Flexible metal–air batteries: An overview

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Flexible metal–air batteries (MABs) are composed of air cathodes, metal anodes, electrolyte/separators, current collectors, and packaging materials (Figure 1). Flexible MABs are divided into many types based on the difference in metal anodes. Among them, flexible Zn–air, Al–air, Mg–air, and Li–air batteries are currently most researched with the hope that they could provide the power for the next-generation flexible electronic devices. Based on type of the electrolytes used in the system, MABs can also be divided into aqueous and nonaqueous air batteries. Particularly, Zn–air, Al–air, and Mg–air batteries compatible with aqueous alkaline electrolytes have been the research focus for decades long, featuring high safety characteristics. Although the theoretical capacity of Al–air and Mg–air batteries is much higher than that of flexible lithium ion batteries (LIBs), their large polarization, low operating voltage, and the reversibility issue in alkaline electrolytes limit their application as an alternative to the current flexible rechargeable MABs. It should be noted that Na–air and Li–air batteries are mainly based on aprotic electrolytes because metallic Li and Na are extremely reactive toward aqueous electrolytes. Currently, rechargeable alkaline Zn–air batteries and aprotic Li–air batteries are of research interest as the representatives for aqueous and nonaqueous MABs systems. Zn–air batteries not only have low manufacturing costs, high theoretical energy density (1218 W·h/kg), and safety but also can be charged more effectively in alkaline electrolytes. On the contrary, aprotic Li–air batteries have attracted widespread attention and research globally as their operation was successfully demonstrated for the first time in 1996 due to their extremely high energy density (11,400 W·h/kg) and operating voltage (2.96 V). Hence, flexible Li–air batteries could be the ideal alternative to flexible LIBs, even surpassing flexible...
Zn–air batteries, given that the technical barriers in Li–air battery can be overcome.\(^1\)

In contrast to traditional rigid MABs, all functional components in flexible MABs need to meet high standards and achieve good compatibility in terms of flexibility, electrochemical performance, safety, cost, and temperature resistance. Therefore, it is still a formidable challenge to commercialize flexible MABs characterized by low-power long-term operations. For better application in flexible electronic devices, an optimized battery structure is required to enable flexible MABs to achieve high electrochemical activity and mechanical stability under repetitive external forces. To this end, flexible MABs with sandwich-type, cable-type, and bamboo slip-type structures have been proposed.\(^3\) Moreover, light and thin metal anodes (single-metal and metal-alloy anodes with different shapes, free-standing metal composite electrodes, etc.) can meet the flexibility requirements such as bending, deformation, and twisting. Therefore, flexible air cathodes and/or electrolytes with high performance and long-term stability have recently become the research focus of flexible MABs.\(^2\)

Compared with flexible all-solid-state LIBs with closed systems, flexible MABs possess a unique semi-open system, which provides a reaction platform for the cathode active materials (oxygen from ambient air or pure oxygen). The semi-open battery structure minimizes the required volume/mass of the air cathode and increases the energy density significantly. A typical air cathode consists of a gas-permeable and liquid-repellent conductive substrate and a catalyst layer (including catalysts, carbon conductive substrates, and binders). Nevertheless, the high overpotential in the air-cathodic process has hindered the large-scale commercialization of rechargeable flexible MABs. During the discharge–charge process \((nM + mO_2 \leftrightarrow M_nO_{2m}, M = Zn, Al, Mg, Li, Na, etc.)\), the redox reactions occurring at the air–cathode (three-phase boundaries) are kinetically sluggish processes that require high-performance catalysts to effectively facilitate the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Clearly, the rechargeability and energy efficiency of flexible MABs largely depend on the bifunctional oxygen electrocatalysts integrated with the air cathode.\(^3\)

Air cathodes have always been a research hotspot as an important component of flexible MABs. At present, flexible air cathodes mainly include the following categories: flexible carbon-based electrodes composed of nanocarbon materials (carbon nanotubes, graphene, etc.), such as carbon nanotube paper and graphite paper; modified carbon cloth or carbon fiber mesh electrodes; flexible metal-based electrodes (such as modified foam metal mesh); and some other flexible electrodes (such as 3D flexible carbon aerogel with hollow structure and polymer or fabric composite carbon-based materials). Among them, the self-supporting flexible air cathode with excellent bifunctional ORR/OER catalytic activity can better meet the requirements of flexible and wearable electronic devices.\(^4\) In recent years, through various technical approaches, such as heteroatom doping, in-situ synthesis, 3D printing and electrospinning, researchers have designed many integrated flexible air cathodes that are hydrophobic, breathable, highly active, and stable. These air cathodes have shown good performance in flexible Zn–air, Li–air, and Mg–air batteries. Moving forward, it is still feasible to load bifunctional catalytic materials on flexible conductive substrates (carbon substrates, metal substrates, etc.) to enhance the electrochemical performance. Similarly, supported non-noble metal bifunctional ORR/OER catalysts with high activity, high stability, and cost-effectiveness are of great interest on flexible air cathodes. Such catalysts include heteroatom-doped carbon-based catalysts, transition metal chalcogenides, and metal single-atom catalysts. The use of these bifunctional catalysts greatly improves the discharge–charge performance and energy efficiency of flexible MABs.\(^1\)

As a bridge between the air cathode and metal anode in flexible MABs, a flexible electrolyte (or electrolyte membrane) is of paramount importance for flexible MABs. In addition to flexibility and mechanical stability, the electrolyte also needs to have good ion (electron) transmission capacity, metal inertness, good electrical

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**FIGURE 1** Schematic illustration and applications of flexible metal–air batteries (MABs)
conductivity, and other traditional liquid electrolyte properties. For flexible Zn–air, Al–air, and Mg–air batteries, alkaline and neutral gel electrolytes (or those with anion exchange membranes) are mainly used. In flexible Li–air and Na–air batteries, the types of electrolytes mainly include nonaqueous gels, solids, and composite polymers. In contrast to the full contact between the liquid electrolyte and electrodes, the solid electrolyte and electrodes are in point contact. Therefore, to improve the electrochemical performance and charge–discharge cycle stability of flexible MABs, interface issues (such as high interface impedance and metal erosion) between electrolytes and electrodes remain a significant challenge. The solid electrolyte greatly reduces the effective reaction interface between the electrolyte and air cathode. For example, in a Li–air battery, the solid lithium peroxide product aggravates the attenuation of the reaction area. Therefore, effective strategies are required to increase the reaction interface area. For the electrolyte–metal anode interface, it is necessary to solve the problems of surface passivation and dendrites. To this end, strategies such as the use of double-layer electrolytes can be adopted. For flexible Mg–air batteries, the use of an organic-aqueous double-layer gel electrolyte can protect the Mg anode and regulate the discharge products so that the battery can obtain high energy density. Moreover, when flexible MABs are deformed, the electrodes and electrolyte membranes may be separated owing to the difference in their mechanical properties. Therefore, a stable interface is the key to ensuring the long-term stable operation of flexible MABs.

In recent years, with technological breakthroughs in flexible wearable electronic products, research on flexible MABs has also made tremendous progress; for example, the energy density, efficiency, and charge–discharge cycle life of these batteries have been greatly improved. Future research should pay more attention to the following fields. (1) CO\textsubscript{2} and other gases entering through the air cathode pollute the electrolyte and metal anode, resulting in the occurrence of battery side reactions and reduced battery efficiency. (2) To meet the requirements of flexible MABs under special conditions such as low temperature, severe deformation, and stretching, flexible electrolytes with good performance and stability need to be developed. (3) To improve a person’s experience of using different flexible and wearable electronic products, new flexible battery structures and encapsulation materials should be extensively designed and developed; at the same time, it is necessary to use a combination of numerical simulation and experimental verification to further clarify the structure–effect relationship among material transport, structural changes, and battery performance and provide important guidance for the rational design and optimization of flexible MABs.

REFERENCES
1. Zhou JW, Cheng JL, Wang B, Peng HS, Lu J. Flexible metal-gas batteries: a potential option for next-generation power accessories for wearable electronics. Energy Environ Sci. 2020; 13(7):1933-1970.
2. Tan P, Chen B, Xu H, et al. Flexible Zn- and Li-air batteries: recent advances, challenges, and future perspectives. Energy Environ Sci. 2017;10(10):2056-2080.
3. Wang HF, Xu Q. Materials design for rechargeable metal-air batteries. Matter. 2019;1(3):565-595.
4. Wu K, Zhang L, Yuan Y, et al. An iron-decorated carbon aerogel for rechargeable flow and flexible Zn-air batteries. Adv. Mater. 2020;32(32):2002292.
5. Li LH, Chen H, He E, et al. High-energy-density magnesium-air battery based on dual-layer gel electrolyte. Angew Chem Int Ed. 2021. https://doi.org/10.1002/anie.202104536

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