A Review on Recent Advancement of Nano-structured-Fiber-based Metal-air Batteries and Future Perspective

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Abstract:

In an era of sustainable development and innovation ecosystem, a high energy density is one of the important requirements for the development of new energy storage modalities, including battery technology. In a metal-air battery (MAB) system, metals function as negative active substances, and oxygen in the air acts as the positive component. Research to date confirms that, MABs have an exceptionally high energy density, durability, and specific power compared to conventional batteries. In addition, they are environmentally friendly, low-cost, and lightweight. In battery construction, fibrous materials have been shown to improve thermal stability, electronic & ionic conductivity, and cyclical performance of MABs. This is due to their outstanding properties that include large surface area-to-volume ratio, controllable morphology and highly porous structure. In this review, the basic working principle of MABs is presented. A critical overview of the usage of a diverse array of fibrous materials related to metal-based, metal oxide-based, and carbon-based fiber shape materials used in MABs such as Li-O₂, Zn-O₂, Mg-O₂, and Al-O₂ systems are comprehensively summarized. We also

identify the most promising systems due to their established scientific database with respect to sustainable development. Finally, the existing challenges and prospects are stressed considering the future perspective of MABs and fiber-shaped structure electrode material.

Keyword: Metal-air battery; Fibrous structure; Electrode; Energy density; Life cycle; Capacity

Graphical Abstract:

1 Introduction

Industrialization and the fast-paced advancement of consumer-based lifestyles have resulted in the disturbance of the equilibrium of our eco-system, leading to climate change. The over-exploitation and over-consumption of irreversible resources, including the use of fossil fuels to grow the economy and accelerate the rate of industrialization, have caused severe environmental damages and exacerbated the greenhouse effect. Energy demand continues to increase, and it will double in 20 years, which could also lead to a global energy shortage. To satisfy the increasing energy demand and to protect further damage to the eco-system, it is necessary to promote more energy technologies that are clean, renewable and sustainable[1]. Since the 1990s, scientists have explored a series of high-performance, pollution-free green energy sources, which have had a profound impact on changes in the energy composition of the world's industrial structure.

In recent years, Lithium ion battery (LIB) is regarded as the power supply in electronic vehicles and power devices, due to the high energy density of 400 W h kg^{-1} theoretically, durable lifespan exceeding 4000 cycles, and efficiency above 400%.[2-4] However, the limited lithium resources on the earth and its associated high extraction cost impedes the further evolution of LIB technologies. Furthermore, their energy densities do not adequately satisfy the requirement of high durability under rapidly changing climatic conditions [5]. These critical limitations have been highlighted in research work on alternative and new energy materials for battery applications. The exploration of potential fungible materials that are relatively abundant on the earth could provide more permanent solutions for battery systems with improved durability and lower cost is the objective of global battery research. The recyclability and versatility of lithium-ion batteries are often debated in all sectors of battery manufacturing, and their user sector value chain, particularly after a recent spike in their usage in electric vehicles. Therefore, emerging challenges of existing battery systems combined with

numerous innovations in new energy materials have resulted in active research in the development of novel battery systems. These systems are not designed to satisfy high energy density demand, but to facilitate comprehensive science-based innovation due to their compactness, durability and sustainable end-of-life solutions.

To address the limitations of closed-system structure batteries such as those of LIBs, MABs attract great attentions. One primary benefit of these systems is their ability to use a half-open system with oxygen from ambient air as a cathode electrode material. Secondly, MAB can also provide an alternative and conceptualized way for fuel cells that use metal as fuel instead of hydrogen energy. They are also designed to achieve a high energy density.[6, 7] In 1979, Burton and his coworkers[8] first reviewed MABs and summarized their development. Subsequently, research in this field intensified in attempt to address key challenges associated with MAB development. Some of the successful developments are related to performance enhancement that includes high energy density, high specific power, environmental friendliness, durability, low-cost and light weight. It has been reported that the high energy density of MABs is mostly ascribed to the component of a complete metal as positive electrode, and the feasibility of the oxidant as an air cathode. [9-11]

Progress has been made in the development of primary MABs such as Zn-O₂, Al-O₂, Li-O₂, and Mg-O₂ systems. According to a recent literature review, many different types of MABs have been proposed and investigated [12]. Some examples include Li-O₂, Na-O₂, Zn-O₂, Mg-O₂, Al-O₂, and Fe-O₂ batteries. The characteristics of several MABs are stressed in **Table 1**.

Table 1. The characteristics of several MABs

Battery System	Fe-O ₂	Zn-O ₂	Al-O ₂	Mg-O ₂	Na-O ₂	K-O ₂	Li-O ₂
Invented date	1968	1878	1962	1966	2012	2013	1996
Cost of metals(\$/kg)	0.40	1.85	1.75	2.75	1.7	~20	68
Theoretical voltage(V)	1.28	1.65	2.71	3.09	2.27	2.48	2.96
Theoretical capacity	763	1086	2796	2840	1106	935	3458

(Wh/kg)							
Electrolyte for batteries	Alkaline	Alkaline	Alkaline or saline	Saline	Aprotic	Aprotic	Aprotic
voltage (V)	~1.0	1.0-1.2	1.1-1.4	1.2-1.4	~2.2	~2.4	~2.6
energy density (Wh/kg)	60-80	350-500	300-500	400-700	Unclear	Unclear	Unclear
Primary (P) or electrically rechargeable (R)	R	R	P	P	R	R	R

All the MABs described in **Table 1** have relatively high theoretical energy densities, approximately two to ten times higher than that of LIBs [13]. As such, they are promising candidates for application in electronic vehicles. Among all MABs reported thus far, Al-O₂ and Zn-O₂ batteries have demonstrated high theoretical energy densities and facilitate high applied voltages. Fe-O₂, Zn-O₂, Na-O₂, K-O₂, Li-O₂ batteries are electrically rechargeable and Fe-O₂ batteries have demonstrated long lifetimes (>1000 cycles). However, research in the field of Na-O₂, K-O₂ and Fe-O₂ batteries is its infancy. Among the aforementioned batteries, Li-O₂, Zn-O₂, Mg-O₂, and Al-O₂ are promising for production scale development in the near future. [12, 14]

With the advent of nanotechnology, nanostructured and fiber-shaped materials are being proposed and designed for use as energy storage devices such as MABs and capacitors [15-18]. Traditional nanoparticles are prone to aggregation, leading to the loss of their nano-structured characteristics including the large surface area-to-volume ratio, porous structure and nanostructure stability. These inherent properties of fibers and nanofibers are significant in the structural design of battery components. Micron-sized powdered electrode materials result in long diffusion distances of metal ions, and limited rate of electron transmission leads to poor cycle and rate performance.

However, fibrous structured materials also possess unique properties such as size effects, piezoelectric effect, thermoelectric effect, and excellent optical, electrical, magnetic, mechanical and

thermal properties. These unique characteristics render them as suitable candidates for nano-devices with superior structural, energy storage, and electrochemical applications. Fibrous structured materials have demonstrated stable performance, enhanced capacity, and low-temperature performance in energy devices. For example, fiber-based shape membranes and electrodes have been shown to improve the energy density and lifespan of MABs. It has been reported that membranes made of porous-structure fibers exhibit significantly improved ion conductivity with high electrolyte uptake [19, 20]. Furthermore, the interfacial resistance increases with the increase of the storage time between the electrolytes and the fibrous membrane absorbed in the electrolytes.

Many different methods are currently used for the preparation of fibrous structure materials. Some examples of important methods include hydrothermal synthesis[21], template synthesis[22, 23], in situ polymerization[24], self-assembly[25], phase separation[26, 27] and electrospinning[28-30]. It has been reported that the optimization of process variables in fiber preparation can lead to tunable properties such as precision control of the nanostructured surface roughness, bulk density, fiber diameter, specific surface area, and connectivity.[31] Moreover, the diverse shapes of fibers including brush-like nanofibers, hollow fibers, core-shell fibers, and other types are also being reported, as shown in Figure 1. This figure provides insight into the physical and chemical properties of these fiber-shaped materials, including their enhanced photoelectric and mechanical properties. Nanostructured fibers prepared from ceramics, polymers, metals, carbon and many other materials were developed and studied for advanced MABs.[32, 33] [20] [18, 33] Since the initial reporting of MABs, researchers have made significant progress with respect to the introduction of fibrous materials in MAB construction. In particular, it has been reported that fibrous materials are used as electrode catalysts, membrane or as a support material for MABs.

This review is aiming to summarize recent progress in MAB development that utilizes fibrous

materials, specifically nano-structured fibrous materials. This report discusses the current developments related to the working principle of MABs, progressive advancement of battery efficacy, durability, and environmental friendliness. Our objective is to provide a critical analysis of recent developments related to various fabricated fibrous materials used for different types of MABs. Finally, existing challenges and future perspective are discussed towards the development of nanostructured fibrous materials for use in MABs.

Figure 1. Various morphologies of nanostructures fiber shape materials: a) brush-like nanofiber. b) Hollow nanofiber. c) Core shell nanofiber. d) multichannel fiber. e) Beaded fiber. f) crimped fiber. g)

Nanosheet-shape fiber. h) Crumpled fiber. i) pearl-like fibers. a) Reproduced with permission.[34] Copyright 2017, American Chemical Society. b) Reproduced with permission.[35] Copyright 2004, American Chemical Society. c) Reproduced with permission.[36] Copyright 2018, The Royal Society of Chemistry. d) Reproduced with permission.[37] Copyright 2018, The Royal Society of Chemistry. e)Open access.[38] f) Reproduced with permission.[39] Copyright 2014, American Chemical Society. g) Reproduced with permission.[40] Copyright 2018, The Royal Society of Chemistry. h) Reproduced with permission.[41] Copyright 2018, The Royal Society of Chemistry. i) Reproduced with permission.[42] Copyright 2016, American Chemical Society.

2 Fiber-shaped material for use in Li-O₂ batteries

2.1 Working principle of a Li-O₂ battery

When the Li-O₂ battery operates, O₂ will be consumed from ambient to produce insoluble metal oxides in the cathode during a discharge process called oxygen reduction reaction (ORR). Conversely, the discharge products are reversibly decomposed during charging to release oxygen in a process called oxygen evolution reaction (OER). On the whole, the following reaction (1-4) will occur:

Total reaction:

The lithium anode transports Li⁺ to the cathode where it is electrochemically reduced. Li-ions react with the superoxide ions of the reduction product to form LiO₂ on the cathode. To achieve high

stability, it must be formed from Li_2O_2 and Li_2O for LiO_2 with more lithium coordination for consideration of thermodynamically unstable LiO_2 . To form a more stable oxide, LiO_2 may be disproportionated ($2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$) or electrochemically reduced ($\text{LiO}_2 + \text{Li} + \text{e}^- \rightarrow \text{Li}_2\text{O}_2$) to form an oxide phase Li_2O_2 . [43-45]

A rechargeable Li-O₂ battery was first reported from the respective groups of Abraham and Jiang.[46] The battery comprising Li metal as positive electrode, electrolyte, and negative electrode is a primary candidate for application as a reusable energy source.[47, 48] The most challenging aspect of enhancing the performance is related to the improvement of the air electrode composition. This determines the capacity, energy density, and efficiency of the whole battery systems.

Thus many materials including porous carbon, carbon nanofibers (CNFs), and carbon nanotubes (CNTs) used as cathode support catalysts are incorporated in lithium-oxygen battery with different metals or metal oxide material catalysts.[49-51] But those cathode materials or their combination is not ideal with respect to practical electrochemical performance, because this is crucial in the design of the electrode structure. Interestingly, fiber-shaped structure is potential for cathode due to their efficient electron pathways, large surface area, and advantageous nanostructures with large spaces for Li_2O_2 deposition, electrolyte uptake, and O_2 diffusion. Most of the fibrous structure materials serve as catalysts are mainly to improve the fundamental kinetics of OER and ORR reactions[52]. Carbon-based nanofibers, and non-carbons including metal and metal-oxides fibers developed as cathode materials for MABs have attracted increasing interest in recent years. To date, Li-O₂ batteries have demonstrated the potential for use as the next generation of battery systems especially for their superior energy density.[53-55]

2.2 Carbon-based fiber-shaped materials used in Li-O₂ battery

2.2.1 Ordinary carbon fiber-based materials for Li-O₂ battery

Owing to the superior conductivity, cost-effectiveness, ease of access, and compatibility characteristics, carbon is considered as the appropriate material for cathode design in Li-O₂ cell, either as a conductive filler or catalyst support. Based on current practice, carbon materials were demonstrated that having a great catalytic effect on ORR. However, their OER is limited. It has been further reported that OER performance can be further improved either via the development of new formulation by compounding or surface modification with carbon materials. [56, 57] Shin and Song [58] fabricated core-shell-structure nanofibers of mesoporous carbon coated CNFs (CNF@mesoCs) as cathode using electrospinning and nano-casting for a Li-O₂ battery. After the coating process, the composite kept its original 1D structure as the original CNFs. Each nanofiber intertwined and formed a 3-D cross-linked network structure. The surface area increased from 708 m²g⁻¹ to 2194 m²g⁻¹ ascribed to the coated mesoporous carbon on the CNFs. Also, it was confirmed that the mesoporous carbon is well-graphitized by Raman spectra characterization. It is considered that better conductivity obtained from the graphitized CNF@mesoCs surface with 4.638S cm⁻¹ compared to the original CNFs (3.0759S cm⁻¹). Moreover, the CNF@mesoCs cathode exhibiting discharging capacitance with 4000 mA h g⁻¹, was much superior to the original CNFs (2750 mA h g⁻¹).

Some carbon materials just like graphene [59, 60] and CNTs [61], are widely adopted as electrode materials with a high discharge capacity. However, industrial progress is still slow because it is costly. To reduce high cost and enhance cycle performance, numerous investigations have conducted and planned new formulations by compounding or surface modification of carbon materials. Among them, Nie et al.[62] prepared carbon nanofibers using PAN and DMF using

electrospinning technology and calcination in air and argon atmosphere. They were then activated under a sealed CO₂ condition for 1 h at 1273 K to obtain self-supporting, binderless, thin network active carbon nanofibers (ACNF) (Figure 2a-d). The micro-sized pores in carbon nanofibers are greatly conducive to the permeability of oxygen. Moreover, in the process of CO₂ activation, mesopores were introduced to expand the Li₂O₂ nucleation sites number. And the reduced particle size was attributed to the flaky Li₂O₂ nucleation formation. Compared to nonactivated CNF cathodes, activated carbon nanofibers as catalysts would greatly enhance the cyclability (Figure 2e and f).

Figure 2. SEM of cathodes incorporated with CNFs (a and b), ACNFs cathodes (c and d) after discharging process. e-f) cycle properties with cathodes of CNFs and ACNFs for Li-O₂ battery as respectively. [62] Reproduced with permission. Copyright 2015, American Chemical Society.

To investigate the effect on lithium-oxygen cell properties when several kinds of carbon-based materials were used, Yamamoto et al.[63] selected four kinds of carbon materials covering Ketjen black (KB), vapor grown carbon fiber (VGCF), Vulcan XC-72R (VX), and acetylene black (AB and AB-S). The effect of carbon electrode stability on the positive electrode in aqueous Li-O₂ batteries

was studied. It was demonstrated that the KB electrode exhibited better stability and has especially stable overpotentials during the ORR process under 2.0 mA cm^{-2} owing to its large specific surface area. Recently, Kim et al used a chemical vapor deposition (CVD) technique to obtain CNF-CB 640, 740, and 840 when CNFs grew on carbon black at 640, 740, and 840 °C, respectively[64]. (Figure 3a) The Li-O₂ battery based on CNF-CB 740 demonstrated high cycle stability with a cut-off voltage (2.5 V to 4.2 V). It was estimated to be stable up to 75 cycles (300 h), with steady charge voltage due to a great number of active sites (Figure 3b and c).

Figure 3. a) Sketch of the grown CNF-CB. b) CNF-CB 740 discharge and charge plots. c) cycle performance of four types of carbon materials. Reproduced with permission.[64] Copyright 2016, The Royal Society of Chemistry.

It has been proved based on the results of many studies that carbon materials doped with nitrogen are efficient and inexpensive with respect to ORR activity [65, 66]. For example, if N and another element are also added to Co-doping carbon materials such as P, B, or S, this would greatly enhance the surface polarity and electronic properties towards the ORR process [67]. Many N-doped CNFs and CNTs are valuable to use as air electrode materials to date [68, 69]. In addition, they have better cycling performance and higher electrical conductivity than undoped carbon. Moreover, it has been

revealed in previous works that N-doped carbon materials could immobilize the active intermediate during the discharging process thus enhance the battery stability [70]. The work by Dai et al.[71] involved a vertical N-doped coral-shaped CNFs (VA-NCCF) array. An energy efficiency was up to 90% between the discharge/charge period and with 0.3 V for voltage gap when embedded in battery system. This represents a significant advancement in Li-O₂ battery research. It could be observed that VA-NCCF grew on Silicon wafer with 20 $\mu\text{g cm}^{-2}$ of density and 20 μm of a thickness supported by a stainless-steel cloth (Figure 4a). The prepared zigzag-like VA-NCCF (Figure 4b and c) had high conductivities and a large free space in different directions between layers for efficient electron, electrolyte, and reactant transporting, in addition to a large uptake of Li₂O₂. After 100 h discharge, the energy was remained about 40 000 mAh g⁻¹. With around 1000 mAh g⁻¹ for the specific capacity, the experimental battery was used with good reversibility for over 150 cycles. It might be ascribed to the minimization of electrolyte decomposition because of catalytic activity induced by N-doping, and facilitated the deposition process of Li₂O₂ and reduced the charging overpotential along the VA-NCCF.

Figure 4 a) VA-NCCF array SEM image growing on a slice of Silicon wafer used CVD method. b) TEM of a single VA-NCCF. c) Schematic of VA-NCCF and with growth of Li_2O_2 on surface. Reproduced with permission.[71] Copyright 2014, American Chemical Society.

With regard to the study on pyrolysis of polyaniline aerogels doped used phytic acid[72], a template-free method was adopted to prepare a novel carbon nanofiber with N and P co-doping (NPCNF). The NPCNF provided capacity of $12,607 \text{ mAh g}^{-1}$ and a large surface area-volume rate. It could potentially be utilized as air electrode in non-aqueous lithium-oxygen cells. Because of the foam microstructure interaction, it also exhibited lower overpotential than pure carbon. Moreover, N, P co-doping induced high electrocatalytic activity.

The formation of a hollow nanofiber shape by different materials is a promising development with respect to air electrode performance. Compared to other ordinary nanofiber-shaped materials,

hollow structure nanofibers that are used as the air cathode of batteries exhibit a greater surface area. This results in a high aspect ratio and high specific capacity, and more active sites to ion adsorption. Moreover, their high surface permeability and high pore volume of hollow structure nanofibers directly enhance the kinetics of adsorption.[18, 73-75]. Research on lithium oxygen battery with hollow CNFs with 30 nm average diameter as cathode and porous ceramic as substrate (Figure 5a and b), it yielded a comparatively high energy discharge of 2500 W h kg⁻¹. This was about 4 times the capacity enhancement compared to many other Li compounds including LiCoO₂ of 600 W h kg⁻¹. The reasons are mainly due to the low-carbon packaging in the grown CNF cathode, the effective immobilization of carbon quality, and the high void volume formed by Li₂O₂. [76]

Figure 5 (a) SEM for cross profile (70°-tilt) of porous anodized aluminum oxide membranes deposited by electron beam evaporation. (b) SEM for cross profile (70°-tilt) of the anodized Aluminum oxide after nanofiber growing on. open access[76]

In a recent publication, Kim et al.[77] fabricated efficient bifunctional electrocatalysts of RuO₂/Mn₂O₃ fiber-in-tube(RM-FIT/KB) and RuO₂/Mn₂O₃(RM-TIT/KB), with a tube-in-nanotube configuration by utilizing electrospinning and carbonization, as shown in Figure 6a. In the OER curves of Figure 6b, RM-TIT/KB exhibits a superior overpotential property ($\eta = 0.96$ V at 2000 mAh g⁻¹) compared to RM-FIT/KB ($\eta=2.01$ V at 2000 mAh g⁻¹), whereas the OER performance of the charge reaction of KB was poor. At 200 mAh g⁻¹, RM-Tit/KB exhibited an overall voltage gap of 1.48 V. The cyclic performance can be seen from Figure 6c. The RM-TIT/KB and RM-FIT/KB underwent

over 100 cycles, whereas KB failed for the 22nd cycle, resulting in obviously discharging capacity decay. The catalytic electrode was expected to be beneficial to the forming and decomposing of Li_2O_2 over a long period, which has been validated through relative uniform discharging and charging behavior of RM-TIT/KB, and RM-FIT/KB (Figure 6d). The rate performance of the catalyst was measured by repeated discharging and charging ranging from 100 mA g^{-1} to 600 mA g^{-1} for different current densities. The Li- O_2 cell using catalytic KBS showed greater rate performance than non-catalytic KB. RM-TIT/KB still exhibited a prominent discharging capability at 600 mA g^{-1} (Figure 6e).

Figure 6. a) Diagram for principle of RM-FIT and RM-TIT formation. b) discharge-charge plots for the first time. c) cyclability, and d) discharging-charging voltage distribution of KB, RM-FIT/KB, and RM-TIT/KB at 400 mA g^{-1} ; e) comparing with the discharging performance of three catalysts (KB, RM-FIT/ KB, and RM-TIT/KB) at various ampere densities. Reproduced with permission.[77]

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2.2.2 Flexible electronics and carbon fiber-based Li-O₂ battery

Flexible electronics are widely concerned because of their flexibility, portability, and wearability, which may lead to transformative design changes in consumer products, automotive, aerospace components, and medical devices.[78, 79]. For this reason, they require a power system with high energy density, and mechanical flexibility. With the rapid advancement of knowledge, flexible Li-O₂ batteries made of carbon have introduced new concepts in flexible and wearable energy devices. Peng et al.[80] created a new Li-O₂ battery in which the air electrodes were assembled using aligned carbon nanotubes. Low-density polyethylene (LDPE) films were modified to prevent water erosion, and LiI was used as the gel electrolyte for a redox media. The results showed that the LDPE film could inhibit the side reactions of Li₂O₂ discharging products in air, and LiI could promote Li₂O₂ electrochemical decomposition in the charging period.

The assembled Li-O₂ battery with fibrous structure electrode showed great flexibility. After 1000 cycles of repeated bending, the charging and discharging curves were initially maintained. The water-resistance was tested using a waterproof LDPE film. The resulting optical fiber Li-O₂ batteries could function as drive yellow light-emitting diodes (LEDs), even if partially soaked water. Furthermore, the charge and discharge performances were still acceptable even after water immersion. The results showed that the LDPE film can effectively enhance the water survival rate of Li-O₂ batteries. They exhibited excellent potential for wearable applications. It was shown that Li-O₂ batteries with a fiber shape woven into cloth could charge smartphones. It is worth noting that these Li-O₂ batteries have a lifecycle in ambient air of up to 610 times. Such designs allow for all-flexible components, which provide opportunities for fiber-shaped Li-O₂ batteries with high flexibility that are very useful in wearable electronic products.

Table 2 summarized the electrochemical performance of different carbon and carbon-based

fibrous structure materials utilized for lithium cells. Obviously, the electrode properties of different carbon materials vary greatly. CNFs with a special structure, high aspect ratio, high conductivity, and favorable flexibility have been shown to be appropriate candidates. Therefore, it is considered as the most attractive air electrode matrix materials. It is very important to control the sintering temperature, sintering time, and the increasing rate of the temperature, which will affect the final morphology and average diameter, porosity, surface area-volume, and other parameters of the fibers. Among them, porosity and the surface area-volume are essential parameters that affect the electrical properties of the cathode materials of batteries.

Table 2. Electrochemical performance of different carbon material and carbon-based composites fibrous structure materials used for Li-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
Activated CNFs	Hierarchically porous structure	CO ₂ activation and Electrospinning		Average diameter of 250 nm/709 m ² g ⁻¹	51 cycles for 1000 mA h g ⁻¹ at 200 mA g ⁻¹ .	[62]
Fluorinated graphite CNF	Porous strip-type structure			168.43 m ² g ⁻¹	979 mAhg ⁻¹ (3rd cycle) at 0.3 mA cm ⁻²	[81]
Nitrogen and phosphorus doped CNF		Template-free method	Calcination for 2 h at the temperatures 1,000 °C in inert Ar atmosphere	Around 80 nm/ 740.96 m ² g ⁻¹	After 16 cycles, huge capacity of 12607 mAh g ⁻¹ maintained at 100 mA g ⁻¹	[66]
CNFs grown on carbon black (CNF-CB 740)	With an entangled and curled structure	Chemical vapor deposition (CVD) method	He gas mixture for 30 min at 740 °C. and dried at the temperature of 80 °C	>10 nm /324 m ² g ⁻¹	The discharge voltage is at 2.5 V after 75 times at 0.5 mA cm ⁻²	[64]
Mesoporous carbon coated carbon nanofibers (CNF@mesoCs)	Self-standing three-dimensional web structure	Electrospinning and nanocasting	Heated at 1273 K in N ₂ atmosphere with heating rate of 2 K min ⁻¹ for 1 h	280 nm/2194 m ² g ⁻¹ .	Discharge capacity was 4000 mA h g ⁻¹ at 0.05 mA cm ⁻²	[58]
Three-dimension open macroporous	Entangled and porous	Ultrasound treatment and	Heated to 800 °C in a N ₂ for 2 h	~50 nm/100.7 m ² g ⁻¹	500 mAh g ⁻¹ after 60 cycles at 300 mA g ⁻¹	[82]

carbon nanowebs (3-DOM-CNWs)	structure	vacuum filtration, following with Freeze-drying						
Low-density polyethylene with low-density polyethylene film	Aligned bar structure						1000 mAhg ⁻¹ after 600 times at 2000 mAg ⁻¹	[80]
Flexible textile fibers with a novel triple-phase structure	Novel triple-phase structure				10–20 μm		Overpotential was 1.15 V, discharge capacity was 8.6 mAh cm ⁻² , and stably ran for 50 times at 0.1 mA cm ⁻² .	[83]
CNFs grafted carbon paper	Cylindrical nanostructure	Chemical deposition method	vapor (CVD)	Heat up to 700 °C with rate of 50 °C min ⁻¹ under 15% H ₂ and Ar	5–10 um		Cycled more than 800 times under 0.01 mA cm ⁻²	[84]

2.3 Metal-based fiber shape materials used in Li-O₂ battery

2.3.1 Precious metal-based fiber materials for Li-O₂ battery

Precious metals are generally thought to be efficient and expensive catalysts for chemical reactions.[82] They can facilitate high catalytic activity, and show excellent properties such as oxidation resistance, corrosion resistance, and high-temperature resistance. Among them, Au, Ag, and Pt are commonly used precious metals for catalysts of MABs, which exhibit excellent catalytic properties and high chemical stability.[61, 85] Precious metals such as Pt group metals have been investigated in this regard for many years, especially the use of Pt as ORR catalysts. This area of research is still attracting attention owing to the excellent electrocatalytic activity and stability of these metals. To utilize these precious metals and their microstructures in MABs, it is essential to investigate the strong electrocatalytic activity of precious metal-based catalysts, especially the OER catalytic performance.

Leng et al. [86] fabricated a non-adhesive and non-carbon Pd/Co₃O₄/NF cathode with a free-standing 3D structure in lithium-oxygen cell. They synthesized Co₃O₄ nanowire clusters on a support

material of a nickel foam (NF) substrate, then incorporated Pd nanoparticles into them using pulse electrodeposition, as shown in Figure 7a. The nanowire cluster presented a flower-like morphology with average value of 60 nm for diameter and about 5 μm length with Pd particles on the surface. It exhibited excellent conductivity and the ORR/OER performance of the cathode because Pd nanoparticles distributed uniformly on the surface of Co_3O_4 nanowires. The Li- O_2 battery adopted Pd/ Co_3O_4 /NF as the cathode demonstrated 70 stable cycles with a constant capacity of 300 mAh g^{-1} , and greater than the 40 cycles that used bare Co_3O_4 /NF cathodes under the same condition as demonstrated in Figure 7b-d.

Figure 7. a) the procedure and mechanism analysis of Pd/ Co_3O_4 catalytic cathode supported with the Ni foam. b-c) different cycles of discharge-charge plots with Co_3O_4 /NF and Pd/ Co_3O_4 /NF air electrodes at 0.10 mA cm^{-2} . d) Relationship between capacity and terminal voltage of various air

cathodes and cycle number. Reproduced with permission.[86] Copyright 2015, The Royal Society of Chemistry.

Recently, Au alloy air electrode materials were demonstrated superior properties including high conductivity, intrinsic chemical stability, a highly porous structure, high surface area volume ratio and mechanical property. [87] Besides, catalytic activity of noble metal-based materials including Pt, Ru, and Pd was systematically investigated.[88] Also, several studies have established that Ag is a suitable ORR catalyst and has reasonable stability and catalytic property. Ag-based catalysts are more suitable for application in alkaline electrolytes and are promising for use in air-electrodes due to their competitive cost and performance balance compared to other precious metals. However, the major shortcomings of precious metals include their high price and lower storage capacity. The price of precious metals and the shortage of resources hinder the industrialization of metal-air batteries, which require high activity and stability, in addition to a reduction of the consumption of precious metals.

2.3.2 Nonprecious metal-based fiber materials for Li-O₂ battery

Although precious metals and their alloys are the most efficient catalysts related to electrochemical activity and stability, high costs and a shortage of resources have hampered the commercialization. It is necessary to investigate electrocatalytic materials with low cost, high stability, and active properties. Recently, researches have been carried on non-noble metal-based catalysts (such as Co, Ni, Fe, Mn). They are similarly to precious metal-based catalysts with low price and excellent performance. For example, Cho et al.[92] fabricated Fe/Fe₃C/N-KB composite catalyst as a kind of air electrode material, and demonstrated high catalytic performance for MABs. A new method for preparing FeN_xC/C nanofiber catalyst was reported by Mu et al. [93] using ferric chloride that can be simultaneously used as an oxidant and iron source. The electrochemical test results revealed

that the FeN_xC/C catalyst possessed higher stability than some Pt/C-based catalysts. Such a development has the potential to replace Pt-based catalysts in ORR.

In a recent publication, it was reported that an iron-nitrogen-carbon nanofiber material[94] was fabricated using an electrospinning and heating process to produce non-noble metal-based nanofibers as a potential replacement for expensive commercial Au and Pt-based catalysts. The (Fe-N-C) nanofiber-based catalysts achieved the optimum half-wave potential value of previously developed non-noble metal catalysts, with a similar value to the marketing Pt/C catalysts. Chen and coworker[95] dissolved iron acetate and polyacrylonitrile (PAN) in dimethylformamide (DMF) and prepared porous non-precious Fe-C based nanofiber catalysts (Figure 8a) using an electrospinning method. The electrospun Fe-C catalysts displayed similar activity to commercial Pt-based catalysts for ORR catalytic activity (Figure 8b). The activity of Fe/PAN and its electrical resistance are comparable at the set current and the limiting current relative to platinum in an aqueous environment. The limiting current of the non-precious Fe/PAN nano-fiber catalyst is commensurate with that of a noble metal. Therefore, a non-precious metal catalyst could significantly reduce cost without an obvious loss of performance. (Figure 8c).

Figure 8. a-b) TEM image of FePAN nanofiber electrode catalysts. c) Contrast of ORR activity of three types of catalyst including FePAN-PL nanofiber electrode, FePAN nanofiber, and Pt/C. Reproduced with permission.[95] Copyright 2012, American Chemical Society.

Fabricating 3D microstructures is a practical way to improve fiber structure porosity and surface area, thus enhancing the electronic performance of batteries.[96] Ramakrishna et al.[97] introduced a facile free-surface electrospinning method. They fabricated non-precious metal 3D layered CNF in batches, in which transition metal-based N and O₂ co-doped CNTs were grown on CNF membranes (MNO-CNT-CNFFs, M = Fe, Co, Ni), followed by in-situ growth and calcination. The synthesized FeNO-CNT-CNFFs exhibited excellent electrocatalyst performance with 0.15 V for low overpotential, 3.4 V for high voltage and long lifespan over 120 h in ambient air tests as cathode when assembled into Li-O₂ battery. It reached up to 220.24 m² g⁻¹ of superficial area in contrast to the presently reported 90.71 m² g⁻¹ of microporous hollow carbon fibers and 205 m² g⁻¹ of overlapped Ti₃C₂ and g-C₃N₄ nanosheets film.[98, 99]

The encapsulation of metal particles into nanofibers was also demonstrated to enhance the CNFs conductivity. Huang et al [100] used electrospinning method and prepared binder-free, graphitized, hierarchically porous CNFs electrodes, encapsulated with Co-Ni catalysts (as shown in Figure 9a-g). In situ coating of Co-Ni nanoparticles formed a porous structure on the CNFs surface, increasing the surface area of Co-Ni/CNFs to 206 m² g⁻¹. In addition, there were more active sites present compared to the CNFs (23 m² g⁻¹). This not only facilitated the graphitization of CNFs and improved the conductivity, but also compensated for the defects of carbon materials in OER performance as an air-electrode catalyst. This composite material exhibited excellent electrochemical performance with its ORR starting points of 0.22 V and OER of 0.70 V. After assembled into Li-O₂ batteries, the maximum discharging capacity was 8635 mAh g⁻¹ (Figure 9h). Moreover, the upper limit capacity could be maintained over 60 times when the terminal charge voltage was less than 4.5 V (**Figure 9i and j**).

Figure 9. a) Diagram of electrospinning procedure. b) image of CoeNi/CNFs and c) CoeNi/CNFs morphology and diameter range of the prepared fibers. and d) TEM of CoeNi/CNFs. e) EDX curves scans for Co, Ni with mesopores. f) A graphite layer around the mesopore g) SAED patterns of CoeNi/CNFs. h) The first discharging and charging curves at 200 mA g⁻¹. i-j) Battery cyclability with Co-Ni/CNF electrodes catalyst. i) discharging and charging curves and j) specific capacity and average voltage vs. cycle. Reproduced with permission.[100] Copyright 2016, Elsevier.

These developments demonstrate their great potential as catalysts and they can be further tuned by adding modifiers or activators to custom-design the ORR and OER properties. Sun et al. [101] mixed PAN, PMMA and FePc in a DMF solvent then used an electrospinning method and obtained FePc carbon nanofiber-based catalysts for Li-O₂ batteries. The prepared PAN/PMMA fiber mats were immobilized at 280 °C with 6 h in ambient, calcined at 650 °C with 3 h in N₂. FePc played a role as a molecular shuttle, with which O²⁻ and ion were transported back and forth between the discharging product Li₂O₂ and the surface of the electronic conductor. (Figure 10) In the discharge process, FePc-O₂ acts as a molecular shuttle of electrons and undergoes a transformation process of (FePc-O₂)→(FePc-O₂)→(FePc-Li-OOLi). In the discharging process, FePc-LiOOLi diffuses to the

nucleation site of Li_2O_2 . LiOOLi and FePc are separated and merge in the Li_2O_2 lattice. This is mainly attributed to the solid-phase catalysts. During the charging process, $(\text{O}_2)_2^-$ in Li_2O_2 is oxidized by Fe^{III} and forms $(\text{FePc}-\text{O}_2)^-$, which then diffuses to the carbon surface via the electrolyte, and is further oxidized to FePc and O_2 , thus completing a reversible process. This process is mainly activated by liquid-phase catalysts. The forming and decomposing process of Li_2O_2 does not directly involve the carbon materials immediately after the addition of FePc , and Li_2O_2 could not react with the carbon materials to produce Li_2CO_3 , thereby inhibiting the deterioration of the cycle performance of the battery.

Figure 10. Diagram of the FePc movement acted as a molecular shuttle between Li_2O_2 and carbon. Reproduced with permission.[101] Copyright 2014, American Chemical Society.

To design an air electrode with high catalytic activity and high conductivity without using a binder, Zhou et al[102] used a multi-walled CNT paper as an adhesive-free and additive-free cathode electrode and exhibited an optimum capacity of $34600 \text{ mA h g}^{-1}$. It was used as an assembled air electrode after further modification of the MWCNTs for $\text{Li}-\text{O}_2$ batteries using Ru NPs catalyst, and the result revealed a fairly low charging overpotential and higher round-trip efficiency.[103] Furthermore, examples of many other metal-based fibrous structure materials as catalysts developed for $\text{Li}-\text{O}_2$ batteries were summarized in **Table 3**. Different preparation techniques exert an important influence on the fiber diameter distribution and final morphology. Electrospinning is a suitable and

effective choice for metal-based fibers. This technology can be used to spin non-spinnable metal and metal-oxide materials to form continuous fibers.

Table 3. Electrochemical performance of different metal-based composites fibrous structure materials used for Li-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
Co-Mn @ CNF	Hierarchical tubular structures	Synthesis of Mn-based MMO HTS and calcination		400–500 nm/60.8 m ² g ⁻¹	Over 900 mAh g ⁻¹ for 30 times at 200 mA g ⁻¹	[104]
Anode Sn@CNFs	Hollow structure	Coaxial electrospinning and heat process		(200 ± 50) nm	737 mAhg ⁻¹ after 200 cycles at 50 mAg ⁻¹	[105]
Fe/Fe ₃ C-CNFs	Including randomly oriented, overlapped, continuous and interconnected	Facile electrospinning method		350 nm	5300 mA h g ⁻¹ for 40 times at 300 mAg ⁻¹	[106]
Co-CNF	Free-standing three-dimensional network	Electrospinning and calcination processes		200–300 nm	Remained 500 mAh·g ⁻¹ after 70 times at 100 mAg ⁻¹	[107]
Iron phthalocyanine loaded on graphite nanofibers (GNF-FePc)	Clear porous structure	Solvothermal process	Vacuum-dried at 80 °C	69.51 m ² g ⁻¹	Specific capacity of ~5500 mAh/g remained on the verge of 90% capacity after 4 cycles.	[108]
Fe-N/CNFs	Highly porous network structure	A mild template-directed hydrothermal carbonization (HTC) method	Calcinated at 800–1000 °C in Ar atmosphere	150 nm/ 584 m ² g ⁻¹	Half-wave potential (0.78 V) and starting potential (0.88 V)	[109]
Co-Ni/CNF	Hierarchical porous structure	Electrospinning and in-situ encapsulation	Stabilization at for 3 h at 220 °C in ambient air and	80–200 nm /206 m ² g ⁻¹	8635 mAh g ⁻¹ for 60 times at 200 mA g ⁻¹	[110]

	with numerous macropores		carbonized for 1 h at 750 °C in N ₂ atmosphere.						
FeNO-CNT-CNFFs 800	Peapod-like and hierarchical and porous structures	Free-surface electrospinning technique followed by in situ growth carbonization.	Carbonized at 800 °C with 5 °C min ⁻¹ of heating rate of in N ₂ atmosphere for 2h	About 600 nm/ 220.24 m ² g ⁻¹		Low overpotential (0.15 V), and more than 120 h of cycling with 30 mAh g ⁻¹ of specific capacity	[97]		
Co ₄ N-decorated CNF (Co ₄ N/CNF)	Brush-like structure	Electrospinning and carbonization	Nitridation at 550 °C for 2 h with ammonia (NH ₃) gas flow	~640 nm		500 mAh g ⁻¹ for 177 cycles at 200 mA g ⁻¹	[34]		

2.4 Metal oxide-based fiber shape materials used in Li-O₂ battery

Metal oxide nano-fiber catalysts used in batteries mainly include perovskite and spinel catalysts.

Perovskite-type catalysts are abundant with good thermal stability, chemical stability, and structural stability. After high-temperature treatment, they easily desorb oxygen to form oxygen vacancies and negative active sites on their surface, thus improving catalytic performance [111].

Due to its high performance to both ORR and OER processes, perovskite oxide is considered to be a bifunctional catalyst used.[112, 113] Perovskite oxides, including La_{0.5}Sr_{0.5}CoO_{3-x}, LaNi_{1-x}Mg_xO₃, La_{0.75}Sr_{0.25}MnO₃, Sr₂CrMoO_{6-x}, LaNi_{1-x}Fe_xO₃, La_{0.6}Sr_{0.4}Co_{0.6}Fe_{0.4}O_{3-δ} are considered as potential candidates as cathodic catalysts in lithium-oxygen battery [111, 114-119] . Xu et al [119] first proposed the use of perovskite La_{0.75}Sr_{0.25}MnO nanotubes (PNT-LSM) via electrospinning way and calcination as air electrode catalysts. It was determined that the lithium-oxygen battery with the PNT-LSM/SP electrode stably exhibited specific capacities above 9000–11000 mA h g⁻¹ which could be cycled over 124 times.

Recently, Wang's group[111] reported on layered microporous/mesoporous La_{0.5}Sr_{0.5}CoO_{3-x} nanotubes as dual-function catalyst for cathode in Li-O₂ battery synthesized using an electrospinning

strategy, and subsequently, using a sintering method. Metal nitrates and polymers were dissolved in DMF and the compound was subsequently electrospun into nanofibers. The obtained nanofibers with layer holes were heated at 60 °C in vacuum atmosphere with 6 h, subsequently sintered for 3 h at 750 °C in ambient air. The assembled battery with HPN-LSC/KB as the air cathode maintains 50 cycles and exhibits large capacity of 5799 mAh g⁻¹ at 0.1 mA cm⁻². However, the lithium-oxygen battery with KB cathode lasts less than 14 cycles. Its excellent catalytic efficiency was mainly ascribed to the interaction of the high surface area-to-volume ratio and stable graded macroporous nanotube structure of perovskite HPN-LSC.

It was proved in previous research that the electrocatalytic activity of perovskite catalysts could be further improved via adding modified materials to produce a bifunctional composite catalyst. [116, 118] Chen et al.[9] prepared a bifunctional catalyst for the combination of N-doped graphene oxide (NRGO) and porous La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ perovskite (LSCF-Pr) using an electrospinning method that was functional to both of ORR and OER. In the electrocatalytic process, La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ was mainly effective on OER, whereas the N-doping graphene mainly acted on ORR. The ORR and OER properties of the composites were similar with that of commercial Pt/C composites. The composites reliability was also greatly enhanced compared to the composites prior to compounding. Recently, Liu et al. [114] synthesized different types of porous nanofibers of perovskite La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_{3-δ} (x=0-1) that could be controlled in a quantified manner by electrospinning technique and then with calcination for 3 h at 700 °C in ambient. Among them, the La_{0.6}Sr_{0.4}Co_{0.6}Fe_{0.4}O_{3-δ} nanofibers (LSCF6464) with diameter in the range of 54-71 nm and a high surface area-volume ratio of 24.2 m² g⁻¹ output a potential of 647 mV at 10 mA cm⁻². It is superior to that of commercial powder-shape IrO₂ catalysts (660 mV) and LSCF (786 mV). It was demonstrated that LSCF6464 nanofibers exhibit approximately eight times higher inner activity compared to that of IrO₂, and triples that of

LSCF. Among all the explored nanofiber samples, it has been shown that LSCF6464 nanofibers provide the highest electrocatalytic activity and reliability. These fibers can maintain their potential throughout a 3-h period. In the same test environment, an IrO₂ nanofibers sample demonstrated rapid potential increase and continuous degradation. It was therefore determined that LSCF6464 nanofibers are prospective OER electrocatalyst candidates for metal-air batteries.

In comparison, spinel-type catalysts are also widely sourced, low-cost, with defects in the structure and vacancies, otherwise interstitial atoms exist in the crystals. A new class of mesoporous Cr₂O₃ nanotubes (Cr₂O₃-MNT) was reported by He's group [120]. In this case, lithium-oxygen battery adopting the catalyst material as cathode exhibited a significant specific capacity of 8278.6 mAhg⁻¹ and a high cyclic performance of 50 cycles. These results indicate that novel Cr₂O₃ nanotubes can both promote the formation and dissociation of Li₂O₂. Alegre et al.[121] introduced bifunctional air electrode materials of Li-O₂ batteries that were also suitable for other MABs. They were synthesized using CNFs based on an electrospinning method and modified using CoO and Co to obtain CoO-Co/CNF. The prepared CoO-Co/CNF exhibited excellent stability and maintained 82% of its performance even if the cycle exceeded 100 h.

Using porous NiCo₂O₄ nanotubes, it was demonstrated that a hollow interior and porous wall with a large surface area-volume ratio could substantially enhance the rate performance, initial discharging capacity, and low overpotential. In a recent publication, Zhang et al.[122] synthesized NCO/CB (Figure 11a-e) and assembled an NCO/CB air cathode in lithium-oxygen battery with specific capacity of 5842 mAh g⁻¹ and charging capacity of 6022 mAh g⁻¹ (Figure 11f and g). One-dimensional hollow mesoporous structures played an important role for electron transmission capability. The diffusion of electrolyte and O₂ and the large contact area between electrodes and electrolytes were also beneficial with respect to enhance the specific capacity. In addition, the

assembled cell can operate steadily for 110 cycles at 2.4 V and capacity of 1000 mAh g⁻¹ (Figure 11h).

Figure 11 a, b) SEM of images for NiCo₂O₄ precursor nanofibers. c, d) TEM images of porous NiCo₂O₄ nanotubes. e1-e4) Elemental mappings show the porous NiCo₂O₄ nanotubes with three elements of Ni, Co, and O uniformly distribution. f, g) Discharging-charging curves of the integrated lithium-oxygen batteries with NCO/CB and CB electrodes at various cycles at 100 mA g⁻¹. h) The cycled performance of the CB and NCO/CB air electrodes 200 mA g⁻¹. Reproduced with permission.[122] Copyright 2015, The Royal Society of Chemistry.

Ramakrishna and his coworker[123] fabricated NiCo₂O₄ tube-in-tube structure nanofibers adopting a simple electrospinning method for lithium-oxygen battery cathode (Figure 12a). NiCo₂O₄ tube in the tube structure exhibited an improved specific capacitance compared to other samples (Figure 12b). The structure maintained a capacitance of 83% even at 20 A g⁻¹ of current density, which revealed a remarkable rate capability. Compared to NiCo₂O₄ nanotubes (28.0 m² g⁻¹) and a solid one-dimensional structure (12.9 m² g⁻¹), the relatively large surface area-volume ratio of the monoculture in the hollow tube structure was 47.3 m² g⁻¹, and it may account for the improved capacitance. As presented in Figure 12c, the NiCo₂O₄ tube/AC ASCS device in the tube exhibited good cycle stability and a specific capacitance retention rate of approximately 87%, even after 10000 cycles.

Figure 12 a) Ternary TMO process diagram with one-dimensional nanostructure, including tube, nanotube and solid one-dimensional nanostructure. b) SEM pictures of NiCo_2O_4 nanofibers. c) cyclability of NiCo_2O_4 tube-in-tube//AC ASCs device. Reproduced with permission.[123] Copyright 2015, American Chemical Society.

Examples of metal oxide-based fibrous structure materials as catalysts material in Li-O_2 batteries that were recently developed are listed in Table 4. Similar with metal-based CNFs preparation methods, electrospinning is also an important preparation process that can be used to prepare hollow-shaped fibers. The structure of hollow fibers is of great significance in improving their specific surface area. The fibers prepared via electrospinning are generally finer and more uniform compared to those using other traditional process. Moreover, the diameter of the fiber is an important parameter that affects

the electrical properties of cathode materials in batteries. A uniform diameter is beneficial to the stability of the electrical properties of the electrodes.

Table 4. Electrochemical performance of different metal oxide-based composites fibrous structure materials used for Li-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
SnO ₂ /NiO CNFs	Hairy-like structure	Forcespinning		100-300 nm / 171.24 m ² g ⁻¹	675 mAhg ⁻¹ after 100 cycles at 50 mA g ⁻¹	[124]
Hollow RuO ₂ CNFs	Macroporous interconnected hollow structure	Electrospinning pre-oxidation carbonization and de-templating	Heated at 240 °C for 20 min	Around 180 nm / 90.71 m ² g ⁻¹	Above 9000 mA h g ⁻¹ after 154 times at 1000 mA g ⁻¹ ;	[98]
ZIF-9 derived Co ₃ O ₄ /CNF composites	Three-dimensional cross-linked web structure	Electrospinning and post thermal treatment		Pores sizes (2–50 nm) /159 m ² g ⁻¹	760 mAh g ⁻¹ after 10 discharge-charge times at 800 mA g ⁻¹	[125]
Co ₃ O ₄ Nanofibers	Spinel structure	Grown on a Ni mesh			800 mAh · g ⁻¹ after 72 times at 2 mA · g ⁻¹	[126]
CoO-Co/CNF	Continuous and with rough surface	Electrospinning and carbonization in a helium flow		250–300 nm	82% of performance for the ORR after cycled for more than 100 h	[121]
CoMn ₂ O ₄ tube-in-tube NFs	Tube-in-tube hollow nanostructures	Single-spinneret electrospinning	600 °C for 2 h in air	227 nm/47.3 m ² g ⁻¹	Limited capacity of 1 A h g ⁻¹ for 115 times at 200 mA g ⁻¹	[123]
La _{0.6} Sr _{0.4} Co _{0.6} Fe _{0.4} O _{3-δ} nanofibers (LSCF6464)	Porous fiber structure	Electrospinning and calcination	Carbonized at 700 °C in air for 3 h	54-71 nm/24.2 m ² g ⁻¹	Potential (vs Ag/AgCl) of 647 mV more than 3 h at 10 mA cm ⁻²	[114]
Perovskite-based porous La _{0.75} Sr _{0.25} MnO ₃ nanotubes (PNT-LSM)	Porous and hollow structure	Electrospinning technique and calcination	Calcination at 650°C for 3 h	300 nm/ 31.34 m ² g ⁻¹	Above 9000-11000 mAhg ⁻¹ of Specific capacities for 5 cycles at a 1000 mAhg ⁻¹	[119]

NiFe ₂ O ₄ -CNF	3D network structure	Electrospinning method	First pre-oxidation at 280 °C in air for 2 h then heated at 650 °C for 30 min in Ar atmosphere, finally at 800 °C for 1 h.	80-150 nm/ 363.40 m ² g ⁻¹ .	Maintained stably over 40 times of the discharge or charge process at 0.1 and 0.5 mA cm ⁻² .	[127]
La _{0.5} Sr _{0.5} CoO _{2.91} nanotubes	Highly hollow porous structure	Electrospinning	Calcined for 2 h at 800 °C with 1 °C min ⁻¹ of heating rate	About 200 nm/ 36.97 m ² g ⁻¹	7205 mAh g ⁻¹ after 85 times at 100 mA g ⁻¹	[128]
La _{0.5} Sr _{0.5} CoO _{3-x} (HPN-LSC)	Hierarchical mesoporous/ macroporous nanostructure	Electrospinning subsequently with post annealing	Calcinated at 750 °C for 3 h in air medium	Average diameter around 118.2 ± 1.2 nm/ 17.18 m ² g ⁻¹	500 mAh g ⁻¹ after 50 times at 0.1 mA cm ⁻²	[111]
Combination of La _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O ₃ with N-doped reduced graphene oxide (LSCF-PR/NRGO)	Porous three dimensional structure		Calcined at 700 °C for 3 h in air	100–300 nm /36.5 m ² g ⁻¹		[9]
Mn ₃ O ₄ /C nanofibers	Porous structure	1D Electrospinning and heat treatment.	First heat-treated at 280 °C in Ar gas, then at 500 °C in a mixture of Ar and ambient air	200–300 nm / 26.3 m ² g ⁻¹	Low overpotential (Mn ₃ O ₄ /C nanofiber + KB) (0.25 V) < [KB] (0.34 V) < [Mn ₃ O ₄ +KB]) at 0.6 mA cm ⁻²	[129]
δ-MnO ₂ /CCFs-K80-XC-72	Continuous and core-shell structure	Electrospinning facile liquid deposition and heat treatment	Heated at 270 °C for 0.5 h in air with a heating rate of 1 °C min ⁻¹ , subsequently	500 nm / 117.5 m ² g ⁻¹	1976 mAh g ⁻¹ stably sustained over 30 cycles at 100 mA g ⁻¹	[130]

			with carbonization at 900 °C for 2h in Ar.			
Mesoporous Cr ₂ O ₃ nanotubes (Cr ₂ O ₃ -MNT)	Hollow mesoporous tubular structured	Electrospinning and calcination	Drying at 500 nm / 53.4 m ² g ⁻¹ 60°C for 12 h ¹ under vacuum, then calcined at 500°C for 3 h in the air with 1 °Cmin ⁻¹ of heating rate		8278.6 mAhg ⁻¹ for 50 cycles at 100 mA g ⁻¹	[120]
Porous NiCo ₂ O ₄ (NCO) nanotubes	Hollow porous nanotube structure	Electrospinning and calcination	Calcinated at 450 °C for 2 h in air	About 100 nm/ 30.2 m ² g ⁻¹	1000 mAh g ⁻¹ over 110 times at 200 mA g ⁻¹	[122]
Carbon nano- paper (CNP) encapsulated by In ₂ O ₃ thin film (CNp@In ₂ O ₃) and catalytic RuO _x nanoparticles (NPs) (RuO _x - Np@In ₂ O ₃)	Porous structure	3D Electrospinning and Carbonization	Heat up to 1000 °C with heating rate of 10 °C min ⁻¹ and Maintained for 2 h in tube furnace surrounded by flowing Ar atmosphere	500 nm–3 um	1000 mAhg ⁻¹ for 165 times at 0.2 mA cm ⁻²	[131]
H-Fe ₂ O ₃ /CNT NFs	Hierarchical porous structure	Electrospinning and calcination	First sintering at 750 °C for 6 h in furnace with reducing atmosphere (H ₂ /N ₂ , 4/96%, v/v) then at 400 °C and heating rate of 5 °C min ⁻¹ for 1 h	166.92 m ² g ⁻¹ ¹	1000 mAh g ⁻¹ remained for 250 times at 500 mA g ⁻¹	[132]

2.5 Concluding remarks and discussion of Li-O₂ battery

In this section, CNFs, precious metal-carbon fibers, and non-precious metal-carbon fibers used for Li-O₂ batteries were presented. They utilize the reversible reaction of lithium metal and oxygen with high-capacity. The theoretical energy density can reach up to 11000 Wh/kg, far exceeding actual state of 200+ Wh/kg of a lithium battery. Therefore, it has gained popularity in academia and the

industry, and it is widely regarded as a subversive technology in the battery field. Many researchers have reported on the advantages of carbon nanofibers in lithium-oxygen batteries. The outstanding electrical conductivity, and easy-to-manufacture processes offer great potential for electrospinning fibrous structure applications in electrochemical energy storage devices. In the process, researchers continue to innovate and produce exciting results, and discussions on the future direction of this approach are ongoing. In summary, we have observed good application prospects of fibrous structure materials in Li-O₂ batteries.

3 Fiber shape material used for the Zn-O₂ battery

3.1 Working principle of the Zn-O₂ battery

Zn-O₂ battery generally comprises a zinc anode electrode, zinc plate, and zinc paste or zinc powder mixed with additive agents. In addition, they include a membrane separator and an air-cathode electrode made from carbonaceous material, metal, or metal oxide-based catalyst material, that are all integrated in alkaline electrolyte. During the charging and discharging process, the following reactions (equations 6-9) occur in the Zn-O₂ batteries:

The theoretical voltage of zinc-oxygen battery is about 1.65V, and the theoretical energy density is 5 times larger compared to the LiBs, which could achieve to a high value of 1086 Wh kg⁻¹[12]. Zn-O₂ batteries technology has been utilized for almost a century. In recent years, it has received increasing attention. Zn-O₂ batteries have a larger storage capacity than lithium-ion batteries, and

their cost is much lower, making them the most viable future option for electric vehicles.[133]

Compared to Li-O₂ batteries, all components of Zn-O₂ batteries are stable with respect to moisture, and the assembly process can be performed in air. It is much simpler to handle Zn-O₂ batteries compared to lithium-oxygen battery. This is because most of the latter components are unstable to water exposure. Since Li-O₂ cells must be assembled in an inert atmosphere, Zn-O₂ batteries have an advantage in that assembling can be done under ambient air conditions. It is much simpler to fabricate Zn-O₂ battery in contrast to Li-O₂ battery. Zn-O₂ batteries are also more competitively priced compared to Li-O₂ batteries because they use aqueous electrolytes, and zinc costs less than lithium. [134] In addition, the Zn-O₂ battery is more practical in terms of technical capabilities and practical application. To date, Zn-O₂ batteries have been used in hearing aids, smartphones, for electronics in defense devices, and laptops. [12] However, these batteries are sensitive to environmental conditions, especially temperature, and require a well-managed hydrophobic-liophilic balance (HLB) in the air electrode to reduce water evaporation losses. At present, the most critical issue associated with Zn-O₂ batteries is the slow oxidation reaction that results from the high overpotential of ORR and OER.[135, 136] Therefore, developing reliable, low cost and efficient fibrous-structure catalysts such as those used in the air cathode electrode for ORR and OER has the potential to facilitate wide-spread commercialization in near future.[134]

3.2 Carbon-based nanofiber-shaped materials used for the Zn-O₂ battery

3.2.1 Ordinary Carbon fiber materials for the Zn-O₂ Cathode Battery

Generally, it has been considered that the most efficient dual-function catalyst are materials that are integrated with precious metals substrates[8]. Whereas, the rarity, poor durability, and costly price limit the ORR and OER properties of these catalysts and hinder their industrial application. Similar

with lithium-oxygen battery, carbon-based electrode was found to be effective for Zn-O₂ batteries. For these batteries, commercial Pt/C catalysts show good performance. However, their widespread application is limited because of their high price and restricted accessibility. Combining the redox ability of polypyrrole (PPy) and the superior electrical conductivity of graphene. A one-step polymerization method of PPy fiber /RGO composite was introduced by Liu Using the modified Hummers method[137]. Go was extracted from natural graphite powder based on an exfoliation process. [138] The prepared PPy fiber/RGO composite exhibited both high energy density of 264 mWh g⁻¹ and high conductivity of 141 S cm⁻¹, with a high area-volume ratio of 561 m²g⁻¹ for the air cathode.

Recent works on N-doping of a carbon plane using a single electron have been reported with respect to enhance the ORR performance, which was comparable to that of commercial catalysts[139-141]. Cho et al. prepared [142] super-porous N-doped CNFs with remarkably high surface areas using a convenient and cost-effective electrospinning process using two component polymers including polystyrene (PS) and polyacrylonitrile (PAN). The polystyrene (PS) formed inner pores, and yielded porous structures resulting in large surface area-to-volume ratio (1271 m² g⁻¹ for N-CNF-1100). The obtained nanofibers firstly with oxidation for 1 h at 400 °C in ambient air, then subsequently calcinated at starting point at 800 °C increasing to 1200 °C under N₂ gas for 1 h. It was determined that 1100 °C was the best calcination temperature that led to the best performance (N-CNF-1100) with energy density plateau of 194 mW cm⁻². The high ORR electrocatalytic activity was ascribed to porosity and large surface area-volume ratio with the increasing number of graphitic-nitrogen groups in the carbon nanofibers. Yu et al.[143] synthesized metal-free and active N-doped CNFs aerogel as electrocatalysts for ORR in Zn-O₂ batteries. The N-CNFs were synthesized by pyrolyzing naturally abundant and green bacterial cellulose (BC). The process is presented in Figure 13a. The Zn-O₂ batteries assembled

with N-CNF aerogel showed outstanding ORR performance for electron-transfer and stable electrochemical performance. The latter far exceeded the performance of RGO aerogels, NH₃-treated CBs, carbon nanotubes most previously proposed non-metal catalytic material. The excellent performance of this Zn-O₂ battery was resulted from the large BET value of 916 m²/g and 3D fibrous net-structure of BC, resulting in numerous N-containing active sites (Figure 13b-d). The results showed that this type of N-CNF aerogel is feasible as the replacement of noble metal catalysts.

Figure 13. a) preparation steps for N-CNF aerogels. b, c) TEM and SEM of N-CNF aerogels for fibrous net-structure. d) HRTEM picture of a single N-CNF. Reproduced with permission.[143]

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Zhang and his coworker [144] stripped graphene in situ using carbon paper and treated it with high-temperature ammonia to prepare a novel bifunctional pyridine-n (PN) bifunctional electrocatalysts containing a new type of nucleus-shell structure DN-CP@G defect. The fabrication process of DN-CP@G involves several steps. First, the original carbon paper-based on graphite

carbon is prepared in a concentrated acidic solution to remove impurities, then heated in an oil bath and carbonized in an inert gas atmosphere. This process produces an abundance of defective sites. Finally, N-CP@G nanocomposites are successfully doped using ammonia treatment. With special 3D porous structure and ORR/OER activity, the DN-CP@G is assembled as a supporting cathode in a Zn-O₂ battery. The battery can maintain a high open circuit voltage (1.43 V) for a long time. It was demonstrated that the maximum energy density could reached 135 mW cm⁻². Based on the consumed zinc foil, the specific capacity at 20 mA cm⁻² is estimated to be 591 mA h g⁻¹. It demonstrated that the cell with DN-CP@G catalytic air cathode exhibited remarkable discharge property. Pt/C+Ir/C electrodes showed better performance compared to the DN-CP@G electrodes in the initial cycle test. However, the performance of DN-CP@G cathode gradually exceeded it after repeated continuous cyclic tests. For the DN-CP@G electrode prepared during this experiment, the discharging and charging voltage can remain highly stable after a long cycle test. Even in the 250 th cycle, the voltage gap of the DN-CP@G cathode was only 0.98 V, which revealed that DN-CP@G exhibited high current efficiency and a long lifespan.

3.2.2 Flexible electronics and carbon fiber-based Zn-O₂ Battery

The Zn-O₂ battery is a promising retractable, flexible and rechargeable device with a high energy density, which is suitable in future electronic products such as wearable electronic products. Wang et al.[145] first reported on a fiber-shaped Zn-O₂ battery. By simultaneously designing cross-stacked, aligned and porous CNTs plates, the plates acted as a catalyst layer. The calibrated carbon nanotube plate has remarkable electronic and mechanical properties similar to an air cathode, which results in a battery with stable electrochemical performance under stretching and bending conditions, as well as high discharge and charge property under the constant ampere density. After testing of the Zn-O₂

battery, it was determined that there was no obvious damage in the structure for bending angles of 30, 60, 90, 120, and 150°. The discharging voltage was kept stable at 1 mA cm⁻². Moreover, a fiber-shaped Zn-O₂ battery provides good tensile property and could reach up to 10% elongation under stretching conditions with a cross-stacking angle of 80° and stable output performance.

Moreover, Wang et al.[146] developed a new kind of mesoporous CNF film(NCNF) that was integrated as cathode substrate in liquid Zn-O₂ cell. The NCNFs with a large surface area was performed using calcinating electrospinning Polyimide(PI) thin slices in Ar. After thermal decomposition, the yellow polyimide film became black, but its structural integrity remained basically unchanged. The obtained NCNF-1000 (pyrolyzed at 1000 °C) exhibited desirable properties including high flexibility and strong mechanical behavior, for example, a tensile strength and tensile modulus of 1.89 MPa and 0.31 GPa, respectively. The assembled Zn-O₂ battery with NCNFs showed an energy density of 776 W h kg⁻¹, a high open circuit voltage of 1.48 V, and a highest power density of 85 mW cm⁻², and simultaneously exhibited a slight charging and discharging voltage gap, high stability and reversibility. The Zn-O₂ battery consists of a separate NCNF1000 air cathode, basic polyvinyl alcohol (PVA) gel electrolyte, zinc foil anode, and a nickel foam current collector (for enhanced conductivity). The all-solid-state battery maintained stably at 1.78 V and 1.0 V of charge and discharging voltage potential of 6 h at 2 mA cm⁻², even if the configuration is folded back-to-front or bent at a large angle. Furthermore, the morphology and structure of the NCNF-1000 did not change significantly after 48 cycles.

Figure 14. a) Diagram for bendable Zn-O₂ cell. b) image of the Zn-O₂ cell assembled with PS-CNF mat as air electrodes. c) image of bendable Zn-O₂ batteries at different bending angles. d) Discharge profiles of the flexible Zn-O₂ battery with PS-CNF for more than 100 cycles, under bent (120°) and nonbent conditions. Reproduced with permission.[147] Copyright 2017, The Royal Society of Chemistry.

Lee et al [147] introduced an extensible and convenient method for in-situ growth of P and S doping carbon nitride fiber structural networks on a carbon cloth. The prepared PS-CNFs used as a three-dimensional flexible cathode for Zn-O₂ batteries exhibited a large surface area (1649 m² g⁻¹), high electric conductivity (165 S m⁻¹), outstanding tensile modulus (B 0.28 GPa), as well as tensile strength (B2.04 MPa). It output an energy density of 785 W h kg⁻¹ and high power density and discharging potential, and a long and stable lifetime without an obvious voltage drop over 240 h. A bendable solid-state Zn-O₂ battery was subsequently assembled from a separable air electrode made from an in situ grown PS-CNFs membrane, electrolyte utilized by a PVA gel polymer and an anode of Zn foil, to demonstrate the device's potential for portability, wearability, and flexibility, as shown in Figure 14a and b. When the battery was bent to different angles of 30°, 60°, 90°, 120°, and 150°, its intrinsic structure remained almost unchanged (Figure 14c). It showed that the potential voltage

remained unchanged before and after bending for a bending angled of 120° over 100 cycles. It revealed that the prepared flexible Zn-O₂ batteries with a PS-CNF air electrode could withstand a certain amount of external stress (Figure 14d). The PS-CNF-based catalyst as the cathode also exhibited superior dual-functional catalytic performance, reversibility that was better than that of most transition metals, precious metals and other metal-free catalysts. The cathode can provide a low over-potential and a long lifespan of more than 120 hours (over 600 cycles) assembled into Zn-O₂ battery. Furthermore, examples of other carbon-based fibrous structure materials as recently developed catalyst materials in Zn-O₂ batteries are summarized in Table 5. The fiber morphology and diameter obtained using different preparation processes are quite different. In addition, it is very important to control the sintering temperature, sintering time and temperature rising rate. This affects the final morphology, average diameter, porosity, specific surface area, and other parameters of the fiber, which then affect the electrical properties of the cathode material of the batteries.

Table 5. Electrochemical performance of different carbon and carbon-based fibrous structure materials used for Zn-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
N-CFs-1100	Churros-like porous structure	Electrospinning and pyrolysis	Carbonized in N ₂ atmosphere at 1000 °C	300-500 nm /1271 m ² g ⁻¹	Exhibiting a 194mW cm ⁻² for maximum power density	[142]
PPy fiber/RGO composite	Highly porous structure	One-step polymerization method	Heated at 60 °C in vacuum for 12 hours	70 nm/561 m ² g ⁻¹	264 mWhg ⁻¹ of energy density in 0.1 M phosphate buffer saline	[137]
Bacterial cellulose derived N-doped CNFs aerogel	3D nanofibrous network structure	Direct porolysis followed by NH ₃ activation	pyrolyzed under flowing N ₂ at 800 °C , reheat under an NH ₃ atmosphere at 700–	916 m2g ⁻¹ / over 10 nm	615 mAhg ⁻¹ at 10 mAc m ⁻² for potential 10000 cycles	[143]

900 °C.					
Nanoporous carbon nanofiber films (NCNFs-1000)	3D randomly entangled network structure	Electrospinning and pyrolysis	Pyrolysis temperature increased to 1100 °C under an Ar atmosphere	≈300 nm/ 1249 m ² g ⁻¹	Cycle over 83 h (500 ctimes) at 10 mA cm ⁻² [146]
PS-CNFs	3D interconnected mesoporous structure	In situ growth and polymerization reaction	Polymerization at 300 °C in N ₂ atmosphere	130-173 nm / 1649 m ² g ⁻¹	698 mA h g ⁻¹ for a 120 h period at 2 mA cm ⁻² [147]
O-CC-H ₂	Coaxial cable-like structure	Facile H ₂ -etching approach	950 °C during H ₂ -etching	Pores size less than 100 nm	Stably ran over 900 cycles (9 hours) at 2.0 mA cm ⁻² [148]
N-CNT-170	Interconnected	Chemical vapor deposition (CVD), spinning and a hydrothermal method	Heated at 170 °C		The voltage efficiency slightly drops to 60.5% after 250 times at 2 mA cm ⁻² [149]
N/F/P-CNFs	3D porous network structure	Electrospinning and annealing	Heated to 1000 °C in Ar with heating rate of 10 °C min ⁻¹	300-500 nm / 1230.1 m ² g ⁻¹	Over 200 cycles (400 s) for a cycle at 10 mA cm ⁻² [150]
DN-CP@G	3D porous structure	High Temperature Ammonia Treatment of Graphene by carbon paper in-situ exfoliating	carbonized at 900 °C under inert atmosphere for 2 h	67.3 m ² g ⁻¹	Over 250 times at 5 mA cm ⁻² [144]
N, F, and B ternary doped CNFs (TD-CFs)	Continuous intersected structure	Electrospinning and annealing	Pyrolyzed at 1000 °C with heating rate of 10 °C min ⁻¹ in Ar	200-300 nm / 14.2 m ² g ⁻¹	Over 120 cycles at 10 mA cm ⁻² [151]

3.3 Metal-based fiber shape materials used in Zn-O₂ battery

3.3.1 Ordinary metal-based fiber materials for Zn-O₂ battery

Similarly to Li-O₂ batteries, the development of air electrode fiber materials for non-noble metal-based Zn-O₂ batteries is very important in addressing the problems of scarcity of metal resources,

high cost, and low output. In this respect, it can be predicted that CNFs based on non-noble metal catalysts and electrodes will be indispensable components of Zn-O₂ batteries in near future. Among different metals, Co is supposed to be potential for both LiBs and metal-based air battery. In many recent publications, cobalt-based sulfur compounds have been investigated for OER and ORR applications for bifunctional performance.

Furthermore, the combination of Co₄N and ORR active Co-N-C (transition metal (Fe or cobalt, etc.)-N)-N is generally supposed to be the best potential substitute for platinum-based catalysts, which may be an advancement for Co₄N for bifunctional OER/ORR electrocatalysis. Nonetheless, some challenges still need to be solved in the synthesis process, for example, the Co precursors and stringent synthesis conditions are temporarily incompatible in many studies. [152, 153] Therefore, there is a need for the effective design of a free-standing three-dimensional bifunctional OER/ORR electrode for Zn-O₂ batteries with the flexibility to exploit Co₄N and Co-N-C.

In this regard, Zhang et al.[42] developed an approach for in-situ coupling of Co₄N in series with Co₄N and interwoven N-C fibers (Co₄N/CNW/CC) via thermal decomposition of a special pearl-shape Zif-67/polypyrrole nanofiber network based on carbon cloth. (Figure 15a). As observed in the SEM images, the PPy nanofibers are intertwined to fabricate a 3-D fiber architecture and numerous Zif-67 particles are wrapped around the fibers, which resembles a pearl necklace. After calcination, the three-dimensional network architecture and polyhedron structure maintained a good original structure (Figure 15b-d). With the interaction of Co₄N, Co-N-C, and the three-dimensional architecture, the integrated flexible bifunctional air electrode exhibited stable OER and ORR electrocatalytic activity, and the current density maintained over twenty hours. Importantly, the prepared battery exhibited a low discharging-charging voltage gap of 1.09 V at 50 mA cm⁻² and a long lifespan of more than 136 h over 408 cycles (Figure 15g). Moreover, the discharging voltage

maintained the initial structure under bending at 0.5 mA cm^{-2} for different angles (Figure 15e and f).

Figure 15. a) Synthesis schematic of $\text{Co}_4\text{N/CNW/CC}$. b-d) SEM images of $\text{Co}_4\text{N/CNW/CC}$. e) current discharging-charging cycle lines at three different current density. f) Discharge plots after several angles bending for every 12 min. g) constant current discharging-charging cycle plots for carbon cloth with the $\text{P-Co}_4\text{N/CNW/CC}$, $\text{Co}_4\text{N/CNW/CC}$ electrode and Pt/C catalyst on carbon cloth of Zn-O_2 batteries at 10 mA cm^{-2} . Reproduced with permission.[42] Copyright 2016, American Chemical Society.

It is noteworthy that the OER activities of cobalt sulfide carbon materials are still low and unsatisfactory for practical application. Due to the synergistic interaction between different catalytically active materials, it is speculated that the transition metal-oxide or metal-sulfide bonding to the doped and co-doped carbon heteroatoms helps to increase the electrocatalytic activity.[154, 155]. Subsequently, doping cobalt sulfide could offer more active sites for N and S co-doped carbon

nanostructures, thus significantly enhancing the OER and ORR performance. Previous studies included NiCo_2S_4 , $\text{Fe}_{0.5}\text{Co}_{0.5}\text{S}$, CoS_2 for OER/ORR activity[155-157] and Co_3S_4 , Co_9S_8 , and $\text{Zn}_{0.76}\text{Co}_{0.24}\text{S}$ for OER/HER activity[158-160].

Therefore, Zhong [161] introduced a two-step synthesis method for Zn-Co-S nanostructures, including nanoneedles (NN), nanoplates (NP) and nanoplates (NS) on carbon fiber paper (CFP) substrates. Zinc-cobalt-S nanostructures were obtained using a straightforward hydrothermal method, and subsequently with a thermal vulcanization procedure, as shown in Figure 16a. Prior to the hydrothermal process, three different forms of zinc-cobalt (NN, NP, and NS) were fabricated through adjusting their urea and NH_4F dosage. A rechargeable Zn- O_2 battery based on Zn-Co-S/NN/CFP is comparable to marketed Pt/C and RuO_2 mixed catalysts with the highest discharging-recharging performance. The initial charging potential using this electrode is 1.18 V and the over-voltage is 0.85 V with a high round-trip efficiency, demonstrating excellent dual-functional catalytic ability (Figure 16b). Surprisingly, the cell with Zn-Co-S/NN/CFP exhibited stable cyclability for over 200 periods as shown in Figure 16c, compared to the 55 cycles of Pt/C+ RuO_2 . Simultaneously, the voltage is 1.71v and the current density of decomposed water is 10 mA cm^{-2} when assembled as positive and negative electrodes for water electrolysis. Numerous H_2 and O_2 bubbles produced could be seen from the electrode surface with scanning rate of 5 mV S^{-1} illustrated in Figure 16d. The service endurance of the aforementioned water diversion system was assessed at 1.90 V using a continuous polarization of 36000 s. Moreover, as shown in Figure 16e, the decay of activity for Zn-Co-S/NN/CFP was relatively more moderate compared to the Pt/C+ RuO_2 . In the entire water separation unit, zinc-cobalt-sulfur-nitrogen/CNF as electrodes exhibited outstanding stability. The results indicated that fabricating and controlling the micro-nanostructure is an effective method for the fabrication of elemental-rich catalysts, and demonstrated that Zn-Co-S/NN/CFP is potential for high-performance

MABs hydro-electrolysis as functional electrode. Moreover, the activity provides the comparability to most noble metal-based catalytic materials.

Figure 16. a) Synthesis diagram of Zn-Co-S NS, NP, and NN on CFP. b) current and voltage polarization profiles of the Pt/C + RuO₂ catalyst and the Zn-Co-S/NN/CFP at 10 mA cm^{-2} . c) Discharging-recharging profiles of Zn-Co-S NN/CFP and Pt/C + RuO₂ as catalysts assembled Zn-O₂ batteries with 400 s per cycle testing. d) the polarized plots of Pt/C+RuO₂ and Zn-Co-S/NN/CFP + Zn-Co-S/NN/CFP. e) time amp responses for 2 integral water separation systems. Reproduced with permission.[161] Copyright 2017, American Chemical Society.

Inspired by the three-dimensional pillar frame fabricated using the pillar layer and the synthesis method of semiconductor nanocrystals, Zhang et al [162] developed a highly efficient Co/CoXSY@S,N- porous Co-doped CNF electrode catalyst. Using the controlled growth of [Co (TDC)(BPY)] N-MOFS solvent effect, the bifunctions of ORR and OER can be obtained. As shown

in Figure 17a, by using S-N that involves Co-MOFs as the precursor, further high temperature pyrolyze was conducted to obtain a precise and controllable doping ratio of S and N. In addition, co-existing Co/Co₉S₈/Co₃S₄ nanocrystals were formed in graphitized carbon structure providing with controllable porous structure and specific surface area. The results revealed that CO/Co₉S₈/Co₃S₄@S prepared using methanol at 120 °C and N porous CNFs at 800 °C have a large surface area-volume ratio (212.1 m² g⁻¹), remarkable mesoporous structure, and biological functional group activity, high power density, and great application stability. During the discharging process, the Zn-O₂ batteries synthesized using Co/CoxSy@SNCF-800 exhibited a high ampere density and comparative to that of Pt/C-RuO₂ Zn-O₂ batteries at the same testing voltage of 1.0 V (Figure 17b). The open circuit voltage was 1.37 V for Co/CoxSy@SNCF-800 (Figure 17c). In the charging-discharging process, the current density of the Co/CoxSy@SCNF-800-based Zn-O₂ battery was similar to the Pt/C-RuO₂ catalytic material, reflecting good charge/discharge performance. (Figure 17d). Durability measurement showed that the starting charge-discharge potentials of the Co/CoxSY@SCNF-800-based rechargeable Zn-O₂ batteries were 1.96 V and 1.26 V, and their initial charge-discharging potentials were 1.98 V and 1.23 V after 468 cycles (Figure 17e). The results demonstrated that the graphitic carbon structure encapsulated with Co/CoxSy nanoparticles could improve the stability of catalysts.

[162]

Figure 17. a) Schematic illustration of Co/CoxSy@SNCF-800. b-c) The influence curves of different catalysts on power density distribution and open circuit voltage. d) The influence curves of different catalysts on discharging and charging polarization of Zn-O₂. e) stability testing of Zn-O₂ battery assembled with Co/CoxSy@SNCF-800. Reproduced with permission.[162] Copyright 2017, American Chemical Society.

3.3.2 Flexible Electronics and metal fiber-based Zn-O₂ Battery

In recent years, Zn-O₂ batteries fabricated with CNFs adopting metal/metal-oxide catalyst materials were widely studied based on their potential to impart flexibility in wearable devices. A new type of nanofiber bifunctional electrocatalytic thin film was developed by Wang's group[163]. The film was composed of Mg sulfide and cobalt coated with N-doped CNF (CMS/NCNF), fabricated using an electrospinning method, and subsequently carbonized. The assembled Zn-O₂ batteries made of thin-film present excellent long-term stability and catalytic performance, and showed stable performance under harsh bending conditions. To investigate the performance under harsh bending conditions, the CMS/NCNF unbonded pads were pressed onto foam nickel and assembled into a binder-free solid-state Zn-O₂ battery (Figure 18a). At three different bending angles, the battery

showed good flexibility and uniformity (Figure 18c and d). Figure 18e depicts the excellent charging and discharge durability at 5 mA cm^{-2} for flat and rolled batteries that lasted for more than 7 hours. As a demonstration example (shown in Figure 18b), two CMS/NCNF batteries are linked together and wound around the finger while maintaining the power supply to LED lamp.

Figure 18 a) The assembled solid-state Zn-O₂ cell. b) testing for the assembled battery. c) discharging and charging polarization plots at several bending angles. d) photography of the bending angle. e) A constant current discharging/ charging cycle curves at 5 mA cm^{-2} at different bending angles. Reproduced with permission.[163] Copyright 2017, The Royal Society of Chemistry.

Currently, porous architectures of active materials embedded with CNFs and the controllable preparation of CNFs with desirable mechanical attributes remain a challenge. Recently, a traditional and scalable method was reported for the preparation of a channel-rich and porous Fe₃C@FeNC-CNF film.[164] The process was followed by the pyrolysis of electrospun optimized PAN/CA nanofibers (Figure 19a). The needleless electrospinning apparatus could mass-produce nanofibers mats (Figure

19b-d). The synthesized Fe-CACNF film showed large surface area-to-volume ratio and good flexibility (Figure 19e and f). The micro/mesopores and channels in Fe-CACNFs provide a large number of fast mass transfer pathways and active centers for interfacial reactions. The excellent performance of Fe-CACNFs enabled ORR to have higher reliability and catalytic activity than Pt/C. It resulted in strong durability and a porous structure, and is promising as a flexible Zn-O₂ battery catalyst. Furthermore, examples of metal-based fibrous structure materials as catalysts in Zn-O₂ batteries developed recently are listed in Table 6. Among the various preparation strategies, in-situ growth and freeze-drying are two commonly used and mature synthetic methods. Fe and CO are two commonly used metal raw materials. They are not only low-cost and abundant, but their oxides also have bifunctional catalytic properties.

Figure 19. a) preparation illustration of Fe-CACNFs. b) photography of Fe-NFF prepared by needleless electrospinning with the size of 180×80 cm. c-d) image of the stabilization and carbonization of Fe-NFFs. e-f) images of the obtained flexible Fe-CACNFs. Reproduced with permission.[164] Copyright 2017, The Royal Society of Chemistry.

Table 6. Electrochemical performance of different metal-based composites fibrous structure materials used for Zn-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
(Fe-CA /CNFs)	Porous and channel-rich structures	Free-surface electrospinning and carbonization	Heated at 800 °C in N ₂ for 2 h with the heating rate of 5 °C min ⁻¹	116.40 m ² g ⁻¹	For 1000 cycles at an accelerated scanning rate of 50 mVs ⁻¹	[164]
Fe1Ni1-N-CNFs	3D porous cross-linked microstructures	Electrospinning technique	Pyrolyzation at 800 °C for 2 h with the heating rate of 5 °C min ⁻¹ in N ₂	98–195 nm/ 252.3 m ² g ⁻¹	A lower onset potential of 1.528 V and a smaller charging transfer resistance of 48.14 Ω.	[165]
Fe-N-CNF	Typical mesoporous structure	Hydrothermal carbonization and pyrolysis	Pyrolysis at 800 °C under N ₂ atmosphere	130 nm/ 425 m ² g ⁻¹	Half-wave potential of -0.140 V and onset potential of -0.02 V and	[166] 重新引用
Co ₄ N/CNW/CC	Pearl-like and 3D Interconnected network structure	In situ coupling of strung Co ₄ N and intertwined N-C fibers	Carbonized at 700 °C under a N ₂ atmosphere	100 nm/ 226 m ² g ⁻¹	More than 408 cycles 50 mA cm ⁻²	[42]
MnS/Co encapsulated by N-doped CNFs (CMS/NCNF)	3D nanoporous network structure	Electrospinning and carbonization	Calcined at 800 °C in Ar atmosphere for 2 h with 5 °C min ⁻¹ of heating rate	200 nm	Cycle over 100 h at 10 mA cm ⁻²	[163]
C-NiPAN900-300		Electrospinning and pyrolysis	Pyrolyzed at 900 °C under a nitrogen atmosphere , then thermally annealing in air at 300 °C	100–500 nm /	Run over 40 times stably at 5 mA cm ⁻²	[167]
Co/CoxSy@S NCF-800	Porous pillared-layer MOF structure	Simple synthesis	Pyrolysis at 800 °C	100–150 nm/ 212.1 m ² g ⁻¹	Discharge/charge potentials were 1.98 and 1.23 V after 468 cycles	[162]
Zn-Co-S nanoneedle	Nanoneedle nanostructure	Facile hydrothermal method and	Calcined to 500 °C for 1 h at a temperature rate of	25.6 m ² g ⁻¹	Long lifespan (~200 cycles), high efficiency (58.1%),	[168]

		thermal sulfidation	5 °C min ⁻¹		and low overpotential (0.85 V) at 10 mA cm ⁻²	
HP-Fe-N/CNFs	Interconnected hierarchically porous structures	Facile pyrolysis	Heated under N ₂ atmosphere to 900 °C for 2 h with heating rate of 2 °C/min	600–800 nm/ 569.6 m ² g ⁻¹	Only 14 mV shift in E1/2 and 0.22 mA cm ⁻² decrease in the limiting current density for HP-Fe-N/CNFs after 1000 cycles	[169]
NiCo@N-CNFs	Tangled porous structure	Electrospinning and calcination	heated in N ₂ atmosphere at 800 °C for 5 h in a tube furnace with 2 °C min ⁻¹ for heating rates	≈100 nm	Run 7 h continuous operation at around 2.57 mA cm ⁻²	[170]
Co-NCNT/Ng	Hierarchical porous structure	One-pot pyrolysis of the mixture of Co precursor, dicyandiamide and glucose	pyrolyzed at 550 °C for 2 h and further heated to 900 °C for 2 h at Ar atmosphere	20–40 nm	Over 5000 cycles.at a sweep rate of 100 mVs ⁻¹	[171]
(Co-Fe carbonate hydroxide hydrate in-situ loaded on 3D porous carbon) ClCHH/Cl@C	3D porous structure	A freeze-drying method then with a calcination	Heat up to 800 °C in N ₂ atmosphere for 1 h	358.5 m ² g ⁻¹	Over 2000 cycles at 10.0 mA cm ⁻²	[172]
porous Cu/N/C fibers	Mesoporous structure	Chemical process and carbonization	Carbonized at 900 °C under Ar atmosphere for 2 h with heating rate of 5 °C/min	500 nm/ 241.22 m ² g ⁻¹	Discharge voltage remained at 1.37 V for over 4000 seconds at 50 mA cm ⁻²	[173]
Fe@C-NG/NCNTs	Framework active sites structure from bamboo-like CNT	Freeze-drying, dicyandiamide, HF leaching	Heated to 800 °C in N ₂ for 1 h at a rate of 3 °C min ⁻¹	117.6 m ² g ⁻¹	Over (1000 cycles) 40 h without obvious voltage change at 10 mAcm ⁻²	[174]
CNF@Zn/Co NC	Core-shell structure	An in-situ growth method	Pyrolysis in N ₂ at 800 °C	500 nm on average / 489.1 m ² g ⁻¹	Energy density of 878.9 Wh kg ⁻¹ , and cycled over 150 h at 2 mA cm ⁻²	[175]

3.4 Metal oxide-based fiber-shaped material used for Zn-O₂ battery

3.4.1 Ordinary metal oxide-based fiber materials for Zn-O₂ battery

As previously stated, the developing of OER and ORR bifunctional electrocatalysts with high catalytic activity is a significant practical issue of Zn-O₂ batteries. The conventional air electrode of Zn-O₂ cell generally need physical deposition of active substances onto carbon gas diffusion layer (GDL) by means of dropping or spraying.[176, 177] These physical procedures usually need auxiliary substrates that degrades the cell property.

To tackle these problems, especially the removal of ancillary materials, Lee et al.[178] introduced a convenient template-free method that was used to synthesize porous Co₃O₄NW arrays that were directly mounted on the SS network current collector without further processing, then packaged as cathode in Zn-O₂ cells. The advanced electrode preparation process avoided some common physical deposition processes such as spraying and dripping. The morphology revealed that the bare SS network collector was densely coated with Co₃O₄NW to form a three-dimensional unbonded NW array without the binder. The results indicated that Co₃O₄NWS was tubular with average diameter of 300 nm, length of 15 μ m, and hollow central diameter of 50 nm. They also revealed circular rounded surface modulation and grew randomly across some of the wires. The large surface area of each unit volume improved the electrocatalytic performance, and was mainly attributed to the facile chemical synthesis method. Furthermore, the Co₃O₄NW was a tubular circular center with a diameter of 50 nm, which resulted from the Kirkendall effect during the NW formation. The advanced electrode exhibited excellent charging/discharging potential at a high current compared to the traditional GDL electrode.

When the SS mesh electrodes were assembled into a single Zn-O₂ battery, they exhibited superior

discharging/charging potentials for ampere density over 20 mA cm⁻². Initial charging/discharging potentials of the direct grown Co₃O₄ NW network electrode were 2.0 V and 0.98 V. In contrast, the conventional Co₃O₄ NW and Pt/C coated gas diffusion layer electrodes exhibited an apparent potential reduction over 100 and 60 times. The great performance was mostly due to the direct coupling CO₃O₄-NW-array of the stainless-steel network that maintained its initial structure and exhibited high activity even after operating for a significantly long period.

Despite these promising results of precious metal or the alloys, their low output and price of N-CNTs and the required precision manufacturing of N-G hinder their practical application. To overcome some of these existing challenges, it is necessary to develop simple, low-weight, cost-effective, and large-scale approaches to produce efficient bifunctional catalysts. Theoretically, the different ways to implement an ORR/OER bifunctional system are as follows: i) a single active layer as a dual functional catalyst; ii) using two electrodes with different catalysts, one for ORR and the other for OER; or iii) a dual-function cathode using two spaced separate active layers inserted using two different catalysts, et al [179].

In consideration of the first approach, to develop a simple and scalable method for bifunctional metal-oxide electrode material, Li et al. reported on metal-based CNFs decorated using Co₃O₄ nanoparticles for the development of composite bifunctional air-cathode catalysts for Zn-O₂ batteries.[180] The bifunctional catalytically active Co₃O₄ NP decorated with CNFs was prepared using an electrospinning method followed by heat treatment. Finally, they were adopted as cathodes without use of conductive additives, adhesives and collectors. Electrochemical tests revealed that the Co₃O₄ NP decorated CNFs was an efficient bifunctional oxygen catalyst and demonstrated superior performance for OER and ORR. There was no apparent increase or voltage-drop even after a continuous period over 160 cycles, the voltage gap was still stable at ~ 0.7 V. This cathode system

had a longer lifespan and higher reliability, compared to the Pt/C electrode assembled in the air-cathode. It is significant that the Co_3O_4 NP decorated CNFs mat without any further modification was adequate for use as an air electrode and can be easily mass-produced. For the second approach, spatial separation of the OER and ORR positions in the cathode is an effective technique. Birgit Pichler et al. [181] developed two kinds of oxide catalysts of spinel-type (NiCo_2O_4) and perovskite-type ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{-Fe}_{0.8}\text{O}_3$) CNFs, for use in bifunctional air electrodes. The bifunctional air electrode of the Zn- O_2 battery showed stable long-period performance for pulse charging/discharging measurements (2 hours per cycle). The stable charging/discharging potential was realized in 700 hours (1 month) and 325 cycles by using a double catalytic bifunctional air electrode to supply oxygen.

3.4.2 Flexible electronics and metal oxide fiber-based Zn- O_2 battery

Among the different catalysts, metal and metal oxide-based catalysts have attracted significant attention because of their flexible and stretchable Zn- O_2 batteries based on abundant and low-cost elements. In particular, metal-oxide fiber shape materials are considered to be suitable candidates in flexible Zn- O_2 batteries with respect to the low price, bifunctional activity and abundance.[182, 183] Recently, Chen et al. [184] introduced a binder-free high-performance air electrode based on the method of in-situ growing an ultra-thin Co_3O_4 layer in carbon cloth (ultra-thin $\text{Co}_3\text{O}_4/\text{CC}$). The well-crystallized ultrathin $\text{Co}_3\text{O}_4/\text{CC}$ was carbonized from ultrathin $\text{Co}(\text{OH})_2/\text{CC}$. A flexible monolithic Zn- O_2 battery was assembled using the ultrathin $\text{Co}_3\text{O}_4/\text{CC}$ cathode. First, a continuous Cu film was produced via thermal evaporation on the back PET, and then via electrodeposition for Zn. Finally, the deposited zinc and air electrodes were combined with the hydrogel electrolyte. Higher discharge voltages and lower overpotentials were observed for charging/discharging processes at higher current densities. Discharge and charge potentials were remarkably lower during the testing of the cycling

performance. Furthermore, both maintained their initial structure at three folding radii of 51, 28, and 13 mm. For Zn-O₂ batteries integrated with the ultra-thin CO₃O₄/CC air electrode, the discharge curve did not change significantly after bending for 300 cycles. This indicated that the self-made flexible Zinc-oxygen cell could operate propitiously with mechanical bending stress.

Moreover, examples of metal oxide-based fibrous structure materials used in recently developed Zn-O₂ batteries are listed in Table 7. Perovskite and spinel-type are commonly used materials to fabricate metal oxide-based air electrode. The diameter of different fibers prepared using different processes varies greatly. They also have a great influence on cycling characteristics, capacitance, and other electrical properties. Perovskite oxides with numerous morphologies such as nanotubes, nanorods, nanocubes, nanosheets, and nanofibers with mesoporous structures, can be prepared using different preparation methods. Many perovskite-type oxides are promising bifunctional electrocatalysts. However, it is necessary to simultaneously increase the surface area-volume ratio and electronic conductivity of perovskite-type oxides so that they can replace precious metals as active catalysts. The development of highly active electrocatalysts will likely be an area of intense future research for in situ growing of perovskite-type oxides on substrates with high porosity and high conductivity. Improving the specific surface area and conductivity for the perovskite-type oxides will help to replace precious metals as active catalysts. The development of highly active electrocatalysts will be a hot topic for the in-situ growing of perovskite-type oxides on substrates with high porosity and conductivity in the future.

Table 7. Electrochemical performance of different metal oxide-based composites fibrous structure materials as cathodes for Zn-O₂ batteries.

materials	Fiber structure	Preparation strategy	Heat process	Diameter & surface area & pore size	Electrochemical performance	Ref
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mesoporous Co ₃ O ₄ NW	Tubular with circular hollow center structure	template-free method		300 nm	Initial charging potentials was 2.0 V and discharging potentials was 0.98 V, stably cycled over 100 cycles at 50 mA cm ⁻²	[178]
Co ₃ O ₄ nanoparticle s-decorated (CNFs) C- CoPAN900	Interconnect ed 3D architecture	Electrospinning and annealing process	first heated in a N ₂ environment at calcined to 900 °C at 5 °C min ⁻¹ of heating rate for 1 h, then re-heated in air to 200 °C for 1.5 h		Cycled over 160 at 2 mA cm ⁻²	[180]
NiCo ₂ O ₄ spinel CNFs	Network structure	Direct impregnation on carbon nanofibers or nickel powder	Calcined at 375 °C in air atmosphere at heating rate 5°C min ⁻¹ for 2 h	150 nm	Stably for 400 h (170 cycles) at 50 mA cm ⁻²	[181]
La _{0.6} Sr _{0.4} Co 0.2Fe _{0.8} O ₃ CNFs	Network structure	Homogeneous dispersion by ultrasonic mixing and then with evaporation	calcined at 300 °C under the pressure of 150 kg cm ⁻² for 20 min in ambient air		Stable for more than 700 h (300 cycles) at 50 mA cm ⁻²	[181]
MnCo ₂ O ₄ /N MCNA	Array and porous structure	Hard templating and surfactant self- assembly approach	First pyrolyzed at 350 °C at a heating rate of 1 °C min ⁻¹ for 2 h in N ₂ , then carbonized to 900 °C at 5 °C min ⁻¹ of heating rate in N ₂ for 2 h	644 m ² g ⁻¹	Reached 100 cycles at 10 mA cm ⁻²	[185]
Mesoporous PrBa _{0.5} Sr _{0.5} Co ₂ - xFe _x O _{5+δ} nanofiber (PBSCF- NF)	Mesoporous structure	Electrospinning and carbonization	annealing at 1100 °C in air for 12 h	300 nm/ ~20 m ² g ⁻¹	Cycled over 150 at 10 mA cm ⁻²	[186]
Ultrathin	Mesoporous	Electrodepositi	pyrolyzed at		1.95 V charge	[184]

Co ₃ O ₄ /CC	3D network structure	on annealing	400 °C for 1 h in ambient		voltage and 1.03 V discharge voltage and at 2 mA cm ⁻²
De-Li (Ni _{0.2} Co _{0.6} Mn _{0.2})O ²	Multi-shelled hollow structure	A simple electrochemical Li ⁺ extraction and intercalation.	Pyrolysis in air	10-15 μm	A stable voltage plateau up to 441 h at 5 mA cm ⁻² [187]
Pod-like Co/CoOx-N-C	Hierarchical porosity pod-like structure	electrospinning and pyrolysis	Carbonized up to 800 °C at 5 °C min ⁻¹ of heating rate under N ₂ atmosphere for 1 h	370 nm / 306.7 m ² g ⁻¹	610 mAh g ⁻¹ at 10 mA cm ⁻² [188]
NiCo ₂ O ₄ @MnO ₂ -CNTs	Highly porous structure	A hydrothermal process	Calcined in air at 350 °C for 3 hours	120 nm / 162 m ² g ⁻¹	794 mAh g ⁻¹ for 380 hours (2290 times) at 10 mA cm ⁻² [189]
Hortensia-like MnO ₂ /CNTs	Hortensia-like and interconnected network structure	A simple two-step hydrothermal reaction	Drying at 70 °C for 6 hours, then heated at 350 °C for 1 hour	345 m ² g ⁻¹	Stably for 500 hours at 20 mA cm ⁻² [190]

3.5 Concluding remarks/discussion of Zn-O₂ battery

Zn-O₂ batteries are pollution-free and safe. In addition, they have high energy density, low cost, and consist of renewable substrates. The discharging current of the Zn-O₂ cells is subjected to the oxygen adsorption and diffusion speed of the activated carbon electrode. The charge of the battery is generally more than three times larger than that of the same volume of zinc-manganese battery. Large Zn-O₂ batteries typically have a charge of 500 to 2,000 mAh and are used primarily for railway and marine light fixtures. The button-shaped Zn-O₂ battery has a charge of 200 to 400 mAh and is widely used in hearing aids. If Zn-O₂ fuel cells are widely used, air and noise pollution can be greatly reduced considering the abundant zinc reserves in the world.

To date, much research has been performed on catalysts, but industrial mass production is difficult to achieve in most cases. However, we have observed broad application prospects in fiber

structure materials. In contrast, fibers have great advantages such as simple preparation method, high fiber porosity, good uniformity, a large surface area-volume ratio of carbonized fibers, high electrical conductivity, and high yield.

4 Nanofiber-shaped material used for Mg-O₂ battery

4.1 Working principle of Mg-O₂ battery

Among different kinds of MABs, there are fewer studies on Mg-O₂ batteries than Li-O₂ and Zn-O₂ batteries.[191] The basic structure of an Mg-O₂ cell comprises Mg anode, air cathode, and electrolyte. The reaction equations (10-12) of the Mg-O₂ battery was shown below:

In battery discharging process, Mg at positive electrode is oxidized to Mg²⁺, and O₂ at the cathode reacts with electrons and H₂O to reduce to OH⁻. The theoretical voltage is 3.1 V and the specific energy density is 6.8 kW h kg⁻¹.

4.2 Fiber-based materials for Mg-O₂ Battery

The Mg-O₂ battery technology has been known since the 1960s[192-194], but no major advancement has been made towards commercialization due to several unresolved technical challenges, such as precipitate control, hydrogen generation, electrolyte composition, air diffusion cathode material, anode material, and the high cost of the manufacturing processes. Based on theoretical analysis, Mg-O₂ batteries can provide high power density, high energy storage, and discharge voltage under neutral conditions[195]. In addition, magnesium metal has good bio-

absorbability, and Mg^{2+} is non-toxic to our human-being and environment.[196] However, the high polarization and low operating voltage compared to the theoretical value during the operational stage limits the wide application of Mg-O_2 batteries [197, 198]. The strong dynamics of air electrode ORR reaction would be a key breakthrough of Mg-O_2 batteries in the near future.

In a recently published work inspired by the fibrous structure of bufo eggs, Cheng et al. [191] successfully prepared Fe-N_x site-coupled mesoporous N-doped CNFs (OM-NCNF- FeN_x) and used them for advanced oxygen electrodes for Mg-O_2 batteries. This method was able to produce OM-NCNF- FeN_x in large quantities. The process of chemical structures of the ZIF-Fe thin layer coated in situ and the generated atomic Fe-N_x sites on OM-NCNF- FeN_x nanofibers were illustrated, as shown in Fig. 20.

Fig. 20 Effect of preparation process of fiber string structure of Bufo spawning apparatus on open mesoporous CNF.

A primary Mg-O_2 battery was integrated and illustrated in Fig. 21a to estimate the practicability of OM-NCNF- FeN_x in Mg-O_2 batteries similar with an air cathode. The SEM images of the Pt/C-Alfa and OM-NCNF- FeN_x inks coated carbon cloth was shown in Fig. 21b. The geometric structure of 3D nanofibers, porous channels, and networks for hierarchical interconnection inherent in the cathode catalytic layer facilitated air diffusion, and thus improved battery performance. Fig. 21c

showed the power density and polarization curves and of liquid Mg-O₂ batteries equipped with different catalysts. The open circuit voltage was approximately 1.77 V for a battery assembled with OM-NCNF-FeN_x. With the increase of current density, the constant current discharge voltage of all catalysts decreased steadily (Fig. 21d). The air cathode with OM-NCNF-FeN_x displayed a lower voltage in contrast to Pt/C-Alfa. The performance of Pt/C-Alfa begins to exceed that of Pt/C-Alfa with the discharge current density at 0.5 and 1 mA cm⁻² (Fig. 21e). When the battery capacity was tested, the OM-NCNF-FeN_x based cell (23 mAh g⁻¹) exhibited larger capacity than Pt/C-Alfa based cell (17 mAh g⁻¹). After discharging for approximately 16.7 h, OM-NCNF-FeN_x did not exhibit an obvious voltage drop, which is indicative of an exceptional air cathode with good durability (Fig. 21f). Furthermore, the discharge performance of OM-NCNF-FeN_x integrated Mg-O₂ micro-battery was very stable under different current densities, similarly to that of a liquid Mg-O₂ battery. The flexibility of this battery under bending without any obvious voltage changes was observed (Fig. 21g). In addition, this kind of single battery can also be assembled in serial. The open-circuit potential of solid-state Mg-O₂ micro-batteries connected in series of five is 7.83 V (Fig. 21h). Moreover, these miniature batteries were shaped into wristbands and no significant performance degradation was observed for a few hours after being utilized to light a LED of 3.5 V (Fig. 21i). These properties confirm that the OM-NCNF-FeN_x-equipped micro-battery could be used as a wearable and flexible power supply for applications in various biomedical and electronic devices.

Fig. 21 (a) Schematic diagram of Mg-O₂ batteries. (b) diagram and SEM images of Pt/C and OM-NCNF-FeNx ink on the carbon cloths. (c) Discharging and power density profiles of the Mg-O₂ batteries with various CNF and Pt/C-Alfa catalysts in DPBS. (d) constant current discharging profiles of Mg-O₂ batteries at different current densities in DPBS with various CNF catalysts. (e) Discharging profiles and (f) discharging capacity of the liquid Mg-O₂ battery in DPBS with OM-NCNF-FeNx and Pt/C-Alfa cathodes. (g) Discharge plots of solid-state Mg-O₂ battery with OM-NCNF-FeNx at 0.05 mA cm⁻², with bending strain every 30-40 min. (h) Open-circuit potentials of five assembled micro-batteries in series with OM-NCNF-FeNx(7.83V) (i) The image of red light-emitting diode (3.5V) driven by wrist band solid-state Mg-O₂ microbattery integrated with OM-NCNF-FeNx. [191]

In addition, carbon nanotube is also a promising material to prepare efficient electrocatalyst for Mg-O₂ battery. Zhao et al.[199] prepared bimetallic catalyst successfully with PdSn nanoparticles and the framework supported by multi-walled carbon nanotubes (MWCNTs) by borohydride reduction

method for magnesium-air battery. The MWCNT diameter was about 10 nm with agglomeration and growth of PdSn nanoparticles on its surface after heat treatment. The heat treatment was adopted at 200 °C under 95% Ar inert gas and 5% H₂ for 4 h, 8 h, 16 h and 24 h, respectively. After the performance testing, it revealed that the 24 h heat-treated PdSn/MWCNTs exhibited best ORR performance with outstanding stability of 1500 cycles and high diffusion-limited current density 6.27 mA cm⁻². After ran for 1500 accelerated degradation test, there was almost no change in the ORR LSV (Linear Sweep Voltammetry) curve which further demonstrated efficient heat treatment that enhanced the stability of PdSn/MWCNTs.

Moreover, a bifunctional hortensia-like MnO₂/CNTs catalyst was developed by Gong and his coworkers.[190] The hortensia-like MnO₂/CNTs was obtained by controlling the crystal structure and morphology electronic arrangement. It owned large BET surface area (345 m²g⁻¹) and strong interconnected conducting network. After the performance testing, the MnO₂/CNTs catalyst output remarkable durability (2000 cycles) and activity (ΔE : 0.850 V) for OER and ORR. The MnO₂/CNTs composite used in Mg-O₂ battery showed large specific capacities of 878 mAh g⁻¹ and power density of 614 mW cm⁻², and could stably ran for 70 hours. It revealed great potential for electrode catalyst of MABs in the near future.

4.3 Advancement and prospects of Mg-O₂ battery

Mg-O₂ batteries have many advantages and have wide application prospects. For example, environmental protection and energy conservation: magnesium and magnesium alloys have a low specific gravity. Magnesium metal fuel cells are not only high in energy, but also light in weight, and are very suitable as portable power supplies and field operation power supplies. Moreover, they are very safe to use: the magnesium air power source reacts with neutral salt water as the electrolyte. The reactants are metal magnesium alloy, water, and oxygen. Most of the products are magnesium

hydroxide precipitates that are non-toxic. The recovered magnesium hydroxide can be reformed into a magnesium ingot for recycling by burning. In addition, the fields of application fields are broad and include medium-power lighting, communication equipment, energy-saving products such as small household appliances, fixed outdoor lighting, emergency standby power supplies carried by vehicles or small ships, etc., that effectively reduce the cost of electricity and address the issues of power shortage, electrical problems and emergency backup power supply current stabilization.[200]

Although there is some progress with respect to the composition and performance of Mg-O₂ batteries, it also exist numerous challenges needed to be solved so that could be produced on a mass scale. Battery durability, recyclability and ease of manufacturing must be addressed in detail. Therefore, future research and development of Mg-O₂ batteries must not be limited to chemists/electrochemists and materials engineers/metallurgists. A broader involvement of scale-up expertise in product development and manufacturing is required. [201] Moreover, fiber-structure also has great advantages as catalysts for Mg-O₂ batteries. The advantages of simple preparation of nanofibers and high porosity can greatly help the development of magnesium air batteries.

5 Fiber-shaped material used for Al-O₂ battery

5.1 Working principle of Al-O₂ battery

For an Al-O₂ battery, aluminum dissolves on the positive electrode surface during the process of discharging (equations 13-14). Electrochemical reduction of oxygen is on the catalyst surface at the air cathode side.

Since the discharge process is an irreversible reaction process, the aqueous aluminum-air cells

could be utilized as primary cells[202]. During the discharging process, the Al anode dissolves to form $\text{Al}(\text{OH})_3$. If it reaches a saturation point, it precipitates on the electrode surface and the reaction equations are described below(15).

The entire reaction equation could be expressed as follows:

However, under the open-circuit condition of aluminum-air batteries, the active material will appear to be self-discharging due to gradual corrosion, as represented by the following reaction:

Although the voltage of the aluminum-air battery is 2.74 V from a theoretical aspect, the actual voltage is limited to 1.2 V and 1.6 V due to the complicated electrode process on the side of the Al anode.[203]

5.2 Fiber-based materials for Al-O₂ battery

In the 1960s and early 1970s, researchers conducted extensive research on Al-O₂ batteries[201]. Al is the richest metal resource in nature and has a very low molecular weight. The Al-O₂ battery has large theoretical specific energy capacity (2980 A h kg^{-1}), only second to the lithium-air battery (3860 Ah kg^{-1}), and can generate a high current density. Therefore, Al-O₂ batteries have great potential in long-term power supply for electronic products.[204, 205]

Nevertheless, the practical energy density of Al-O₂ cells is far below the practical target of electric vehicles and marine batteries. This phenomenon is mainly confined to the performance and development of current electrode materials. Among them, the electrochemical performance is mainly restricted by the oxygen electrode material.[206-208] In recent years, the development of carbon

materials and metal or metal oxide composites with high conductivity and tensile strength has been demonstrated, and aligned carbon nanotubes have been shown to be promising for oxygen electrodes materials.[209, 210] In this regard, Xu et al. [211] developed cross stacking aligned CNT/Ag sheets as cathode for Al-O₂ cell. The unique structure integrated with aligned CNT sheets enhanced gas diffusion, ORR catalytic activity, and improved electrons transportation. During the fabrication process, the special fiber-shaped Al-O₂ batteries were assembled with electrolyte gel made from a gel and a spring-like Al metal substrate as the air cathode, coated with aligned CNT/silver-nanoparticle hybrid sheets. This design offers various advantages including a framework with high porosity to assimilate O₂, and coated Ag particles as effective catalysts. Therefore, the Al corrosion decreases while the safety and stability increase, thereby facilitating flexibility and stretchability. It was observed that a fibrous porous Al-O₂ battery maintains its intrinsic structure when the bending angles are varied, and its shape is deformed at various times. The output voltage is maintained at a near-constant value of 1 mA cm⁻². The Al-O₂ cell could not be broken up and was stretched by 30% when the output voltage exceeded 1 V during the stretching process. The unique fiber shape of the battery is favorable for weaving into fabrics, which can potentially be used to weave "energy textiles." It was also demonstrated that the power density and output voltage could double if two batteries were installed into a porous tube and connected sequentially. More practically, such batteries could be woven into a stretchable textile to provide electricity for an LED light.

Figure 20. a) Fabricating process diagram of Ag/CFP air cathode. b) Diagram of a primary Al-O₂ cell. c) discharging plots of primary batteries adopting different oxygen electrodes, in contrast with that using marketing QSI-Nano as air cathode. d) Polarizing and power density plots of the battery integrated with Ag/CFP-3 and QSI-Nano oxygen electrodes. e) Specific capacities of Al-O₂ battery integrated with Ag/CFP-3 and QSI-Nano as oxygen electrodes. Photograph represented a LED light with power supply by two serials connected Al-O₂ batteries integrated with Ag/CFP-3 air cathode. Reproduced with permission.[212] Copyright 2017, Nature.

Apart from carbon-based fiber materials, the use of metal-based fibers as air cathode materials of Al-O₂ batteries also provides alternative routes. Hong and Lu [212] prepared a batch of CNF paper-supported Ag catalysts, Ag/CFP, via a simple in-situ method using a binder-free green catalyst for Al-O₂ battery. As shown in Figure 20a, Ag precursors were self-integrated on the functionalized CFP surface using concentrated acid pretreatment and electrostatic interaction of silver ions and negatively charging practical groups. Silver particles were then formed via a slow reduction process.

To test the practical electronic performance of the electrodes, the prepared Ag/CFP electrodes were directly used to assemble a primary Al-O₂ battery as the air cathodes (Figure 20b). The discharge plot in Figure 20c reveals that the performance of the Al-O₂ battery based on the Ag/CFP electrode was significantly enhanced when Γ_{Ag} increased. The discharge polarization profiles (Figure 20d) demonstrated that the discharge voltage and highest power density of Ag/CFP were better than those of the QSI-based cathode battery at a lower mass load. This was mainly ascribed to the powerful coupling effect among the prepared silver particles and the super ORR performance of the CFP matrix. As shown in Figure 20e, an LED light was powered using two serially connected Al-O₂ batteries integrated with an Ag/CFP-3 oxygen electrode. As the discharge continued, the aluminum plate became thinner and increasingly, soluble metal aluminates were accumulated in the electrolyte. When the aluminum plate was exhausted, the battery finally stopped working.

The Al-O₂ battery is very promising for high-performance, low weight, and low-cost energy-storage systems. It has attracted significant attention in recent years. However, the actual operating voltage is far less to the theory value because of the overpotential and water consumption of the two electrodes. The electronic performance of Al-O₂ batteries could be further improved to surpass the energy efficiency and durability of most existing battery systems. In summary, Al-O₂ batteries have broad application prospects and will become a leading technology in many fields.

5.3 Advancement and prospects of Al-O₂ battery

The specific energy of the Al-O₂ battery can reach as high as 8100 Wh/kg in theory. As a special fuel cell, the Al-O₂ battery has great commercial application potential in military, civil, underwater power systems, communication system standby power supplies, portable power supplies, and other fields. However, the development of aluminum anode is hindered by some problems, because aluminum is a very active amphoteric metal. At present, Al-O₂ batteries are not extensively used in

industrial and civil aspects, mainly because of the need to improve material preparation technology and the concept of secondary charging and discharging. The development and application of nanofiber technology have also promoted the development of Al-oxygen cell. And its safety and environmentally friendly characteristics mean that it will have broad developmental prospects, and will be applied to mobile devices such as power vehicles and mining in the future. Nanofibers have broad application prospects in Al-O₂ batteries. The combination of nanofibers and gel electrolytes can be assembled into flexible aluminum-air batteries. The method is simple and has broad application prospects.

6 Advantages of metal-air batteries and environmental challenges:

6.1 Advantageous characteristics of MABs

MABs are lightweight, clean and safe. The important performance parameters of several MABs that are widely investigated currently are shown in **Table 8**. These batteries can greatly reduce the weight of equipment while significantly improving their endurance, and can also be served as power supply for electric vehicles, replacing traditional fuels such as gasoline, alleviating the resource utilization crisis, and achieving zero-row release pollution-free travel[213]. The discharge reaction of MABs could be controlled. The metal electrode can be replaced, which can prolong the service time and improve the lifespan of the battery. Metal-air batteries are non-toxic to the humans and recyclable. Increasing attention has been recently directed to the development of small, fast, and portable electronic devices. It is therefore essential to develop lightweight and flexible energy storage systems. Fibrous shaped-based batteries are becoming increasingly important due to their combined advantages of miniaturization, adaptability and woven properties. Electrode with fibrous structure is one of the most efficient ways for flexible energy storage system [214]. For example, one-dimensional

fibrous structures have excellent flexibility, and can be woven into any shape that conforms to the human body. The preparation of high-performance woven fibrous zinc-air batteries has a strong promotion effect on the development of flexible energy storage systems [215].

Table 8. Some performance parameters of Li-O₂, Zn-O₂, Mg-O₂ and Al-O₂ batteries

Metal-air battery	Theory open circuit voltage (V)	theoretical specific energy (Oxygen containing) (KWh/kg)	Theoretical specific energy (No Oxygen) (KWh/kg)
Li-O ₂ [216]	2.96	5.210	11.14
Zn-O ₂ [217]	1.65	1.090	1.35
Mg-O ₂ [218, 219]	3.09	2.789	6.462
Al-O ₂ [220]	2.71	2.3	8.100

Moreover, it has a rich storage of several metal reserves for use in metal-air batteries, in addition to mature smelting technology, and the production cost is lower. And these metals are low-pollutant and their recovery costs are also low. Gold, the electrolyte of the air battery, is often an ordinary alkaline solution that is convenient for processing and has a significant cost advantage.

6.2 Environmental challenges in the present development of MABs

Although the MAB has several advantages, the actual application and mass production are mainly hindered by problems and technical difficulties associated with the following aspects [221]. At present, the current MABs suffers from self-corrosion problem of metal electrode. When the electrode is exposed to air and the electrolyte, some metal-air cells react with air or the electrolyte to cause their own corrosion, such as the reaction between zinc and air[222, 223]. The process of discharging the battery under alkaline conditions occurs in addition to a hydrogen evolution reaction. The air cell causes the reaction rate to change due to the formation of a thin film of aluminum in the air, and the ability of the aluminum electrode to lose electrons is slow. As a result, the potential increases and the entire cell voltage drops. If the oxide film is damaged, the hydrogen reaction occurs along with a

hydrogen evolution reaction, and the magnesium in the air cells is oxidized in the air. In addition, an oxide film is generated from the magnesium surface that prevents the electrode from discharging normally, thus resulting in a reaction[224]. When used in aqueous solutions, the rate decreases, and the self-corrosion phenomenon of hydrogen evolution is also present for magnesium electrode. In addition, long exposure of the secondary Li-O₂ cell to moist air causes the lithium electrode to degrade, and a water-proof packaging process is required.

Moreover, the electrolyte used in the metal-air cell is alkaline and is environment-dependent. The environment has a significant influence and has a certain volatility, such as the case of zinc and air[225]. A tank is used in a semi-open state and is affected by the ambient temperature. If the temperature is too high or too low, this will cause the electrolyte to be volatilized, thereby causing damage to the cell structure. When CO₂ in the ambient air reacts with an electrolyte to generate a carbonate, this leads to irreversible charging, which limits the re-use of metal-air cells. The service life, and even some of the cells only form a disposable battery [224]. At present, the metal air battery used in the battery system is usually heavy, bulky, expensive, and easy to corrode after long-term operation. However, carbon-based materials such as bamboo, carbon fiber, and chitosan are eco-friendly and non-toxic. Carbon-based fibers will be one of the trends in battery development in the future [226, 227].

Apart from these potential problems, air electrode blockage is also another critical challenge. Current metal-air batteries are sparse and porous to increase the contact area with the air. However, a series of reactions in the discharge process produces insoluble substances. As the reaction proceeds, these insoluble substances block the holes of the air electrodes and lead to battery failure[8] [228, 229]. For example, the hydroxide produced is insoluble and eventually covers the cathode and catalytic active point. This hinders the continuation of the reaction and result in great energy reduction

and battery endurance. Moreover, due to the variation of the chemical properties of the product after the reaction, it is impossible to charge and discharge multiple times.

The MABs that run on oxygen or air feedstock are an innovative new class of potential energy storage technology, given that they facilitate a high-energy efficiency, high open-circuit voltage, low self-discharge property, and long lifespan. Wind and solar power are also extensively researched areas in the quest to reduce our reliance on the energy generated by non-sustainable fossil fuels and to develop sustainable green energy technology. However, there are still some concerns with respect to the consistency of the power generated by these methods. As a result of the use of cathode material O_2 from the air, MABs can serve as a reliable power source for the transport sector, especially for HEVs and EVs. Despite their useful attributes, resolving their weaknesses such as poor cyclability, low practical performance against their theoretical energy density, and improving their air electrode composition remain as challenges to the commercial viability of this technology. Moreover, it is difficult for some of the materials used in MABs to maintain their supply chain and recyclability after their end-of-life. In addition, safety issues related to organic electrolyte system integration and costs are of concern.

For instance, it is suggested in the literature that the demands for MAB is expected to rise globally due to the increase in the demand for electric vehicles. It is envisaged that this demand will increase dramatically in the next decade as many countries and automobile companies transition from fossil fuels to electric-powered vehicles. Therefore, the optimization of performance and the maintenance of environmental sustainability is significant. After the end-of-life, batteries cannot be landfilled because they leach potentially harmful chemicals. Similarly, incineration must be used with maximum care. The end-of-life management of these batteries is a major challenge, given that the material system (MAB) and its components are not easily recycled and recovered.

Although research and development on the enhancement of the overall efficiency of MABs continue, achieving high energy densities, high-performance electrolytes, and safe and environmentally sustainable materials with strong structural stability and durability in the long term are still key challenges in the development of cost-effective, safe, and commercially viable systems.

7. Conclusions and future perspective

The continued development of MABs technology presents an exciting opportunity to achieve sustainable clean energy demand using an energy-efficient system. To realize this objective, it is essential to design and select the advanced materials with high catalytic activity, the cost-effective manufacturing processes, and the investigation of the fundamental relationships between the electrochemical behavior and atomic structure of the devices must be fully understood. Admittedly, the current development of alternative fiber-based lightweight new energy materials and their technological innovation in MABs development will allow the shortcomings of metal-air batteries to be effectively addressed.

In this review, the highlighted studies illustrated the pros and cons of the development of metal-air batteries with special reference to fiber-based structure design. These investigations confirm that compared with conventional batteries, metal-air batteries have exceptionally high energy densities, durable and high specific power. In addition, they are environmentally friendly, low-cost and lightweight. The advancements in fiber-based metal materials used for metal-air batteries, including the next generation of Li-O₂, Zn-O₂, Mg-O₂, and Al-O₂ batteries, are based on various fabrication processes and synthesis strategies for relative fiber-shaped structure materials, as well as electrochemical performance. In addition, we also focus on the composition of nanofiber-based nanostructure electrode materials and the evolution in structures for metal-air batteries, in addition to

the recent progress in the improvement of electrochemical performance.

For metal-air batteries, fiber-shaped structures have been shown to enhance thermal stability, electronic and ionic conductivity, in addition to the cyclical performance. This is attributable to their outstanding properties including their large specific surface area, tunable morphology, and porosity. These characteristics imply that there is excellent potential for the practical application of next-generation MABs based on rational structural designs to realize high-energy. Nevertheless, it still exists some problems and challenges. These include: (a) batteries electrochemical performance, including the capacity, cyclability, rate capability and efficiency, need to be further improved and developed, especially in the design of suitable cathode materials. In addition, it is imperative that more efficient catalysts should be developed with bifunctional catalysis. In particular, cathode materials should be environmentally friendly and exhibit the functions of catalysis and discharge products, which will lead to a broad space for development. (b) With the development of intellectualization, flexible MABs fabricated using nanofiber-based materials are a current trend and an area of significant research interest. It is challenging to effectively integrate nanofiber-based materials into smart devices to improve their flexibility, lifespan and safety, especially when the batteries are frequently bent. Moreover, flexible MAB has great potential for flexible electronic systems as a future power source. (c) To meet practical application requirement, large-scale and scalable manufacturing methods are also needed for fibrous structured electrode materials. In industrialization aspect, the main concern is the efficiency and cost of preparation. As a potential fabrication method, electrospinning is promising in the realization of mass production. (d) Developing the MABs requires a significant structured air electrode design and fabrication process development. Metal-air batteries usually use carbon materials as substrates, such as Toray carbon paper. However, these materials are prone to carbon corrosion during repeated charging and

discharging processes. Moreover, the preparation of air electrodes is very complicated, and the addition of auxiliary components will have some adverse effects. It could be resulted in the degradation of battery performance when the interaction force between the catalyst and a substrate is weak. Therefore, it is essential to design novel air electrode structures to control the morphology and the diameter of the cathode fiber materials to prolong the cycle life of batteries. (e) With the popularization and industrialization of MABs in the near future, the end-of-life management of these batteries is a major challenge, considering that the material system (MAB) and its components are not easily recycled and recovered. Moreover, some of the materials used in MABs have difficulty maintaining their supply chain and recyclability beyond their useful life. Also, the safety issues are related to the organic electrolyte system. Therefore, it is of great significance to find safe and harmless recycling methods for the sustainable application of MABs and the protection of human environment.

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Declaration of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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