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Efforts towards practical and sustainable Li/Na-air batteries

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What is the most favorite and original chemistry developed in your research group?

Li-N₂ battery for both electricity storage and artificial N₂ fixation.

How do you get into this specific field? Could you please share some experiences with our readers?

I have paid close attention to metal-air battery since I was pursuing my PhD because it holds much higher energy density than that of Ni-MH battery (my research topic of PhD). When I started my own research group at CIAC early 2010, I decided to focus on The Holy Grail of Batteries - Lithium-Air, trying to address the daunting challenges that limit the application of Li-air battery.

What is the most important personality for scientific research?

Curiosity to the unknown and persistence to explore.

How do you keep balance between research and family?

I usually keep a timetable in my mind so I know what to do at specific time. In this way, I know the dividing line between work time and family time.

What is your favorite journal(s)?

Journal of the American Chemical Society, Angewandte Chemie International Edition, and Advanced Materials.

What's your hobby?

Playing football and reading.

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Abstract The Li-O₂ batteries have attracted much attention due to their parallel theoretical energy density to gasoline. In the past 20 years, our understanding and knowledge in Li-O₂ battery have greatly deepened in elucidating the relationship between structure and performance. Our group has been focusing on the cathode engineering and anode protection strategy development in the past years, trying to make full use of the superiority of metal-air batteries towards application. In this review, we aim to retrospect our efforts in developing practical, sustainable metal-air batteries. We will first introduce the basic working principle of Li-O₂ batteries and our progresses in Li-O₂ batteries with typical cathode designs and anode protection strategies, which have together promoted the large capacity, long life and low charge overpotential. We emphasize the designing art of carbon-based cathodes in this part along with a short talk on all-metal cathodes. The following part is our research in Na-O₂ batteries including both cathode and anode optimizations. The differences between Li-O₂ and Na-O₂ batteries are also briefly discussed. Subsequently, our proof-of-concept work on Li-N₂ battery, a new energy storage system and chemistry, is discussed with detailed information on the discharge product identification. Finally, we summarize our designed models and prototypes of flexible metal-air batteries that are promising to be used in flexible devices to deliver more power.

Keywords Li-O₂ battery, Na-O₂ battery, Li-N₂ battery, flexible battery, anode protection, cathode engineering.

Contents

1. Introduction	Page No.
2. Li-O ₂ Batteries	Page No.
2.1. Working principle of Li-O ₂ batteries	
2.2. Cathode design for Li-O ₂ batteries	
2.3. Li anode protection	Page No.
3. Na-O ₂ Batteries: Promising Alternative to Li-O ₂ Batteries	
3.1. Why Na-O ₂ batteries?	
3.2. Cathode design for Na-O ₂ batteries	
3.3. Na anode protection	
4. Li-N ₂ battery	
5. Flexible Li-air batteries	
6. Conclusions	Page No.

1. Introduction

Nowadays, Li-ion batteries play an increasingly important role in the society and permeate ubiquitously in our daily life, from the phones, laptops and tablets to the popular electric cars. But the anxiety on the endurance time after one charge circumvents us all the time because their energy density cannot meet our demand. The current energy density of advanced Li-ion batteries is 300-500 Wh/kg. There is small space to further lift by the optimizations based on intercalation type Li-ion batteries even replacing graphite with silicon or developing high-nickel, Li-rich cathodes or LiNiCoAlO₂ materials. The rejuvenation of Li metal based batteries is promising to solve this anxiety, where cathode can be same as that Li-ion battery or changed by others, like Li-S and Li-O₂ batteries. [1]

Among the emerging new battery technologies, Li-O₂ batteries have the highest energy density (~3500 Wh/kg), because the consumed O₂ can be extracted from open air, reducing the weight of battery components, and the Li metal anode possesses a high specific capacity and a low electrochemical potential. Unlike the cathodes in current Li-ion batteries which include scarce and expensive cobalt materials, cathodes in Li-O₂ batteries are mostly abundant and cheap carbon-based materials with sustainability, making the cost of Li-O₂ batteries lower than that of current Li-ion batteries. However, the high demand on Li resource has pushed the rise of Li price and Li is likely to be exhausted in the future 20 years. Taking this into account, Na-O₂ batteries will be a good substitution because of the abundant Na resource and relatively high energy density. Actually, Na-O₂ batteries have been studied extensively since 2012 and the performance has been much improved. During the past 10 years, our group has devoted in the research of metal-air batteries and made substantial contributions to this field. Considering the main components of air are O₂ and N₂, this review will focus on the introduction of Li/Na-O₂ (N₂) batteries and flexible batteries. In this review, we will summarize the cathode design and anode protection strategies of Li-O₂ batteries and Na-O₂ batteries followed by the proof-of-concept Li-N₂ batteries and the future direction for metal-N₂ batteries. Then, prototypes of flexible Li-air batteries are displayed to demonstrate potential applications. Finally, we discussed the problems remain in this area and provide advancing directions for the years to come.

Figure 1 Schematic of a typical aprotic Li-O₂ battery.

2. Li-O₂ Batteries

2.1. Working principle of Li-O₂ batteries

Like traditional Li-ion batteries, a Li-O₂ battery comprises three parts, namely anode, electrolyte and porous cathode (Figure 1). Unlike the close system of Li-ion battery, the Li-O₂ battery is semi-open to let O₂ permeate into the porous cathode to proceed electrochemical reactions. During discharge, Li is oxidized to Li⁺ and O₂ is reduced at cathode. The reduced O₂ can combine with Li⁺ to form LiO₂ (Equation 1) followed by the disproportionation reaction in Equation 2 (solvation-mediated route) or further reduction in Equation 3 (surface-adsorption route) to form insoluble Li₂O₂ product deposited on the cathode surface. Typically, the solvation-mediated route can result in large Li₂O₂ particle thus a larger discharge capacity is achievable, while the surface-adsorption route tends to form small Li₂O₂ particle or film covering the cathode surface, leading to poor electron conductivity and reduced active reaction sites, giving rise to small capacity.^[2] During charge, the Li₂O₂ is decomposed to release O₂ and Li⁺ at the cathode and the Li⁺ is reduced to Li at the anode.

The basic operation principle of Li-O₂ batteries is very simple if you ignore their severe side reactions. However, parasitic reactions happen through the whole life of Li-O₂ batteries actually, making the system rather complicated. On the cathode side, the commonly used carbon-based materials tend to decompose at high voltage to form Li₂CO₃ and other species. In addition, Li₂O₂ is not stable towards carbon thus Li₂CO₃ can be formed by the reaction between Li₂O₂ and C.^[3] These side products are difficult to be decomposed and will continuously accumulate on the cathode surface as the cycling goes on, impeding electron and O₂ transfer and finally leading to the battery failure. For the electrolyte, the generated superoxide and singlet oxygen during cycling can attack electrolyte to produce side products depositing on the cathode as well. The

constant consumption of electrolyte can also deteriorate the kinetics in the battery. On the anode side, the active Li metal is unstable towards O_2 and H_2O . The O_2 shuttled from cathode and H_2O brought by gas or electrolyte decomposition can corrode the Li anode, as a result, the long cycling performance is unsatisfactory if no proper strategies are adopted to stabilize Li anode. In addition, the rate capability is limited by intrinsic sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), catalysts should be adopted to improve rate performance as well as round-trip efficiency. From the above, we conclude that even Li- O_2 battery can provide high energy density, the challenges still exist on the way to make it applicable.

2.2. Cathode design for Li- O_2 batteries

Among the three parts of Li- O_2 batteries, cathode structure optimization has been mostly investigated in the past years, because cathode determines the discharge energy density and charge efficiency. Most reported cathodes are based on carbon materials due to their light weight, good conductivity, abundant source, low price, high surface area and tunable properties. Although cathode design strategy evolved in the past years, we have been keeping pace with the trend of cathode evolution. The usually used cathode designing strategies can be broadly classified into four stages based on previous publications with our works included in each stage. The four stages do not appear one by one in the order of time, but the design art is utilized better and battery performances are much improved at lifted stages because of improved catalytic effects, high accommodation surfaces and tuned Li_2O_2 deposition behaviors endowed by the designed cathodes.

At stage 1, the cathode is a mixture of carbon and catalysts. The carbon can be super P, KB (Ketjenblack), carbon nanotube

(polytetrafluoroethylene) and lithiated Nafion onto the current collector, which are typically carbon paper, carbon cloth, nickel/copper foam. On the basis of this, we constructed hierarchical Co_3O_4 porous nanowires along with super P to make a cathode for Li- O_2 battery.^[4] The battery can run 73 cycles and deliver a full discharge capacity of $11160.8 \text{ mAh g}^{-1}$ at a relatively low current density of 100 mA g^{-1} . For this cathode, most of the super P particles are buried, and only the surface super P can be sufficiently used. The poor contact between the super P particles also leads to high charge overpotential. Then, in 2016, RuO_2/CNT was synthesized and used as cathode in Li- O_2 battery in our group.^[2a] Due to the good catalysis of RuO_2 , high conductivity and special structure of CNT, the battery displays a full discharge capacity of 29900 mAh g^{-1} and achieves 171 stable cycles. The high discharge capacity has been proved to originate from the RuO_2/CNT promoted solvation-mediated Li_2O_2 growth.

At stage 2, researchers have realized that the binders used in Stage 1 can reduce the electronic conductivity of cathode and be decomposed during cycling the battery.^[5] As a result, binder-free, self-standing catalytic cathodes are designed using simple hydrothermal or chemical vapor deposition methods to avoid the usage of binders. Different kinds of catalysts with varied shapes, like nanoarrays, nanowires, nanowalls, grown on carbon cloth, carbon paper and nickel foam have been reported. For our group, we developed two kinds of this type cathode: Ru-modified Co_3O_4 nanosheets on carbon textiles and Co_3O_4 nanosheets on carbon paper, which realized 70 and 50 cycles, respectively.^[6] However, the insulating nature of the metal oxides hinder the good electron transfer in the cathode, increasing the overpotential. What's more, the poor-conductive side products formed on the catalyst exacerbate this problem in the long run. To further optimize the composition and structure of the cathode, in 2018, we successfully

Figure 2 Four stages of cathode design strategies that deepen our understanding on cathode designing art.

(CNT), graphene or other carbon materials, while the catalysts are synthesized nanoparticles, nanowires, nanosheets and nanowalls. For preparing the cathode, the carbon and catalysts are just bound by certain binders, like PVDF (polyvinylidene fluoride), PTFE

demonstrated that hierarchical N-doped carbon nanotubes grown on stainless steel mesh could enable the Li- O_2 battery to deliver 232 cycles at 500 mA g^{-1} and a discharge capacity higher than 11000 mAh g^{-1} .^[7] The good conductivity of CNT and the hierarchical

structure facilitate the electron transfer and mass transport, thus a high performance is achieved. Another advantage of this cathode is that it can be used in flexible batteries because of the intrinsic bendable nature of stainless steel mesh.

In the process of designing the cathode, we observed that current collectors, like carbon cloth and carbon paper, could contribute to the overall capacity of Li-O₂ batteries, because the active catalytic particles cannot fully cover all the fibers of these current collectors and the discharge product would also deposit on the uncovered fibers. Since the typical diameters of the fibers of carbon paper (carbon cloth) and stainless steel mesh are ~10 and ~20 μm , respectively, their surface areas are very low, thus, the capacity contribution is limited. To further increase the capacity, we used electrospinning technique to design integrated electrodes with decreased fiber diameters (300-400 nm) but enlarged overall surfaces. This makes up stage 3, and we have prepared a Co-N-CNT/CNF (carbon nanofiber) composite cathode through electrospinning and chemical vapor deposition methods.^[8] Thanks to the special structure, large discharge capacity (>11000 mAh g⁻¹), high discharge potential (> 2.8 V), low charge overpotential (0.61 V) and 130 cycles were achieved. Besides, our another work based on Mo₂C-decorated carbon nanofiber also displayed 124 cycles.^[9] Effective porous nanofiber catalytic cathode, like tubular La_{0.75}Sr_{0.25}MnO₃, could also be obtained if the carbon fiber was calcinated in air.^[10]

Stage 4 gives a more comprehensive and in-depth devisal for constructing cathodes with periodic macroporous frameworks by template replication method. This architecture enables large surface area, good contact between electrode and electrolyte, fast gas diffusion and increased electrolyte permeability. These advantages promote battery performance in every aspect including capacity, life and rate capability. Inspired by honeycomb structure, we fabricated Pd-hollow spherical carbon on carbon paper through electrophoretic technique without the use of binder.^[11] This free-standing structure could enable favorable electron transfer route and tailor the product morphology for the weak binding to LiO₂ induced by Pd nanocrystal. The battery presented 5900 mAh g⁻¹ at 1.5 A g⁻¹ and 213 cycles. Apart from this, we designed 3D macroporous LaFeO₃ as a catalyst for Li-O₂ battery using polystyrene spheres template.^[12] A long life of 130 cycles was realized at a high current density of 0.15 mA cm⁻² and a fixed capacity of 1000 mAh g⁻¹. As a comparison, the battery adopting LaFeO₃ catalyst without using template only exhibited 75 cycles. We can thus know the tremendous improvement brought by the structure tuning. In 2016, we further reported a macroporous, binder-free, open-pore, self-standing, catalyst-imbedded, flexible, and highly conductive nanofiber cathode for Li-O₂ battery through electrospinning.^[13] The Li-O₂ battery with this multi-functional cathode that combined the advantages of stage 2 and 3 discharged 3290 mAh g⁻¹ at a high current density of 1000 mA g⁻¹. When the current density was doubled, the discharge capacity was still astonishingly 9112 mAh g⁻¹. The excellent rate capability and long life (154 cycles) proved the fast Li⁺ transfer and O₂ diffusion, good catalysis and high conductivity brought by this multi-functional cathode.

In addition to carbon-based cathodes, carbon-free cathodes have been investigated as well because of their chemical stability.^[14] The instability of carbon cathodes has been recognized early,^[15] so carbon-free cathode can be an important supplement to cathodes to avert the side products accumulation arising from carbon decomposition. Among the carbon-free cathodes, all-metal materials have received much attention because of their high conductivity that metal oxides cannot reach. However, the high mass density and low surface area of metal will undermine the specific capacity, therefore, rational design of metal-based cathode using nano-engineering is critical to improve the performance of Li-O₂ batteries. In 2017, we reported a robust and ultralight all-metal cathode based on Ni foam.^[16] By combustion and Au-Ni alloying, the Ni foam was endowed with high surface area and good catalytic effect. The battery delivered a capacity of 22551 mAh g⁻¹ at 1.0 A g⁻¹ and a 286 cycles lifetime, which are the best performance in the Li-O₂ batteries adopting carbon-free cathodes. Besides, the Li-O₂ batteries with this cathode showed negligible reactivity toward Li₂O₂ and the intermediates, enabling a low charge potential and highly reversible electrochemical reactions.

Based on the above discussion, we know that materials with various structures and components have been adopted in Li-O₂ batteries. However, in some cases, complex cathode structures do not necessarily lead to better performance. The structure of cathode and how the cathode influences the discharge and charge processes should be investigated in coordination with electrolytes. Moreover, porous structures are synthesized by tedious procedures, which bring high costs. Developing simple ways for constructing effective cathodes is important.

Figure 3 A map of strategies for Li anode protection.

2.3. Li anode protection

The Li anode protection in Li- O_2 batteries did not receive people's concern until J-L Shui identified porous LiOH formation on the surface of Li using synchrotron X-ray diffraction and 3-D μ -tomography in 2013.^[17] After that, people realized that a long-life Li- O_2 battery must keep a stable anode rather than only optimizing the cathode. Compared with the numerous investigations in cathode, reports on anode protection are much fewer. Based on the published papers, we classify the protection strategies into four categories (Figure 3).

The first one is surface modification of Li plates. Our group noticed the importance of Li anode stability in the Li- O_2 batteries as early as 2015. We developed an electrochemical way to fabricate an artificial protective film on the surface of Li metal by charging symmetric Li battery with TEGDME-FEC (Tetraethylene glycol dimethyl ether-Fluoroethylene carbonate) electrolyte (Figure 3a). The decomposition of FEC during charging resulted in a LiF-rich film on Li surface, which could protect Li anode to expand the battery life from 40 to 100 cycles. In our recent work, to stabilize the interphase between Li plate and the designed plastic crystal electrolyte, the Li plates were pre-cycled in 6 M LiFSI/DME to achieve a LiF coating layer before usage, thus a highly stable all-solid-state lithium-oxygen battery was achieved.^[18] To suppress dendrite and serious corrosion, we developed a LiF/F-doped carbon gradient protection layer by one-step reaction between molten Li and polytetrafluoroethylene (PTFE)^[19]. This layer enables

uniform Li^+ capture and quasi-spontaneous diffusion so that Li aggregation and dendrite can be avoided. Z. Zhou further developed a simple method by immersing Li into 1,4-dioxacyclohexane (DOA) for 10 minutes to form a poly-DOA surface film (Figure 3b).^[20] Similarly, H-S Zhou's group reported that immersing Li in organic GeCl_4 -THF steam for several minutes could create a "water-defendable" film consisting of Ge, GeO_x , Li_2CO_3 , LiOH, LiCl and Li_2O on Li (Figure 3c).^[21] With this Li anode, the symmetrical cell cycled for 500 cycles and the Li- O_2 battery ran for 150 cycles in humid O_2 . Recently, Keegan R. Adair made a protective zirconium coating film on Li anode by molecular layer deposition, and a long life of 500 cycles in Li- O_2 batteries was achieved (Figure 3d).^[22] These artificial films are nanoscale in thickness and constructed directly on the Li surface in a simple way. However, the films can be damaged by aggressive intermediates and cannot be repaired during rigorous cycling in Li- O_2 batteries.

Another strategy is surface coating of Li plates with a thicker film, like Al_2O_3 /PVDF-HFP (vinylidene fluoride-hexafluoropropylene) (Fig 3e)^[23] and graphene-polydopamine composite (Fig 3f).^[24] We designed an integrated separator and protection film simultaneously by facial solution-casting based on tissue (Fig 3g)^[25]. This electrochemically and mechanically stable film enabled the Li- O_2 battery to run for 300 cycles. In 2019, H-S Peng's group reported a three-dimensional CNT network with deposited Li as anode in Li- O_2 battery (Fig 3h).^[26] The porous structure of CNT network can promote even, dendrite-free Li deposition and alleviate volume change. This strategy is even

easier than the surface modifying strategy but the coatings will induce larger interfacial resistances, which may compromise the discharge plateau and cycling performance.

The next strategy is electrolyte tuning with specific additives. The above anode protection methods are usually adopted before assembly of Li-O₂ batteries, the formed protection film can be destroyed during cycling in Li-O₂ batteries. It is important to develop a continuous protection strategy. For this, we added tetraethyl orthosilicate (TEOS) into the electrolyte to react with the surface LiOH of Li plate to generate a protective film.^[27] Even though new LiOH will form in the following cycling, the TEOS can continuously consume it thus the protection can be maintained (Figure 3i). Redox mediators (RMs) are very useful in decreasing the charge overpotential and enlarging the discharge capacity. However, the shuttle effect of RMs is prone to attack Li anode, thus anode protection in the presence of RMs is vital. The dual-functional RMs like InI₃ and triethylsulfonium iodide (TESI) were reported to act as both homogeneous catalyst and anode protection additive.^[28] For InI₃, during charging, In³⁺ will firstly deposit on Li anode to form a layer of In. This film can protect the anode from shuttle effect. As to TESI, the cation TES⁺ can decompose by electron attack, forming an organic SEI-like film (Figure 3j). This protection layer is a good Li⁺ conductor but an electron insulator. So the film can defend the Li anode against dendrite growth and I₃⁻ attack. The above electrolyte tuning methods use additives to chemically produce a film on Li. We can also physically tune the electrolyte to achieve a similar effect. H-S Zhou's group reported a MOF-based separator to act as a RMs sieve to restrain the shuttling effect (Figure 3k).^[29] With the help of RMs and MOF-protected Li, the battery achieved a long life of 100 cycles at a high current density of 5000 mA g⁻¹. Recently, we adopted the rheological properties of the electrolyte by adding 10% hydrophobic silica to make it solid-like (Figure 3l).^[30] Due to the electrostatic interaction between CF₃SO₃⁻ and silica particles, the viscosity of the optimized electrolyte was increased for 980-fold, thus the diffusion of H₂O or other contaminants was much slower. The Li anode in this Li-O₂ battery achieved a long life of 550 cycles, showing good protection effect. In addition, we recently fabricated Li-air batteries with a hydrophobic composite polymer electrolyte film to expel moisture and enhance the stabilization of Li, which greatly improved the safety and performance.^[31] Regulating the species and concentration of salts in electrolytes can optimize Li⁺ solvation structure and adjust SEI film to strengthen Li anode. We successfully adopted 2 M LiTFSI, 1 M LiNO₃/DMA (N,N-dimethylacetamide) electrolyte in Li-O₂ batteries with suppressed Li dendrite and corrosion.^[32] This kind of strategies can be effective ways to tailor the SEI on anodes by sacrificing additives and the amount of the additives should be controlled precisely.

Li metal alloys have been successfully used in Li metal batteries and Li-S batteries because of their chemical stability and dendrite prevention effect (Figure 3m, n).^[33] H-S Zhou's group employed Li/Si alloy, prepared by charging the Li|Si half cell, as the anode in Li-O₂ batteries.^[34] By introducing FEC into the electrolyte in half cell, the anode/electrolyte interphase could be stabilized (Figure 3o). This battery avoided the formation of Li during charge so that the dendrite and Li corrosion is absent naturally. Similarly, Q-H Yang reported a Li-O₂ battery with Li/Al alloy anode by pre-lithiation

(Figure 3p).^[35] Thanks to the stable alloy anode and SEI formed during pre-lithiation, the battery held 100 cycles at 100 mA g⁻¹ for a reversible capacity of 1000 mAh g⁻¹. The alloy strategy can stabilize the anode but the energy density is undermined because the exotic metal cannot deliver energy. Moreover, the alloying procedure is tedious and complicated compare the above mention three ways.

In addition to the above common strategies for anode protection, we recently found that CO₂ in O₂ can facilitate the formation of a protective and self-healing Li₂CO₃ film on Li surface. Further more, CO₂ can stabilize the electrolyte and cathode due to the capture of the aggressive intermediates thus the Li-O₂/CO₂ battery can run for 715 cycles and only 6.23% Li is lost after 500 cycles.^[36] Solid-state electrolyte (SSE) can be effective in restraining Li dendrite and avoid safety issue. However, the contact between Li and SSE is not satisfying. To tackle this, a hybrid solid electrolyte with rigid Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) core and poly (PVDF-HFP) shell is designed.^[37] The rigid core can sustain mechanical strength and homogenize Li⁺ diffusion and the soft shell can enable stable and close contact with Li anode thus a long life of 146 cycles was realized.

3. Na-O₂ Batteries: Promising Alternative to Li-O₂ Batteries

3.1. Why Na-O₂ batteries?

The continuous development of Li-based batteries has resulted unprecedented consumption rate of lithium resource, especially in the surging electric car industry. It is estimated that lithium resource will be depleted in two decades at such an increasing demand on Li-ion batteries. Sodium-based batteries have attracted people's concentration because of the high abundance and low cost of sodium, thus it is a promising alternative of Li-based batteries. Like Li-O₂ batteries, Na-O₂ batteries can deliver a higher energy density than their corresponding metal-ion batteries, attracting intense research interest. In 2012, a reversible Na-O₂ battery was first reported with an ultra-low overpotential (<200 mV) without using any catalyst based on the formation and decomposition of NaO₂.^[38] After that, the researches in Na-O₂ batteries are burgeoning. Table 1 shows a comparison on the characteristics of Na-O₂ and Li-O₂ batteries. Compared with Li-O₂ batteries, Na-O₂ batteries offer lower energy density and discharge voltage yet higher round-trip efficiency because of low overpotential. We note that the Na⁺ radius is larger than that of Li⁺, which hinders the life of Na-ion batteries. But for Na-O₂ batteries, the size influence is minimal. Further, B. D. McCloskey reported

Figure 4 Schematic illustrations of porous cathode synthesis: (a) vertical Co_3O_4 grown on carbon textile (COCT), (b) graphitic nanoshell embedded in mesoporous carbon (GNS/MC), (c) Co-embedding/coating N-doped carbon fibers (Co-ECNCFs), (d) CoB nanosheets and (e) porous carbon spheres (PCS).

at less decomposition of electrolyte and cathode happened in Na-O_2 batteries than that in Li-O_2 batteries.^[39] So, besides cost, Na-O_2 batteries indeed have other advantages over Li-O_2 batteries, which motivate us to improve the performance of Na-O_2 batteries.

Table 1 A comparison on the characteristics of Na-O_2 and Li-O_2 batteries.

	Na-O_2 batteries	Li-O_2 batteries
Energy density	1108 Wh/kg (NaO_2)	3458 Wh/kg (Li_2O_2)
Discharge voltage	~2.2 V	~2.7 V
Discharge product	NaO_2 or/and Na_2O_2	Li_2O_2
Overpotential	~0.2 V for NaO_2	~1.5 V for Li_2O_2
Element abundance	2.3% of earth's crust	0.0065% of earth's crust
Element metal price	3000 \$/metric ton	16500 \$/metric ton
Metal ion radius	0.98 Å	0.69 Å
Side reactions	Less	Complicated

For Li-O_2 batteries, the discharge product is generally Li_2O_2 , while the product may be NaO_2 , Na_2O_2 , $\text{Na}_2\text{O}_2 \cdot x\text{H}_2\text{O}$ or their composites for Na-O_2 batteries. This has increased the complexity of discharge product identification and discharge mechanism. Until now, scientists in this field still have not yet understood the control parameters for the selective formation of solely NaO_2 or Na_2O_2 . The low overpotential without using any catalysts is only reported in Na-O_2 batteries based on NaO_2 discharge product.^[38,40] But once the product involves Na_2O_2 or its hydrates, the overpotential climbs thus catalysts are needed. In addition, like the situation in Li-O_2 batteries, porous cathodes with catalytic effect are

indispensable to enlarge the capacity of Na-O_2 battery. In this circumstance, the challenges to drive the facile proceeding of OER and ORR can be shared by Na-O_2 and Li-O_2 batteries. In the anode side, Li and Na are both active towards H_2O and O_2 , so Na corrosion should also be paid close attention.

3.2. Cathode design for Na-O_2 batteries

The researches on cathode design in Na-O_2 batteries are less than those in Li-O_2 batteries, because these two cousins show many similarities in cathode properties. To facilitate the OER and ORR in Na-O_2 batteries, we have designed a series of cathode materials to optimize the electrochemical performances including cycle life, overpotential and discharge capacity. Binder-free cathodes have received attention due to their stability but catalyst is still needed to provide deposition sites and driving force for ORR and OER. On the basis of this, we designed a binder-free, flexible cathode using carbon textile as support to grow vertical Co_3O_4 nanowire arrays (COCT) by a simple hydrothermal method (Figure 4a).^[41] The synthesized COCT made the Na-O_2 battery deliver a high capacity up to $4687.2 \text{ mAh g}^{-1}$ at 100 mA g^{-1} , four times that of the bare carbon textile. The cycle life was also prolonged from 16 cycles to 62 cycles at 100 mA g^{-1} . The discharge product was confirmed as Na_2O and Na_2O_2 . J-Y Cheon assembled a mesoporous carbon embedded by graphitic nanoshell (GNS/MC) for aqueous Na-air battery, which is the first example for aqueous Na-air battery (Figure 4b).^[42] The prepared cathode showed very high catalytic activity for both OER and ORR, leading to a very low overpotential of 115 mV, while the overpotentials for Pt/C and Ir/C are 179 mV and 364 mV, respectively. However, the long cycling stability of the aqueous Na-air battery was not shown, thus leaving the comparison difficult on the life of aqueous and non-aqueous Na-air batteries.

To further promote the performance of Na-O_2 batteries, we

Fig. 4. (a) Schematic of the Na anode, GF separator, blocking layer, and f-PVDF. (b) Top-view SEM image of blocking interlayer after depositing 3 mAh cm⁻² (c) with and (d) without f-PVDF blocking layer after the 1st charge. (e) Cycling interlayer at different current densities. (f) Illustration of dendrite symmetric batteries and (h) metal-O₂ batteries.

catalytic activity.

Since side reactions in Na-O₂ batteries are less than those in Li-O₂ batteries (Table 1) and the charge overpotential for NaO₂ decomposition is low even without catalysts, carbon-based cathodes are promising in Na-O₂ batteries. In 2017, B Sun designed hierarchical porous carbon spheres (PCS) using MnCO₃ sphere as template (Figure 4e).^[45] The obtained unique structure greatly promoted the O₂ diffusion and electrolyte infiltration. As a result, conformal film-like NaO₂ deposited on the surface of porous carbon instead of cubic NaO₂, which made the NaO₂ decomposition more complete and a low charge overpotential was achieved. This special cathode configuration enabled the Na-O₂ battery run for 400 cycles, the highest cycle number in Na-O₂ batteries.

3.3 Na anode protection

To achieve a long-life Na-O₂ battery, all battery components, including cathode, anode and electrolyte, should play a role. The Na anode suffers severe dendrite growth, oxygen crossover and water corrosion during cycling. Thus, it is vital to take action to protect Na anode to improve battery lifespan.^[46] Even though the protection methods for Li and Na are alike, Na is more active and difficult to handle. As a result, specific protection strategies are very important for Na anode. We proposed and demonstrated that fibrillar polyvinylidene fluoride film (f-PVDF) coating on Na could effectively suppress dendrite growth (Figure 5a).^[47] After depositing 3 mAh cm⁻² Na, the surface of f-PVDF was still very clean, no evidence of dendrite at all (Figure 5b). Moreover, the film could prevent cracks on anode surface during cycling while the bare Na plate endured severe cracks and corrosion (Figure 5c,d). Figure 5e gives the cycle performance of the Na-O₂ batteries with and without f-PVDF film, from which we can find the life is doubled when using the film. The improved performance can be ascribed to the following advantages: (1) the strong polar C-F groups in the f-PVDF enable an affinity to Na ions and thus Na deposition is

constructed a carbon textile with decreased string diameter and increased surface area by electrospinning PAN (polyacrylonitrile) and Co(NO₃)₂ precursors to improve the catalytic effect (Figure 4c).^[43] As a result, the discharge capacity was amplified to 6102 mAh g⁻¹ at 200 mA g⁻¹, proving that the surface area enhancement could increase the capacity. In addition, long life up to 112 cycles was sustained due to the good catalytic N-doping and Co nanoparticles. As well known, transition metal oxides are commonly used as catalysts for OER and ORR because of their low cost, but the intrinsic low conductivity or insulating nature can block the electron transfer, leading to high overpotentials in metal-O₂ batteries. Therefore, it is critical to explore catalytic cathodes that keep the low cost, but possess high conductive. Transition metal borides can meet these demands. We developed a controllable synthesis of porous CoB nanosheet by calcinating inorganic molten salts (Figure 4d).^[44] The metallic nature of CoB was proved by calculating the density of states and band structure, both passing the Fermi level. The CoB together with CNT was used as cathode for Na-O₂ batteries, a much higher capacity of 11428 mAh g⁻¹ and a longer life of 74 cycles with a high fixed capacity of 2000 mAh g⁻¹ were obtained due to the good catalysis and conductivity of CoB. After examine the charged cathode, we found the discharge product could be removed completely even after 30 cycles. A deeper calculation showed that a stronger interaction between Na₂O₂/CoB interfaces was the origin of enhanced

homogeneous; (2) the f-PVDF film with porous structure can absorb more electrolyte to improve ion conductivity; (3) the good electrolyte wettability of the f-PVDF film help dendrite suppression. Our another work on anode protection adopted Li-Na alloy as anode, which could prevent dendrite growth through electrostatic shield effect (Figure 5f).^[48] Unlike other strategies using Cs⁺ or Rb⁺ to induce shield effect, this does not involve costly additives.^[49] The alloy could also avoid sacrificing the anode specific capacity because Li and Na were both charge carriers in the cell. To alleviate the corrosion on the alloy anode, 1,3-dioxolane (DOL) was added in the electrolyte to form a stable SEI. As a result, the symmetric battery could cycle more than 800 h (Figure 5g) without obvious overpotential increase and the metal-O₂ battery could run 137 cycles (Figure 5h).

5. Li-N₂ Battery

5. Flexible Li-air Batteries

The surging demand for flexible and wearable electronics has

Figure 7 Prototypes of flexible Li-air batteries. Batteries with (a) paper-ink cathode and (b) recoverable carbon textile cathode. (c) A battery inspired by bamboo slips. (d) A PDMS-encapsulated integrated flexible Li-O₂ battery. (e, f) 1D flexible, water-proof Li-air batteries.

It is well known that O₂ makes up 21% of the air while N₂ does 78%. Since Li-O₂ batteries have demonstrated great potential for energy storage, however, when O₂ is replaced by air in Li-air batteries, we must consider the role of N₂. Besides, the price of pure N₂ is much cheaper than O₂. If we can combine N₂ into a battery, it would be another important innovation in energy storage as well as nitrogen fixation. As a proof of concept, we successfully presented a rechargeable Li-N₂ battery based on the reaction of $6\text{Li} + \text{N}_2 \leftrightarrow 2\text{Li}_3\text{N}$ (Figure 6a).^[50] The discharge potential was around 1.0 V during N₂ fixation. The successful N₂ fixation and release were confirmed by SEM, XRD (Figure 6c), N1s XPS spectrum and FT-IR spectra (Figure 6d). This battery system has offered a greener route for nitrogen fixation compared with Haber-Bosch process and is considered as a promising candidate for next generation energy-storage system. Inspired by our work, a Na-N₂

promoted the energy storage devices to be bendable, rollable and foldable. To this end, flexible Li-air batteries with high energy density have been developed. Unlike the closed Li-ion battery, the Li-air battery is semi-open, thus making the designing principles vary from that of Li-ion battery. The challenges to construct flexible Li-air batteries include the selection of sealing materials that can endure rigorous bending and hold close contact with battery components simultaneously, novel closure design of batteries, anode protection strategies and the integration of components. Our group has committed to the development and application of Li-air batteries since 2012 and we have designed many prototypes of flexible Li-air batteries with different characteristics.

In 2015, inspired by Chinese traditional writing using a brush and ink, we prepared a paper-ink cathode by facial painting ink on the paper and then drying (Figure 7a).^[53] This novel way for

cathode preparation can reduce the cost and simplify the tedious electrode preparation procedures. Because of the foldability of paper, we designed a proof-of-concept flexagon Li-air battery that could control the light on/off freely. At the same year, we reported a recoverable cathode by growing TiO_2 nanoarrays on carbon textiles (Figure 7b).^[54] The softness of the carbon textiles made the battery work normally at different shapes without performance fading. Due to the anti-acid TiO_2 nanoarrays, the cathode can be reusable for more than 10 times (more than 1100 cycles) after acid wash. A bamboo-slips-like Li-air battery model was then demonstrated in 2016 (Figure 7c).^[55] The newly designed battery was free of package and air diffusion layer, thus made a record high energy density. The flexibility of bamboo slip structure also made the battery wearable and could be bent or folded. This thought can be further developed by taking smaller batteries to configure a larger cell for higher endurance ability for bending and folding.^[56] Different from the “dividing” strategy, we later developed a highly compact, integrated flexible Li-air battery with specially designed electrodes and electrolyte based on Polydimethylsiloxane (PDMS) package (Figure 7d).^[57] The anode was a composite film of Cu foil, Li foil and stainless steel mesh, while the cathode was carbon cloth with $\text{RuO}_2/\text{TiO}_2$ nanowires. The cathode ensured a high electrochemical capability and the unique structure of anode, electrolyte and PDMS promised a great mechanical property. As a result, the battery sustained its capacity even after being bent for 5000 times.

Among various forms of flexible batteries, one-dimensional (1D), cable-like battery shows great potential to be first used in commercial applications, because it is the most deformable one and can be assembled easily. Some contributions to the configuration of 1D flexible Li-air batteries have been made in our group. We reported a water-survivable flexible Li- O_2 battery with a lithium stick, hydrophobic polymer electrolyte with a contact angle of 98.8° to H_2O , super P cathode and nickel foam sealed by thermal shrinkage rubber (Figure 7e). The hydrophobic polymer electrolyte can protect the Li from water attacking so that the battery can survive in water. When the battery is used in open air, the polymer can ensure the battery run for a longer time. The easily deformable cable battery can be bent or twisted randomly without structure breaking. Our another work on 1D Li-air battery took an inverse structure with cathode in and anode out (Figure 7f).^[58] The heat-shrink tube sealing can enable the battery work in water and bear high temperature. The battery gave a discharge capacity of 115 mAh at 0.2 mA and 218 cycles were achieved at 1 mA with a fixed capacity of 4 mAh. Furthermore, as demonstrated in our recent work, solar energy and flexible Li- O_2 battery could be combined to realize low overpotential and high energy efficiency.^[59] The outstanding performance of the flexible battery proved the prototype was very successful.

6. Conclusions

In this review, we have retrospected our efforts in metal-air batteries in the past decade, including the cathode design optimizations and anode protection strategies in Li/Na- O_2 batteries, a proof-of-concept Li- N_2 battery and flexible metal-air batteries. We have demonstrated that through rational design of cathode and anode, the discharge capacity, life and rate capability of metal-

air batteries can obtain huge improvements. Flexible metal-air batteries with good fatigue resistance and high electrochemical performance are promising to be used in wearable devices.

Even though great advances have been made in the fundamental researches, the road to real-world application of metal-air batteries is still far away. Currently, almost all works claiming metal-air batteries are tested in pure O_2 atmosphere with a heavy gas storage bottle or continuous gas-purging instrument. This has greatly reduced its gravimetric energy density and impeded its way to practical applications. When realizing metal-air battery, all components (N_2 , H_2O , CO_2 , NO_x , SO_x et al) and O_2 partial pressure in the open air should be considered. It is crucial to conduct investigations on Li/Na- O_2 batteries working in real air, including understanding how these air components affect the electrochemical performances and optimizing the battery performance in this specific situation. Fast charge has raised research recently because of the demand in smart phones and electric cars. However, the intrinsic sluggish OER process hinders the fast charge ability of Li-air batteries, thus exploring ways to realize fast charge is challenging, but the research in this respect should continue. Safety of metal-air batteries is an extremely critical problem due to the highly active nature of Li and Na. Proper ways in anode protection and sealing technique are urgently required to keep them safe and avoid the moisture and CO_2 influence from open air. Furthermore, most previous works focus on one part of the batteries to optimize thus the performance cannot improve greatly. Only when the battery was optimized comprehensively, including anode protection, electrolyte tuning and cathode engineering, can the battery deliver a better capability. Finally, metal-air batteries are not likely to replace current Li-ion batteries completely thus looking for the application scenarios and make a supplement to Li-ion batteries are critical.

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Entry for the Table of Contents

Page No.

Title: Efforts towards practical and sustainable Li/Na-air batteries

Kai Chen, Gang Huang, Xin-Bo Zhang*