anodes in Li-O₂ batteries⁶⁹⁻⁷¹.

3) The electrolyte is one of the pivotal factors ensuring the operation of Li-O₂ batteries. The inevitable decomposition of organic electrolytes induced by reactive oxygen species has reduced the cycle stability of Li-O₂ batteries⁷²,⁷³. Therefore, the electrolyte in Li-O₂ batteries must possess the dual capability of stabilizing the lithium anode and withstanding superoxide attack and decomposition facilitated by the presence of the catalyst.

Finally, comprehensive consideration of the cathode, lithium anode, and electrolyte is essential in the design of practical Li-O₂ batteries.

References


Entry for the Table of Contents
锂氧电池中钌基电催化剂的研究进展

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摘要: 可充电锂氧 (Li-O2) 电池因其高能量密度而受到广泛关注。然而, 缓慢的阴极动力学导致较高过电压和较差的循环性能。为了克服这一问题, 不同种类的阴极催化剂已经开始被探索。其中, 钌基电催化剂已被证明是促进析氧反应 (OER) 的极具前景的阴极催化剂。由于钌基催化剂与超氧根阴离子 (O2−) 中间体之间存在强相互作用, 因此可以通过调节 Li2O2 的形态来促进过氧化锂 (Li2O2) 的分解。本文介绍了钌基电催化剂的设计策略, 以提高其在锂氧电池中的 OER 催化动力学。不同结构的钌基催化剂已经被总结, 包括金属颗粒 (钌金属和合金)、单原子催化剂和不同底物 (碳材料、金属氧化物/硫化物) 负载钌的化合物, 以调节钌基电催化剂的电子结构和基体结构。这些钌基电催化剂调节了对 LiO2 的吸附, 提高了 OER 活性, 抑制了副产物的形成, 从而提升了 Li-O2 电池的可逆性和循环稳定性。然而, Li-O2 电池仍然面临着许多挑战。其中之一是锂金属阳极的问题, 锂的不稳定性和安全性一直是 Li-O2 电池研究的一个关键问题。此外, 电解质的选择和阴极材料的优化也是当前研究的重点之一。为了提高 Li-O2 电池的性能, 还需要对添加剂 (即氧化还原介质) 进行更深入的研究, 以提高电池的循环寿命和能量密度。这些挑战的克服将需要跨学科的合作和持续的研究努力, 以推动 Li-O2 电池的进一步发展。

关键词: 锂氧电池, 钌基电催化剂, 反应机理, 反应速率, 过电压