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

Authors: Kai Chen, Gang Huang, and Xin-Bo Zhang *

This manuscript has been accepted and appears as an Accepted Article online.

This work may now be cited as: Chin. J. Chem. 2020, 38, 10.1002/cjoc.202000408.

The final Version of Record (VoR) of it with formal page numbers will soon be published online in Early View: http://dx.doi.org/10.1002/cjoc.202000408.
Efforts towards practical and sustainable Li/Na-air batteries

Kai Chen,a,b Gang Huang,c and Xin-Bo Zhang,*a,b

a State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China.
b University of Science and Technology of China, Hefei, Anhui 230026, China
c Materials Science and Engineering, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia

Cite this paper: Chin. J. Chem. 2019, 37, XXX—XXX. DOI: 10.1002/cjoc.201900XXX

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)?

What’s your hobby?
Playing football and reading.

Xin-Bo Zhang
Director of State Key Laboratory of Rare Earth Resource Utilization, CIAC, CAS.
E-mail: xbzhang@ciac.ac.cn
Homepage: http://energy.ciac.jl.cn/

Birth: Feb. 18, 1978
Education:
1999 BSc, Changchun University of Science and Technology
2005 PhD, Changchun Institute of Applied Chemistry, CAS.
Experience:
Xin-Bo Zhang joined CIAC as a professor of “Hundred Talents Program” of Chinese Academy of Sciences (CAS) in the spring of 2010. He received his PhD degree in inorganic chemistry from CIAC in 2005. Then, during 2005-2010, he worked as a JSPS and NEDO fellow at National Institute of Advanced Industrial Science and Technology (Kansai center), Japan
Awards:
2019 Jilin Provincial Natural Science Award (First Prize, first place)
2019 Highly-Cited Researchers, Clarivate Analytics
2018 Leading Talents in Science and Technology Innovation (Ten Thousand Talents Program)
2017 National Science Fund for Distinguished Young Scholars, NSFC
2016 Young and Middle-aged Leading Scientists, Engineers and Innovators, MOST, China
2015 Young Top-Notch Talent (Ten Thousand Talents Program)
2014 Excellent Young Scholars of NSFC
2011 “Hundred Talents Program” of CAS
Interests: Energy materials chemistry; Metal-air batteries; Electrocatalysis and electrosynthesis
Abstract The Li-O$_2$ 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-O$_2$ 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-O$_2$ batteries and our progresses in Li-O$_2$ 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-O$_2$ batteries including both cathode and anode optimizations. The differences between Li-O$_2$ and Na-O$_2$ batteries are also briefly discussed. Subsequently, our proof-of-concept work on Li-N$_2$ 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.

**Key words** Li-O$_2$ battery, Na-O$_2$ battery, Li-N$_2$ battery, flexible battery, anode protection, cathode engineering.
Contents

1. Introduction
2. Li-O2 Batteries
  2.1. Working principle of Li-O2 batteries
  2.2. Cathode design for Li-O2 batteries
  2.3. Li anode protection
3. Na-O2 Batteries: Promising Alternative to Li-O2 Batteries
  3.1. Why Na-O2 batteries?
  3.2. Cathode design for Na-O2 batteries
  3.3. Na anode protection
4. Li-N2 battery
5. Flexible Li-air batteries
6. Conclusions

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 up 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 prototype 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.

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 Li2O2 (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.

\[ \text{Li}^+ + O_2 + e^- \rightarrow \text{Li}_2\text{O}_2 (1) \]
\[ \text{Li}_2\text{O}_2 (\text{sol}) + \text{Li}_2\text{O}_2 (\text{sol}) \rightarrow 2\text{Li}_2\text{O}_2 + O_2 (2) \]
\[ \text{Li}_2\text{O}_2 (\text{solid}) + \text{Li}^+ + e^- \rightarrow 2\text{Li} + O_2 (3) \]

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$_2$O. The O$_2$ shuttled from cathode and H$_2$O 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$_2$O$_2$ 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 (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 (polytetrafluoroethylene) and lithiated Naion onto the current collector, which are typically carbon paper, carbon cloth, nickel/copper foam. On the basis of this, we constructed hierarchical Co$_3$O$_4$ 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 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$_2$O$_2$ 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$_3$O$_4$ nanosheets on carbon textiles and Co$_3$O$_4$ 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 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 electrosprinning technique to design integrated electrodes with decreased fiber diameters (300-400 nm) but enlarged overall surface. This makes up stage 3, and we have prepared a Co-N-CNT/CNF (carbon nanofiber) composite cathode through electrosprinning 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 Mo\(_2\)C-decorated carbon nanofiber also displayed 124 cycles.\(^{[9]}\) Effective porous nanofiber catalytic cathode, like tubular La\(_{0.75}\) Sr\(_{0.25}\)MnO\(_3\), 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 LiO\(_2\) induced by Pd nanocrystal. The battery presented 5900 mAh g\(^{-1}\) at 1.5 A g\(^{-1}\) and 286 cycles lifetime, which are the best performance in the Li-O\(_2\) batteries adopting carbon-free cathodes. Besides, the Li-O\(_2\) batteries with this cathode showed negligible reactivity toward LiO\(_2\) 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-O\(_2\) 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.
2.3. Li anode protection

The Li anode protection in Li-O2 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-O2 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-O2 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 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 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 GeCl₄·THF steam for several minutes could create a “water-defendable” film consisting of Ge, GeOₓ, Li₂CO₃, LiOH, LiCl and Li₂O on Li (Figure 3c).[21] With this Li anode, the symmetrical cell cycled for 500 cycles and the Li-O₂ battery ran for 150 cycles in humid O₂. Recently, Keegan R. Adair made a protective zircon coating film on Li anode by molecular layer deposition, and a long life of 500 cycles in Li-O₂ 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-O₂ batteries.

Another strategy is surface coating of Li plates with a thicker film, like Al₂O₃/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-O₂ 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-O₂ 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...
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 CO\(_2\) in O\(_2\) can facilitate the formation of a protective and self-healing Li\(_2\)CO\(_3\) film on Li surface. Further more, CO\(_2\) can stabilize the electrolyte and cathode due to the capture of the aggressive intermediates thus the Li-O\(_2\)/CO\(_2\) 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\(_{1.2}\)Al\(_{0.3}\)Ge\(_{1.5}\)(PO\(_4\))\(_3\) (LAGP) core and poly (PVDF-HFP) shell is designed.\(^{[27]}\) 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-O\(_2\) Batteries: Promising Alternative to Li-O\(_2\) Batteries

3.1. Why Na-O\(_2\) 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-O\(_2\) batteries, Na-O\(_2\) batteries can deliver a higher energy density than their corresponding metal-ion batteries, attracting intense research interest. In 2012, a reversible Na-O\(_2\) battery was first reported with an ultra-low overpotential (<200 mV) without using any catalyst based on the formation and decomposition of Na\(_2\)O\(_{2}\).\(^{[36]}\) After that, the researches in Na-O\(_2\) batteries are burgeoning. Table 1 shows a comparison on the characteristics of Na-O\(_2\) and Li-O\(_2\) batteries. Compared with Li-O\(_2\) batteries, Na-O\(_2\) 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-O\(_2\) batteries, the size influence is minimal. Further, B. D. McCloskey reported 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-O\(_2\) batteries, the formed protection film can be destroyed during cycling in Li-O\(_2\) 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 protection in the presence of RMs is vital. The dual-functional RMs like InI\(_3\) and triethylsulfonium iodide (TESI) were reported to act as both homogeneous catalyst and anode protection additive.\(^{[24]}\) For InI\(_3\), during charging, In\(^{3+}\) will first 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 I\(_3^-\) 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 shutting 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 CF\(_3\)SO\(_3^-\) and silica particles, the viscosity of the optimized electrolyte was increased by 980-fold, thus the diffusion of H\(_2\)O or other contaminants was much slower. The Li anode in this Li-O\(_2\) 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.\(^{[33]}\) 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 LiNO\(_3\)/DMA (N,N-dimethylacetamide) electrolyte in Li-O\(_2\) batteries with suppressed Li dendrite and corrosion.\(^{[34]}\) 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-O\(_2\) 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-O\(_2\) battery with Li/Al alloy anode by pre-lithiation (Figure 3p).\(^{[35]}\)
that less decomposition of electrolyte and cathode happened in Na-O2 batteries than that in Li-O2 batteries.[39] So, besides cost, Na-O2 batteries indeed have other advantages over Li-O2 batteries, which motivate us to improve the performance of Na-O2 batteries.

Table 1 A comparison on the characteristics of Na-O2 and Li-O2 batteries.

<table>
<thead>
<tr>
<th></th>
<th>Na-O2 batteries</th>
<th>Li-O2 batteries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density</td>
<td>1108 Wh/kg (NaO2)</td>
<td>3458 Wh/kg (Li2O2)</td>
</tr>
<tr>
<td>Discharge voltage</td>
<td>~2.2 V</td>
<td>~2.7 V</td>
</tr>
<tr>
<td>Discharge product</td>
<td>NaO2 or/and Na2O2</td>
<td>Li2O2</td>
</tr>
<tr>
<td>Overpotential</td>
<td>~0.2 V for NaO2</td>
<td>~1.5 V for Li2O2</td>
</tr>
<tr>
<td>Element abundance</td>
<td>2.3% of earth's crust</td>
<td>0.0065% of earth's crust</td>
</tr>
<tr>
<td>Int metal price</td>
<td>3000 $/metric ton</td>
<td>16500 $/metric ton</td>
</tr>
<tr>
<td>Metal ion radius</td>
<td>0.98 Å</td>
<td>0.69 Å</td>
</tr>
<tr>
<td>Side reactions</td>
<td>Less</td>
<td>Complicated</td>
</tr>
</tbody>
</table>

3.2. Cathode design for Na-O2 batteries

The researches on cathode design in Na-O2 batteries are less than those in Li-O2 batteries, because these two cousins show many similarities in cathode properties. To facilitate the OER and ORR in Na-O2 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 Co3O4 nanowire arrays (COCT) by a simple hydrothermal method (Figure 4a).[41] The synthesized COCT made the Na-O2 battery deliver a high capacity up to 4687.2 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 Na2O and Na2O2. 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-O2 batteries, we...
constructed a carbon textile with decreased string diameter and increased surface area by electrospinning PAN (polyacrylonitrile) and Co(NO$_3$)$_2$ precursors to improve the catalytic effect (Figure 4c). 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-O$_2$ 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). 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-O$_2$ 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 Na$_2$O$_2$/CoB interfaces was the origin of enhanced catalytic activity.

Since side reactions in Na-O$_2$ batteries are less than those in Li-O$_2$ batteries (Table 1) and the charge overpotential for Na$_2$O$_2$ decomposition is low even without catalysts, carbon-based cathodes are promising in Na-O$_2$ batteries. In 2017, B Sun designed hierarchical porous carbon spheres (PCS) using MnCO$_3$ sphere as template (Figure 4e). The obtained unique structure greatly promoted the O$_2$ diffusion and electrolyte infiltration. As a result, conformal film-like Na$_2$O$_2$ deposited on the surface of porous carbon instead of cubic Na$_2$O$_2$, which made the Na$_2$O$_2$ decomposition more complete and a low charge overpotential was achieved. This special cathode configuration enabled the Na-O$_2$ battery run for 400 cycles, the highest cycle number in Na-O$_2$ batteries.

### 3.3 Na anode protection

To achieve a long-life Na-O$_2$ 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. 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). 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$_2$O$_2$ 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...
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 supression. 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).

4. Li-N2 Battery

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 6Li + N2 ↔ 2Li3N (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 batteries was developed, which could run ~80 cycles with high discharge potential (>2 V).[51] The higher discharge potential of this Na-N2 battery than that of Li-N2 battery (~1 V) contradicts the enthalpy of formation (∆H°f) values for Li3N (-164.56 kJ/mol) and Na3N (+64 kJ/mol).[52] The positive formation enthalpy (+64 kJ/mol) and negative entropy change also mean the reaction (6Na + N2 → 2Na3N) cannot proceed spontaneously. In addition, Na3N is extremely unstable and no reports have claimed its synthesis by directly reaction of Na and N2 at room temperature. We emphasize that researches in metal-N2 batteries are very primary. In the future, more works should be conducted to elucidate the hidden complex mechanisms and explain the contradiction between experiment and theory.

5. Flexible Li-air Batteries

The surging demand for flexible and wearable electronics has...
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 hexagon 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). 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). 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.

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). The anode was a composite film of Cu foil, Li foil and stainless steel mesh, while the cathode was carbon cloth with RuO$_2$/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 commercial applications, because it is the most deformable one and can ensure the battery run for a longer time. The easily deformable flexible Li-air batteries are not likely to replace current Li-ion batteries, 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.

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$_2$O, 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.

Acknowledgement

The authors thank the National Key R&D Program of China (2017YFA0206700), the National Natural Science Foundation of China (21725103, 51702314), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21010210), the K. C. Wong Education Foundation (GJTD-2018-09), Jilin Province Science and Technology Development Plan Funding Project (201801012031C), Changchun Science and Technology Development Plan Funding Project (1955010), National & local united engineering lab for power battery.

References

Kai Chen received his BS degree in material chemistry from Liaoning University in 2017. He is currently pursuing a PhD at Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences. His research focuses on resolving the problems of Li-air batteries in practical condition.

Gang Huang received his PhD in applied chemistry from CIAC in 2016. Now he works at King Abdullah University of Science and Technology (KAUST) as a post-doctoral fellow and his research focuses on the development and characterization of nanoporous materials for Li-ion and Li-O2 batteries.
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*