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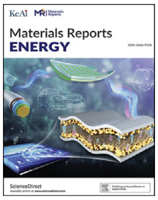

Review

An overview of non-noble metal electrocatalysts and their associated air cathodes for Mg-air batteries

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ABSTRACT

Although metal-air batteries (MABs) including Mg-air batteries possess high theoretical energy densities and are promising in energy storage systems, the poor performances and high cost of corresponding electrocatalysts and air cathodes significantly limit practical application. Based on this, the present review gives a summary of the recent progress in the development of cost effective non-noble metal electrocatalysts and their associated air cathodes for MABs, with a particular focus on Mg-air batteries including the aspects of corresponding catalyst synthesis and characterization, catalyzed oxygen reduction reaction (ORR) mechanism, air cathode fabrication and performance validation. The paper also provides an analysis on the issues that challenge the development of advanced electrocatalysts and the associated air cathodes for Mg-air batteries, as well as a discussion of potential research directions that may help resolve these issues and facilitate the practical application of Mg-air batteries.

1. Introduction

Global CO_2 emissions have been increasing in recent years, and currently about 80% of them come from fossil fuel consumption.[1] This leads to fossil fuel exhaustion, additional CO_2 emission and global warming, and thus highlights the urgency of promoting humanity's ability of utilizing renewable energy sources. And although renewable energies are inexhaustible resources that can be continuously replenished by nature (e.g. solar, wind, biomass, geothermal, tide, hydro) and can potentially meet global energy demands, their intermittent and non-dispatchable nature are significant challenges. To accommodate variations in energy demand and storage of generated power therefore, the development of energy storage systems is necessary for the practical utilization of renewable energies to uncouple power generation and utilization along with the enabling of suitable integration within electrical networks. Similarly, many transportation systems require energy to be stored and carried within electric vehicles (EVs) either in the form of batteries to start engines, battery banks for EVs or fuel cells to propel vehicles in different operation modes to reduce greenhouse gas emissions related to transportation.

Energy storage systems can also be used to balance the asymmetry of daily variations between power production and power demand, and it is expected that increasing energy demand and energy management will stimulate storage system usage with research activities related to renewable energies further promoting industrial development. In 2017, the global energy storage system market was valued at approximately $194.3 billion U.S. and is expected to generate approximately $296.0 billion U.S. in revenue by the end of 2024, growing at a compounded annual growth rate (CAGR) of around 6.2% between 2018 and 2024.[2] And because energy storage processes require the conversion and storage of electrical energy from one energy source to another form that can be converted back into electrical energy as needed,[3] electrochemical technologies are recognized as the most efficient and reliable option.[4–26]

1.1. Electrochemical batteries for energy storage and conversion

Since the invention of the first battery by Allessandro Volta in the eighteenth century,[27] advancements in energy storage technologies have continued to evolve, resulting in unique battery products that are considered to be common devices to store and convert energy. In general, batteries can be categorized as primary or secondary batteries in which primary batteries cannot be electrically recharged and need to be replaced/disposed. Representative primary batteries, including alkaline and lithium batteries as well as Zn-air and silver oxide batteries, are often used in applications such as remote controls, watches, toys, flashlights, etc., and constitute 20% of the global battery market. A major issue for existing primary batteries involves environmental pollution resulting

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from battery disposal. Alternatively, secondary batteries, exemplified by lead-acid batteries, nickel-cadmium batteries, nickel metal hydride batteries and Li-ion batteries (LIB), are rechargeable. In the portable consumer device market, LIBs are currently the most successful secondary batteries in production,[28,29] accounting for 37% of the total share, followed by lead-acid starter batteries (also known as SLI) (20%) and alkaline batteries (15%) with nickel metal hydride (3%) and carbon zinc (6%) batteries representing a small fraction and metal-air batteries (MABs) representing less than 1% of the total global battery market.[30]

Nowadays, batteries are not only expected to power portable electronics, but also facilitate medium and/or large-scale energy storage such as in EVs and grid storage systems, in which the global market of the former has experienced remarkable growth in recent years. In addition, the value of the EV market is expected to grow from $2.25 billion in 2017 to $5.33 billion in 2022 at a CAGR of 18.83%[31] and EV productions are projected to grow from 5.77 million units in 2017 to 13.64 million units by 2022.

1.2. *Metal-air batteries*

The uncertain prospect of further improvements in current battery technologies such as LIBs has given opportunities for MABs to expand into the EV and stationary power markets. For pure EVs, batteries need to achieve a practical specific energy density of 1700 Wh/kg, which is the usable specific energy density of gasoline (theoretical specific energy density of fuel is 13 kWh/kg, energy conversion efficiency of tank-to-wheel of fleet is only 12.6%), and a volumetric energy density of 417 Wh/L to achieve a driving range of 500 miles (125 kWh capacity is required for a maximum 300 L battery).[32–35] However, current batteries such as LIBs based on intercalation chemistry can only provide a capacity of ~200 Wh/kg, and it is generally believed that further improvements to LIB technology can only increase energy densities by up to 30% and may reach 400 Wh/kg in the future.[32–35] As a result, researchers are exploring other practical high energy density alternatives that cost less than $100/kWh for EVs. Here, the theoretical energy densities of MABs (1–11 kWh/kg, calculated based on the thermodynamics of active materials, not counting cathode oxygen and associated components and systems) are much higher than those of LIBs and therefore are often advocated as a promising solution for next generation electrochemical energy storage systems in EV or grid energy storage applications[36] if high utilization efficiency, capacity and rate performance can be realized. Despite this, MABs remain in initial research stages due to associated challenges involving metal anodes, air cathodes and electrolytes, and their potential has yet far from been fully identified. These challenges must be properly addressed before large-scale adoption. Being expected to help to address these limitations, this review aims to improve the understanding of MAB technologies, with special attention to primary Mg-air batteries.

In general, MABs are open electrochemical systems that use metal anodes (Li, Na, Mg, Fe, Zn, Al, etc.), ambient air open cathodes and electrolytes (aqueous or non-aqueous electrolyte depending on the nature of the anode employed). And different from other batteries, MABs can combine the design capabilities of conventional batteries with the design capabilities of fuel cells. In addition, MABs possess larger theoretical energy densities (~3–30 times) than LIBs (Fig. 1) in which only the active component of the anode (metal) is stored and the reactant (O_2) from the air cathode during discharge is extracted from air through a reduction reaction,[37] meaning that the main weight factor dominating the specific energy density of MABs is the anode metal.[38] For example, the theoretical specific energy density of Li-air batteries can reach 11 kWh/kg excluding the oxygen cathode and other cell components, which is close to that of gasoline[39] whereas the theoretical specific energy density of Zn-air batteries excluding the oxygen cathode and other components can reach 1.3 kWh/kg,[40] which is still much higher than those of LIBs. Moreover, the oxygen electrode in MABs is always accessible and its amount is unlimited, allowing inexpensive batteries with high specific energy densities.[41] As a result, MABs are considered to be promising candidates for large-scale energy storage applications such as in EVs. Phynergy (Israel)[42] developed a mass-producible Al-air battery that can significantly extend the range of current EVs before recharge. Companies such as Eos Energy Storage (NYC, USA), Fluidic Energy (Scottsdale Arizona, USA) and Powair (Europe) are also involved in the testing of Zn-air batteries in grid energy storage systems in pilot plants and Tesla Motors has filed eight patent applications involving the use of MAB packs (Zn, Al, Fe, Mg, Li or V) as range extenders for traditional LIB packs. In 2009, IBM further launched the “Battery 500” program with the aim of developing Li-air batteries with an ambitious target of 500 miles (800 km) driving range. Mg-air batteries are also being actively developed to power EVs.

Table 1 gives a comparative summary of the electrochemical properties of main anode metal materials (Li, Zn, Mg, Al, and Na) in MABs (calculations are based on the weight of anode materials only),[35,40,43–50] all of which are promising with corresponding advantages and disadvantages. Among these metals, Li and Zn have been widely used as anode materials for MABs, yet Mg-air, Al-air and Na-air batteries deserve more attention. Though Li is the theoretically most attractive anode material in MABs due to its most negative standard electrode potential and highest specific capacity and specific energy density, the scarcity and high production cost of Li limit its application to high-end products, and the high reactivity of Li to atmospheric conditions makes Li-air open systems unsafe. Compared with Li, Zn shows no advantages in terms of standard electrode potential, specific capacity and specific energy density. However, Zn is more abundant, cheaper and safer to handle in ambient conditions, and, in addition, is superior to Al in corrosion resistance in alkaline media, all of which contributes to the success of primary Zn-air batteries using alkaline electrolytes.

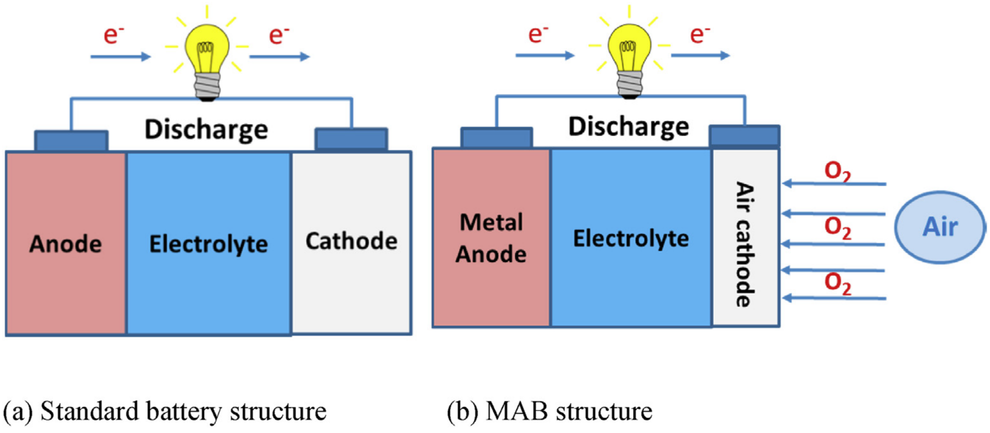

Fig. 1. Schematics of the structure of a metal-air battery (MAB) as compared with a standard battery.

Table 1
Electrochemical properties of Li, Zn, Mg, Al and Na anodes. [46–55]

Metal	Standard electrode potential (V vs. NHE)	Specific capacity (Ah/kg)	Volumetric capacity (Ah/L)	Specific energy density (kWh/kg)
Li	−3.04	3862	2062	11
Zn	−0.77	820	5851	1.3
Mg	−2.37	2205	3833	6.8
Al	−1.66	2980	8046	8.1
Na	−2.71	1166	-	3.4

Among the many possible MAB chemistries, MABs can generally be divided into two categories based on the electrolyte in which one uses aqueous electrolytes[39,46–51,56–59] while the other uses non-aqueous electrolytes, including organic solvents, ionic liquids and all solid-state electrolytes.[37]

The research into MABs began much earlier than LIBs in which Maiche[60] designed the first primary Zn-air battery in 1878 with commercial products entering the market in 1935[61] with water-based Fe-air, Al-air and Mg-air batteries being developed in the 1960s.[46,62–64] And although metals such as Zn, Fe, Mg and Al are thermodynamically unstable in aqueous environments, their surfaces can in some cases be passivated with corresponding oxides or hydroxides, making them to some extent compatible in aqueous electrolytes in which, during discharge, metals are oxidized at the anode and O_2 from the atmosphere is reduced at the cathode by the following equations[55]:

$$\text{Anode: } M \leftrightarrow M^{n+} + ne \tag{1}$$

$$\text{Cathode: } O_2 + ne + 2H_2O \leftrightarrow 4OH^- \tag{2}$$

Here, M represents a metal and n is the oxidation number of the metal ion. During recharge, the above electrochemical reactions get reversed as the metal is re-plated on the anode and O_2 is evolved on the cathode. As a result, air cathodes need to be able to effectively catalyze the oxygen reduction reaction (ORR) and the reverse oxygen evolution reaction (OER).

To date, although high theoretical energy density (1.3 kWh/kg excluding oxygen) has provoked considerable interest for Zn-air batteries, the achievable energy density of Zn-air batteries is usually between 350 and 500 Wh/kg, and the inefficiency of catalysts on air cathodes also leads to insufficient rate capabilities of commercial Zn-air batteries. Besides, rechargeable Zn-air batteries are much inferior to traditional LIBs in energy efficiency (<60% vs. > 90%), resulting from the large overpotentials[65–67] at the air cathode, which is a serious disadvantage. And due to the lack of stable dual-function electrocatalysts and cyclable metal anodes, the cycle life of rechargeable Zn-air batteries is also far from satisfactory, which will be further exacerbated if batteries need to experience high-current deep cycling. On the other hand, individual ORR and OER catalysts, though sufficiently durable under respective operating conditions, generally cannot tolerate alternating reduction-oxidation environments during discharge-charge cycles, and thus are particularly incompatible with ORR active ingredients.[68–73] Furthermore, metal anodes also need to be specifically designed to suppress corrosion as well as uneven dissolution and deposition to circumvent long-term cycling instabilities in rechargeable Zn-air batteries.

Aside from Zn-air batteries, other aqueous MABs also face similar challenges. For instance, Fe-air batteries are rechargeable, and yet their actual energy densities are much lower (60–80 Wh/kg) than current LIBs.[74] Despite this, their long cycle life (>1000 cycles), lower costs (<$100/kWh) and eco-friendly nature make them suitable for stationary energy storage applications. As for Al-air and Mg-air batteries[75,76] with high theoretical energy densities, only small amounts of their total energy density are available because of the severe parasitic corrosion of these metal anodes in contact with aqueous electrolytes. Here, common solutions[54,55,68,69,73] include alloying these metals with other metals such as Cd, Pb, etc. or introducing additives such as polymers, metal oxides, etc. However, none of these solutions can resolve all the issues. Alternatively, mechanical charging involving the rapid and simple replacement of discharged anodes and used electrolyte slurries with fresh metal electrodes and electrolytes[77,78] can achieve high Faradaic efficiencies at the anode in which battery re-charging can be completed in a matter of minutes instead of hours like in secondary battery systems. Here, waste electrolyte slurries containing metal oxides and hydroxides can also be recovered and regenerated into metal through electrolysis or even through solar thermal decomposition.[79–81] Moreover, mechanically chargeable MABs only need to operate in discharge mode and are therefore not limited by the availability of stable dual-function air cathodes, which is particularly attractive due to the difficulty in developing stable air electrodes that are resistant to oxygen evolution during battery charging. In this regard, some companies[82] have demonstrated re-charged Zn-air batteries with the mechanical refueling of zinc anodes for EV applications (e.g. all-electric passenger cars and electric scooters)

Most MABs such as Na-air and Li-air batteries use aprotic electrolytes in which ORR proceeds through a mechanism distinct from that in aqueous electrolytes[55]:

$$\text{Anode: } M \leftrightarrow M^{+} + e \tag{3}$$

$$\text{Cathode: } xM^{+} + O_2 + xe \leftrightarrow M_xO_2\ (x = 1 \text{ or } 2) \tag{4}$$

Here, this reaction involves the one- and/or two-electron reduction of O_2 (Equation (4)) depending on the metal cation (e.g. one electron for Na, two electrons for Li) to form corresponding metal super-oxides or metal peroxides. These metal oxides possess limited solubility in electrolytes and can deposit on air cathodes, the accumulation of which can cause the gradual blockage of available cathode surface area and render batteries inoperable. In consequence, the discharge capacity of non-aqueous MABs depends on the storage capacity of air cathodes to discharge products, and thus is much lower than that of theoretical values.[55] As compared with aqueous MABs, non-aqueous MABs are more immature and face even greater challenges. For example, because metal super-oxides or metal peroxides are oxidizing and can induce the decomposition of most common electrolytes used in MABs, it is necessary to find suitable electrolytes.[49,83]

Despite early beginnings, no MABs are currently in large-scale industrial deployment with only primary Zn-air batteries[42] being commercialized, mainly for low-power applications such as hearing aids, watches and electronic calculators. However, if practical energy densities and power densities can be further improved, primary MABs may be a short-term solution that can replace traditional LIBs. And rechargeable non-aqueous MABs, by virtue of the higher theoretical energy densities, can provide long-term solutions for large-scale electrochemical energy storage applications if associated technical problems can be effectively resolved. But despite this, electrically rechargeable non-aqueous MABs may not be suitable for high-power applications (such as EVs) because corresponding ORR rates in aprotic solvents are orders of magnitude slower than ORR rates in aqueous electrolytes.

In general, primary MABs with aqueous electrolytes possess many disadvantages, and their performance is dependent on environmental conditions such as atmospheric humidity and temperature in which, due to their open system nature, water drying from electrolytes can limit shelf life whereas water flooding in electrolytes from air can limit power output due to atmospheric changes. Issues such as limited power output and operating temperature range, anode corrosion, hydrogen release from anode corrosion and alkaline electrolyte carbonation also affect the performance of MABs with aqueous electrolytes.[32,36,84–88] Other major deficiencies of primary MABs include the low utilization of anodes and the slow kinetics of ORR in air cathodes, both resulting in limited actual energy densities.[32,36,84–88] As for MAB anodes, if exposed to electrolytes, they will get passivated and corroded, and metal oxides, hydroxides or other substances will then form and accumulate on anode surfaces. This will in consequence prevent the entry of electrolytes and therefore cause the incomplete discharge of active materials. Moreover, the self-discharge and corrosion of metal anodes can further reduce the Coulombic efficiency of anodes and shorten battery shelf life. As for air cathodes, main issues are the inherently slow reaction kinetics of oxygen reduction with high overpotentials. Overall, solutions to these problems involve the rational design and engineering of cathode and anode materials and structures.

1.3. Air cathodes of metal-air batteries

Because both ORR and OER are sluggish reactions, air cathode dominantly affects the performance of rechargeable MABs, and therefore is pivotal to the commercialization of MAB technologies. On air cathodes, both ORR/OER occur at the three-phase boundary in which the solid electrode is in contact with not only the liquid electrolyte but also the gaseous O_2. Here, the development of active bi-functional electrocatalysts can accelerate ORR/OER kinetics and the design of appropriate electrode architectures can expand the three-phase interface, all of which can greatly benefit the charge/discharge performance of corresponding batteries.

The operation of primary MABs involves only ORR on the air cathode, making electrocatalysts easier to function, yet there are several issues remain. Therefore, it is vital that metal anodes and air cathodes be improved to enhance the general performance of primary MABs. And although both anode and cathode electrochemical reaction kinetics influence largely the performance of MABs, the sluggish ORR on air cathodes is the most challenging aspect. Based on this, efforts should be directed to the study of high-performance air cathodes adaptable to different pH electrolytes. Overall, MABs are currently receiving increasing attention in resolving present energy demands. Nonetheless, more work is required before commercialization can be realized.

2. Status of primary Mg-air batteries

Mg is the fifth most abundant element in the earth's crust with a content of 3%.[88] As a result, widely available and inexpensive Mg (about 5% of Li metal costs) is an attractive candidate anode material for MAB applications. And despite being less well-known than Zn-air batteries, Mg possesses high reaction activities and is non-toxic, biocompatible and environmentally friendly. In addition, the use of Mg encounters significantly less safety and processing issues as compared with Li if exposed to air. Furthermore, Mg has a large negative standard electrode potential (-2.37 V vs. NHE), and the theoretical specific energy density for the reaction between Mg and O_2 (6.80 kWh/kg) ranks second among all MABs, far exceeding that of Zn-air batteries (Table 1). Mg also possesses a specific capacity of 2205 Ah/kg, making it almost twice superior to Li in volumetric capacity (3833 Ah/L vs. 2062 Ah/L). This can impart Mg-air batteries a huge advantage in applications, especially for cases with limited in installation space such as mobile devices and EVs. Currently, Mg-air batteries have mainly been used in small, lightweight consumer-friendly portable power systems up to 100 W, although power is generally limited up to 5 kW,[28,44,89–91] with important markets including small-sized devices such as emergency lanterns and emergency power backup systems for hospitals and schools[37,76,92–94] as well as subsea instruments such as lighthouses, monitoring equipment and buoys.[95,96] Mg-air batteries have also found applications in military field, as the hybridization of Mg-air batteries with Ni–Zn batteries has been proposed as detector energy providers that can provide 25 kW of power for two weeks.[76]

In general, current Mg-air batteries are primary batteries based on either alkaline or acidic aqueous electrolytes with relatively few studies[37,51,53,93,94,97–100] concerning the possibility of electrically rechargeable Mg-air batteries based on non-aqueous electrolytes due to difficulties in realizing simultaneous reversible Mg dissolution/deposition and oxygen reduction/evolution electrochemistries. To achieve higher performance of air cathodes, most MABs, including Mg-air batteries, use alkaline electrolytes which can easily absorb atmospheric carbon dioxide and consequently cause the precipitation of carbonate in the pores of air cathode electrocatalysts. This issue will get exaggerated in secondary MABs due to the lack of electrolyte replacements,[101] and has already prompted attention to acid electrolyte batteries with early attempts at Al-air and Mg-air batteries using weakly acidic chloride solutions.[85] However, these batteries experienced high cathodic polarizations that resulted in increased heat generation and anode self-discharge.

Mg-air batteries, unlike Zn-air batteries, notwithstanding their irreversibility in aqueous media (most Mg compounds are both electrically and ionically non-conductive), can be reused by mechanically replenishing/replacing spent anodes[102] and consumed/evaporated electrolytes. This enables not only Mg-air batteries to remain stable for significant periods of time with the removal of electrolyte and subsequently to be rendered operational through the re-addition of electrolyte, but also battery charging that consumes just a few minutes instead of hours as in secondary battery systems and the centralization of anode replenishment in large processing plants that ensures higher quality. Such easy operations make Mg-air battery applications convenient and can provide high Faradaic efficiencies and high degrees of safety. In addition, mechanically rechargeable Mg-air batteries operate only in the discharge mode, and therefore are not limited by the availability of stable dual-function air cathodes, which is particularly important since the development of air cathodes that are stable against oxygen evolution during charge is quite challenging.

Under this background, Mg-air batteries using neutral aqueous electrolytes such as NaCl solutions, which are non-aggressive, safe, environmentally friendly and exempt from the current issues bedeviling both alkaline and acidic electrolytes, deserve researchers' interest. Furthermore, with the rapid growth of EVs and grid-scale energy storage systems, significant opportunities have arisen for primary Mg-air batteries, and have highlighted the importance of realizing in practice high rates and capacities in neutral electrolytes.

Primary Mg-air battery systems involve the electrochemical coupling of Mg anodes to air diffusion cathodes through suitable electrolytes to provide high-performance batteries with inexhaustible cathode reactants from atmospheric oxygen (Fig. 2). During discharge, the Mg anode is oxidized to generate Mg^{2+} and two electrons whereas atmospheric oxygen reacts with water through the air diffusion cathode and is reduced to generate OH^- through electrochemical reactions, resulting in the outflow of electrons via an external circuit.

Overall, the discharge reaction in primary Mg-air batteries and corresponding standard electrode (anode and cathode) potentials and cell voltages can be represented as follows[76,104–109]:

$$\text{Anode: } Mg \rightarrow Mg^{2+} + 2e \quad E^\circ = -2.37 \text{ V (vs. NHE)} \tag{5}$$

$$\text{Cathode: } O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad E^\circ = +0.40 \text{ V (vs. NHE)} \tag{6}$$

$$\text{Overall: } 2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2 \quad E_{cell} = 2.77 \text{ V} \tag{7}$$

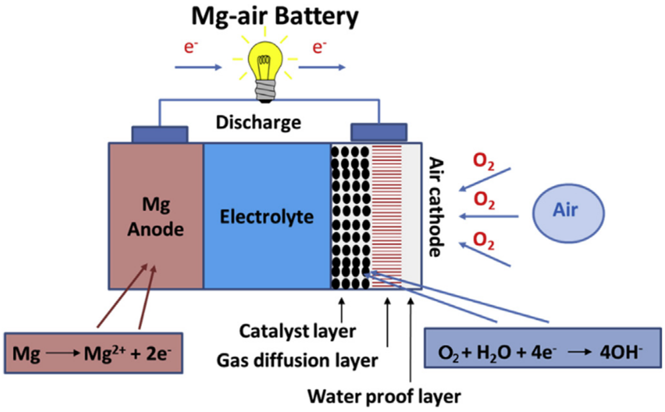

Fig. 2. Typical structure of a Mg-air battery. Adapted from Ref. 103.

Here, the high theoretical cell voltage (2.77 V) is far beyond practical values which are normally below 1.2 V in conventional saline aqueous electrolytes. This can be ascribed to high levels of anodic and cathodic polarization and low Coulombic efficiencies during discharge, resulting mainly from the parasitic corrosion of Mg and the sluggish kinetics of cathodic ORR. And because Mg^{2+} is stable under a pH below 11 while $Mg(OH)_2$ is stable under a pH above 11,[110,111] Mg can spontaneously convert to Mg ions in both neutral and acidic aqueous environments and these generated Mg ions can further react with water through electrochemical mechanisms to generate magnesium hydroxide and hydrogen. Specifically, Mg can spontaneously react with water as a parasitic reaction to form interfacial $Mg(OH)_2$ film on electrodes as well as hydrogen. This interfacial $Mg(OH)_2$ film can subsequently block electronic and ionic conduction and terminate the discharge process of corresponding batteries due to high interfacial impedance. Equations listed beneath show the main parasitic corrosion reaction of Mg with water[112]:

$$Mg \rightarrow Mg^{2+} + 2e \tag{8}$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{9}$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \tag{10}$$

and the overall corrosion reaction:

$$Mg + H_2O \rightarrow Mg(OH)_2 + H_2 \tag{11}$$

Several strategies have been applied to overcome the corrosion of Mg and inhibit the evolution of H_2, including alloying Mg with other metals to reduce H_2 evolution,[113–119] improving Mg intrinsic properties through altering Mg grain size, morphology and nanostructure to optimize the electrochemical performance of Mg in aqueous electrolytes,[41,120,121] as well as modifying electrolyte compositions to reduce Mg corrosion in aqueous electrolytes. And because the formed $Mg(OH)_2$ films on Mg electrodes can provide higher corrosion resistances in alkaline media but is also passivated and can hinder further discharge reactions,[122] electrolyte pH levels should be controlled close to neutral to which the salt concentration in electrolytes is important. For instance, the corrosion rate of pure Mg in seawater is 1200 times slower than that in 3 mol/L $MgCl_2$ solution and therefore, lower salt concentration is usually required.[122] In addition, hydrogen inhibitors can be introduced to electrolytes to suppress hydrogen evolution.[84]

Aside from anodic corrosion, the low Coulombic efficiency of Mg-air batteries is also caused by the slow kinetics of ORR. As a complex process in Mg-air batteries, ORR involves the diffusion of atmospheric oxygen to catalyst surface, the absorption of oxygen on catalyst surface, the transfer of electrons from anode to oxygen molecules, the breakage of oxygen bonds, and the removal of products from catalyst surface to electrolyte. Here, the reaction mechanism depends on pH environments, and to facilitate ORR, protons or hydroxyls are necessary (i.e. an acidic or alkaline environments).[123,124] And neutral media (pH = 7) has been reported to have negative influence on ORR kinetics under high overpotentials due to lower proton and hydroxyl concentrations (10^{-7} mol/L).[125–128] Overall, the electrical reduction of oxygen in neutral electrolytes is mainly carried out through: i) the direct four-electron reduction of oxygen to generate OH^- (Equation (12)); ii) the two-electron reduction of oxygen to generate OH^- and HO_2^- (Equation (13)) and subsequent reduction to OH^- (Equations (14) and (15)), all of which can be represented as follows[129]:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{12}$$

$$O_2 + H_2O + 2e \rightarrow OH^- + HO_2^- \tag{13}$$

$$HO_2^- + H_2O + 2e \rightarrow 3OH^- \tag{14}$$

$$2HO_2^- \rightarrow 2OH^- + O_2 \tag{15}$$

Here, the two-electron reduction of oxygen not only reduces system efficiency, but also produces strongly oxidizing substances (such as peroxides) which will further reduce catalytic activities.[130–132] Therefore, electrocatalysts which can effectively promote the direct four-electron reduction of oxygen to generate hydroxyls are necessary to develop promising Mg-air battery systems.

3. Development of ORR electrocatalysts and associated air cathodes for primary Mg-air batteries

The air cathode is a basic component of primary Mg-air batteries; however, several issues can cause inefficiencies in existing air cathodes. Table 2 summarizes these issues along with the corresponding solutions.[46]

The main reason for low Coulombic efficiency of primary Mg-air batteries is the slow ORR kinetics, which, as mentioned in Section 1.2, results from the high overpotential. Efforts aiming to overcome this demerit can focus on the activity of catalysts and the architecture of air cathodes.

3.1. ORR electrocatalysts for Mg-air batteries

Compared with the many types of electrocatalysts that have been explored for ORR in acidic or alkaline media,[13,133–143] there lacks specifically designed electrocatalysts active in neutral media[95,96,144,145] for MABs including Mg-air batteries. However, catalysts effective in weak alkaline media are also effective in neutral media because the catalysts' performances under the two circumstances are often comparable,[71] and to date, several examples have been explored, mainly for microbial fuel cells or bio-fuels.[76,126–128]

The first type of electrocatalysts involve precious metals (e.g. platinum group metals (PGMs): Pt, Pd, Ru, Rh, Ir, etc.) and corresponding alloys with unique structures (Pt_5M (M = lanthanide or alkaline earth metals), hollow Pt_3Ni nano-frames, PtNi, etc.) based on acidic or alkaline fuel cells and batteries.[146–153] Here, these core-shell bimetallic catalysts are special alloys in which the precious metal shells can act as protectors of transition metal cores[154,155] against core dissolution. Moreover, the catalytic behavior is usually enhanced on bimetallic catalysts as compared to monometallic catalysts due to changes in the structure and surface between the interaction of two types of metal atoms. And because

Table 2
Summary of issues impairing air cathodes and the corresponding solutions.[46]

Issues	Cause	Effect	Countermeasure
Slow oxygen reaction kinetics	High overpotential required for ORR	Low energy/power density and efficiency	Explore effective and durable electrocatalysts
High internal resistance of air cathodes	Cathode structure	Low energy/power density and efficiency	Proper optimization of air cathode structures
Air cathode flooding	Electrolyte penetration into the pores of air cathodes	Limited oxygen accessibility	Treatment of carbon electrodes with wax Appropriate optimization of gas diffusion layers (GDLs)
Carbonate	Reaction of CO_2 with alkaline electrolyte	Reduced electrolyte conductivity and air cathode activity	Using pure O_2 instead of air
Electrolyte dry-out	Water evaporation	Decreased battery life	Appropriate optimization of GDLs

only small amounts of precious metal are used in surface shells for catalytic reactions, precious metal loadings can be minimized. Despite this, the high price and scarcity of these precious metals can elevate battery cost to a high level, hence developing practical and economically competitive MABs still require the search for non-precious metal catalysts, including carbon-based materials, transition metal oxides, carbides, nitrides and atomically dispersed catalysts (ADC) with and without pyrolysis. Here, non-precious metals can easily form effective nanostructures and establish important interactions with support materials such as carbon to improve activity and stability.

Carbon-based materials have been introduced in recent years as non-precious metal catalysts for ORR. Though generally far from successful in reducing overpotentials and expediting reaction kinetics,[156–161] novel carbon-based materials do provide opportunity to construct promising ORR catalysts, as the combination of different types of carbon materials may incorporate the advantages and properties of individuals. For example, by coating mesoporous carbon onto carbon nanofibers (CNFs) to form a carbon nanofiber@mesoporous carbon core-shell composite catalyst,[162] the resultant structure can possess not only an enlarged surface area, but also a highly conductive graphitized surface to increase electrical conductivity, thus promoting catalytic activity and chemical/electrochemical stability. The doping of carbon with heteroatoms such as nitrogen, phosphorus, boron, sulphur or fluorine can also greatly improve ORR activity due to the formation of conductive pathways, especially for high surface area mesoporous carbons, nanotubes and graphene. However, the production of graphene and nanotubes remains expensive.

Transition metal oxides are another important type of non-precious metal ORR catalyst[22,129,163,164] that have been extensively studied in terms of their crystal structure, morphology and doping effect. In general, transition metal oxides are abundant, inexpensive, easy to prepare, environmentally benign and more importantly, possess catalytic activities that rival Pt-based catalysts. These transition metal oxides include i) perovskite oxides with the general formula of ABO_3 in which A refers to a rare alkaline earth metal cation and B represents a 3D transition metal cation, and ii) spinel oxides with the general formula of $A_xB_{3\text{-}x}O_4$ (A, B=Co, Zn, Ni, Fe, Cu, Mn, etc.), as well as iii) other transition metal oxides including single metal oxides and mixed metal oxides such as MnO, MnO_2, Mn_2O_3, Mn_3O_4, Co_3O_4, Fe_3O_4, etc. A major obstacle in the application of transition metal oxides involves their low electronic conductivity, which can hinder charge transfer and result in low catalytic performances. As a countermeasure, the composition of transition metal oxides with conductive carbon materials is an effective strategy to ensure rapid electron transport and enhance interactions between oxides and carbon to improve catalytic performances.

Carbides and nitrides are also promising ORR electrocatalysts for MABs. For example, titanium nitride (TiN) is a typical transition metal nitride that possesses high electronic conductivity and good electrochemical activity and therefore has been widely used in electrochemical devices.[165] Graphite carbon nitride (g-CN) is also an attractive metal-free electrocatalyst because of its rich source and negligible metal pollution. And to address the poor conductivity and ORR activity of g-CN, carbon[166] and P-doping[167] have been combined with porous graphitic g-CN to obtain catalysts with excellent ORR activities in MABs. Recently, researchers even attempted to improve the capacity, chargeability and round-trip efficiency of MABs by using carbon composite catalysts prepared from carbides such as tungsten carbide (WC)[168] and boron carbide (B_4C).[169] And according to their studies, WC coatings can enhance ORR and OER activities and limit discharge-charge overpotentials due to the enhanced catalytic performance and electrical conductivity of carbon-WC composites. B_4C nanowire-carbon nanotube composite cathodes also exhibits improved ORR/OER activity, chargeability and round-trip efficiency due to the synergistic effects between B_4C and carbon.

Catalytic performance is closely related to active site exposure, as more exposed surface areas can provide more active sites. Based on this, the fabrication of electrocatalysts with optimal nanostructures and large surface areas is important in which both theoretical and experimental studies have confirmed that the reduction of particle or cluster size to uniformly distributed single atoms is an effective method to obtain more active sites and better catalytic activities.[170,171] As a result, various single (e.g. Co, Ni, Fe, Cu, Mn) or binary (e.g. CoCu, CoNi, Fe–FeC, $FeNi_3$) non-precious metals have been studied as catalysts for MABs, and binary metals are expected to produce stronger synergetic effects.[172–176] M-N-C-type molecular catalysts (M is a non-precious metal such as Mn, Fe, Co, Ni) have also been thoroughly studied as ORR catalysts in acidic and alkaline media[142,143,177] as well as neutral media,[178,179] in which, as compared with Pt in alkaline and neutral media, can show high performances and durability in long-term operations.[145,180,181] Cobalt and iron tetramethoxyphenylporphyrin (CoTMPP and FeTMPP) catalysts supported on carbon or pre-pyrolyzed can also produce higher and similar ORR activities in alkaline media.[136,182–188] And because the chemical and electronic environments associated with the active sites of such molecular catalysts are usually more pronounced and more easily tunable as compared with solid state metal catalysts such as Pt,[189,190] ligand environments around transition metals can be modified and molecular catalysts can be fixed on high-surface-area conductive carbon to produce homogeneous catalysts capable of mediating ORR. In addition, these catalysts can be used as model systems to provide basic understandings of the ORR mechanism in terms of active sites and interactions between catalysts and supports.

For M-N-C type catalysts, the type of nitrogen was found to be a vital element in the formation of active ORR catalysts in addition to the metal source, carbon support and high temperature heat treatment method. Typically, there exist four types of nitrogen ligands in the graphene sheet, i.e., pyridinic, pyrrolic, nitrile and graphitic, where only pyridinic and pyrrolic nitrogen are active towards ORR.[191]

Optimal metal loadings in M-N-C non-precious metal catalysts depend on the active nitrogen content in carbon supports in which if the active nitrogen atom is saturated with coordinated metal ions, metal loadings reach a maximum. Here, excessive metal can form inactive materials (e.g. metal carbides and nitrides)[192,193] that can inhibit ORR activity.[194,195] As for the choice of carbon support materials, this depends on its ability to coordinate nitrogen atoms and not its other properties.

Dodelet et al.[196–199] also used XPS and time-of-flight secondary ion mass spectrometry (SIMS) to study the decomposition of metal macrocycles adsorbed on carbon supports and proposed the existence of two active sites on heat-treated M-N-C catalysts, mainly in Fe-based catalysts, in which one involves $Fe–N_4$ active sites and the other involves $Fe–N_2$. And although $Fe–N_2$ may not possess a complete structure with complete coordination, it is still considered to be able to form a complete active site through coordination with two other N or O atoms. These researchers further proposed that under a low-temperature heat-treatment condition (500–600 °C), the resultant catalytic active site contains a moiety of $Fe–N_4$, where the nitrogen type in $Fe–N_4$ is pyrrolic nitrogen, while at a higher heat-treatment temperature (>800 °C), $Fe–N_2$ is the active site, where the nitrogen type is considered as pyridinic nitrogen.[199] And because the high-temperature active sites were the functional groups with the highest ORR activity, Dodelet et al. deemed that the heat treatment of metal complexes containing N at 800 °C to increase metal-coordinated pyridinic nitrogen content is key to improving the ORR activity of non-noble metal catalysts.

Although heat-treated M-N-C catalysts have superior activity and stability to the untreated ones, the nature of the corresponding active sites, along with the mechanism by which their morphology and chemical parameters controlling the activity and stability, remain unclear. For example, the role of N-containing moieties such as pyridinic type N, pyrrolic type N, etc. as ORR active sites in M-N-C electrocatalysts, the impact of various carbon morphologies on π-electron delocalization and nanostructure stability, and the temperature dependence of heat treatment effect, all deserve further investigation. In addition, the kinetic behavior of M-N-C catalysts remains elusive and is not well understood.

Furthermore, most M-N-C catalysts can only reduce oxygen to hydrogen peroxide through the two-electron route instead of the four-electron route to H_2O, and the resultant hydrogen peroxide can corrode catalysts and other cathode components and consequently reduce catalytic activities and cathode lifespans. There has been conducted significant research on the mechanisms and kinetics of ORR catalysis in M-N-C catalysts using CV and RDE/RRDE technology,[200,201] but most have focused on ORR with limited concern over catalytic hydrogen peroxide reduction in which if a catalyst can reduce H_2O_2, H_2O_2 produced by the process can be eliminated to mitigate its negative impact on cathode life and performance. Moreover, most previous research has been performed in strong acid or alkali media aiming at hydrogen fuel cell applications, while neutral media that are widely used in Mg-air batteries acquired little attention.

3.2. *Air cathodes for Mg-air batteries*

In general, the air cathode of primary Mg-air batteries must form a three-phase (gas-solid-liquid) interface with gas, catalyst/carbon and electrolyte contact to promote the reduction of gaseous oxygen.[19,32,36,37,66,68,84,89,202–212] Typical air cathodes possess a sheet-like structure with opposing faces exposed to two different environments (atmosphere O_2 and electrolyte) and consist of four layers, i.e. a waterproof layer (WPL), a GDL, a current collector layer and a catalyst layer (CL).[212–239] Here, the atmospheric side needs to be air permeable but hydrophobic to avoid electrolyte leakage. As a result, the WPL layer is in direct contact with the air side and is usually composed of a hydrophobic porous substance (such as paraffin or Teflon) that can separate electrolyte from air and allow only O_2 to pass and block out CO_2 and H_2O. Alternatively, the GDL possesses high porosity, high electrical conductivity and is usually composed of carbon materials and hydrophobic binders such as polytetrafluoroethylene (PTFE) so that the diffusion layer is only permeable to air and prevents water from penetrating. The CL, comprising an electrocatalyst, a conductive carbon material and a binder, enables ORR and is dispersed on the surface of the GDL near the electrolyte. As for the current collector, it is embedded into the air cathode and is usually made of a metal mesh that can be connected to an external circuit and can enhance the electron transfer process and provide structural support for the air cathode. As a result, the four layers of the commonly used air cathodes for MABs are a Teflon film layer, an active CL, a metal mesh layer and another active CL. The two active CLs contain conductive carbon additives, catalysts, dispersants and binders, and are usually bonded to each side of the metal mesh via heat-sealing of a coating adhesive that is pre-coated onto the surface of the active layer or metal mesh. A microporous Teflon film is also laminated onto a sandwich cathode. Despite high performances however, this four-layer air cathode configuration is expensive and is usually designed for alkaline media rather than neutral media (sodium chloride). In addition, the coating adhesives between active layers and metal meshes increases internal resistances and therefore limit air permeability and water transport, meaning that the heat-sealed bonding method is detrimental to electrode performances.

As an alternative, a two-pass lamination method has been developed to fabricate air cathodes comprises four layers,[240] including a hydrophobic film layer facing the atmosphere, a carbon sheet embedded with a CL, a metal mesh layer as a current collector and a carbon sheet embedded with a CL facing the electrolyte. However, this method still involves the heat sealing of a coating material to bind the above-mentioned carbon and mesh layers together, and the heat sealing process used to apply the hydrophobic film layer in the second pass can produce highly inconsistent results in terms of air permeability throughout the cathode structure as evidenced by testing the corresponding air cathode sample. To address this, there has been proposed an air cathode which is constructed by applying multiple pastes onto porous metal foam[241] and composed of a hydrophobic layer facing the atmosphere, a first catalyst embedded layer, a metal foam layer and a second electrolyte embedded layer facing the electrolyte. Another air cathode was also prepared through sandwiching a hydrophobic paste layer and a catalyst paste layer between two mesh current collectors,[242] in which one mesh current collector touched the hydrophobic paste on one side and faced the oxygen environment on the other side whereas the other mesh current collector adjoined the catalyst paste on one side and faced the aqueous electrolyte on the other side. Furthermore, an air cathode constructed with a current collector layer, two sintered diffusion layers and a sintered activation layer[243] was also studied focusing on the use in fuel cells or electric capacitors, particularly zinc-air fuel cells with isolating membranes and potassium hydroxide or polymer electrolytes. And the two or more sintered diffusion layers in the cathode can act as obstructions to prevent water/electrolyte loss.

On the whole, currently the proposed air cathodes are constructed by sandwiching together multiple layers through adhering, heat sealing or sintering, and these multiple layers include hydrophobic layers, current collectors and CLs that are often separated by adhesives or sealing components. Here, each layer is a standalone element or structure (e.g. in the form of sheets or webs) that must be prepared in advance separately and be independently applied to the current collector. As a result, existent air cathodes and corresponding fabrication methods are unnecessarily complex. In addition, although successes have been achieved in the fabrication of air cathodes, limitations remain such as: i) their susceptibility to corrosion in acidic or neutral media, ii) high internal electrical resistances partly because of their multilayer configuration, iii) high material and manufacturing costs due to the multilayer fabrication process, and iv) uneven catalyst distributions over cathode structures due to direct deposition into current collectors. As a result, further development of Mg-air batteries do need cost-effective air cathodes that can be prepared through continuous manufacturing processes, withstand corrosion, and possess satisfactory performance in neutral media.

To address these requirements, we recently investigated systematically the pyrolyzed Co-N_x/C composites derived by heat-treating CoTMPP/carbon precursors at high temperatures, in the anticipation of finding a well-performed non-noble metal catalyst for air cathode of Mg-air battery.[103,244,245] Three representative carbon supports, including Black Pearl 2000 (BP), ordered mesoporous carbon (MPC) and monolayer graphene oxide (GO), were chosen to adsorb CoTMPP, a non-noble metal material mentioned in Section 3.1, to form the precursors and to prepare Co-N_x/BP, Co-N_x/MPC, and Co-N_x/GO. A series of tests and characterizations suggested that Co-N_x/BP was the best one among the three electrocatalysts for ORR in neutral medium.

For further fundamental understanding, DFT calculations were also carried out in our study to identify the catalytic ORR active centers, leading to both Co–N_2 and Co–N_4 being confirmed (Fig. 3). And to facilitate further investigations, based on measurements and analyses, an ORR mechanism was proposed as follows[244]:

$$\text{Co-N}_x\text{/C} + O_2 \rightarrow O_2\text{–Co-N}_x\text{/C} \tag{16}$$

$$O_2\text{–Co-N}_x\text{/C} + e + H_2O \rightarrow \text{(OOH)–Co-N}_x\text{/C} + OH^- \tag{17}$$

$$\text{(OOH)–Co-N}_x\text{/C} + e + H_2O \rightarrow H_2O_2\text{–Co-N}_x\text{/C} + OH^- \tag{18}$$

$$H_2O_2\text{–Co-N}_x\text{/C} \rightarrow \text{Co-N}_x\text{/C} + H_2O_2 \tag{19}$$

$$\text{(OOH)–Co-N}_x\text{/C} + 3e + H_2O \rightarrow \text{Co-N}_x\text{/C} + 3OH^- \tag{20}$$

Here, Equation (16) represents the chemical reaction between catalysts and O_2; Equation (17) represents the reaction determining step of ORR on the surface of three different carbon-supported Co-N_x/C catalysts; Equation (18) represents the formation of peroxides, which occurs only if catalyzed by Co-N_x/MPC or Co-N_x/GO; Equation (19) represents the chemical desorption of H_2O_2 to form free H_2O_2 that can enter the bulk solution as detected by a ring electrode; and Equation (20) represents the complete 4-electron transfer mechanism of the Co-N_x/BP catalyst in which the total number of electrons detected is 4. Despite these findings, more evidence is needed to validate the catalytic mechanisms. Overall

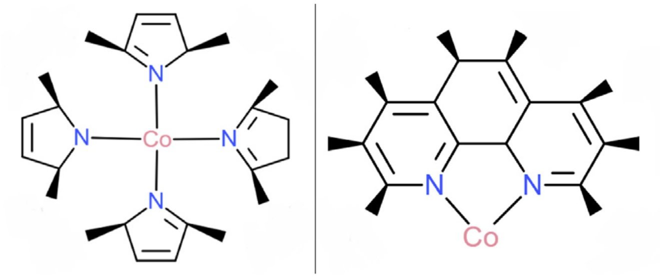

Fig. 3. ORR active site structures of heat-treated CoTMPP. Left: Co–N_4 structure; Right: Co–N_2 structure. ▲ represents the bulk carbon support.

however, these can improve the understanding of non-precious metal catalysts supported by various carbon supports for ORR and the obtained results and conclusions can provide reference for the proper selection of carbon supports.

The integrated MAB air cathode designed and fabricated by using the Co-N_x/BP electrocatalyst and adopting an innovative method was proved preliminarily to be suitable for ORR in alkaline or neutral media and superior to commercially available air cathodes in terms of material costs, air cathode and corresponding system components, system internal resistances, gas flow limitations, and manufacturing processes. Here, metal current collectors were used to maintain corrosion resistance to alkaline or neutral (e.g. NaCl) media and achieved the same or better performances than commercially available cathodes. Detailed manufacturing steps were also outlined in our study, including paste/ink preparation, bonding methods and hot-pressing conditions. Moreover, performance evaluation carried out using a custom built three-electrode electrochemical half-cell and a Mg-air single-cell battery demonstrated the high ORR activity and stability of the air cathode in which electrochemical tests performed after immersing the air cathode in 10 wt% NaCl solution for 30 weeks revealed no degradation. And because the performance results obtained in a single Mg-air battery based on this developed air cathode were comparable to or better than those using commercially available air cathodes but with significant cost reductions in terms of materials and manufacturing, our study provided a route to the production of low-cost, high-performance MAB air cathodes that can easily be transferred to continuous industrial manufacturing processes.

4. Conclusion and perspective

Among various battery technologies, MABs (a combination of high-energy-density metal anodes and atmospheric oxygen as the cathode reactant) possess theoretically high specific energy densities that are comparable to gasoline, making them attractive technologies for sustainable energy storage and conversion applications. Despite early development however, current MABs have yet achieved large-scale industrial deployment and among different types of MABs, primary MABs may be a short-term solution if corresponding practical energy/power densities and lifetimes can be further improved, allowing them to replace conventional batteries in many power-intensive applications.

And for the various MABs (e.g. Li/Mg/Zn/Al-air batteries), Mg-air batteries possess the second highest specific energy density and the second largest cell voltage. However, this battery technology is currently in developmental stages and its potential has not yet been fully realized due to challenges related to anodes, cathodes and electrolytes. These challenges must be properly addressed before Mg-air batteries can achieve large-scale deployment. Here, the development of suitable air cathodes for Mg-air batteries and other MABs is particularly challenging due to the sluggish kinetics of ORR in which the ORR reaction at the air cathode mainly occurs at the three-phase boundary where the solid electrode is in contact with the liquid electrolyte and gaseous O_2 at the same time. Because of this, the development of active catalysts to accelerate ORR kinetics and the design of appropriate electrode structures to expand the three-phase interface are vital in improving battery performances. Moreover, most MABs including Mg-air batteries use alkaline aqueous electrolytes in which air cathodes perform better than in lower pH electrolytes, hence issues related to corresponding anodes and cathodes must be addressed, including the formation of passivated $Mg(OH)_2$ films on anodes and the precipitation of carbonate in cathodes due to the adsorption of atmospheric carbon dioxide, which can form interfacial films on anodes and block electrocatalyst pores in cathode CLs to terminate discharge processes due to high interfacial resistances.

And although great progress has been made in air cathodes for primary Mg-air batteries, several challenges must be overcome to achieve commercialization, including: i) insufficient fundamental understanding of the reactions and synergy mechanisms of ORR, particularly the effects of supports on the local nitrogen coordination environment of catalyst active sites. The fundamental understanding of intrinsic ORR mechanisms is also an important aspect in the development of high-performance electrocatalysts, particularly the elucidation of catalyst active sites for O_2 activation and catalyst support interactions; ii) insufficient strategies for catalyst design, raw material selection, scalable synthesis and catalyst performance optimization; and iii) unoptimized electrode/cell designs and fabrication methods that are incompatible with newly developed catalysts in which electrocatalytic reactions occurring at the three-phase boundary of solid-liquid and electrolyte-gas at the catalyst layer for cathodic ORR as well as corresponding mechanisms are complex and are primarily dependent on catalyst surface properties and air cathode structure designs and optimizations.

To overcome these challenges, several research directions are promising, including:

(1) The combination of experimental characterization with theoretical research. Overall, a basic understanding of the relationship between catalytic mechanism and catalyst composition/structure is needed to allow for the proper selection of different materials to optimize design, synthesis and performance. In addition, the combination of molecular/atomic modeling and experimental characterization is necessary to understand the close relationship between ORR catalytic mechanisms and catalyst electronic structures/compositions to further improve ORR catalytic performances in MABs. Here, theoretical research and experimental verification of electrocatalytic ORR reactions are important aspects in the development of ORR electrocatalysts and to study electrocatalysts at the molecule/atom/electron level, powerful computing and advanced modern characterization techniques are needed. For example, DFT calculations can be used to study ORR kinetic processes, including the electrocatalytic mechanism of each basic step as well as the rate determining steps, transition states, activation energies and the catalytic activity of different catalysts. Diagnostic tools such as *in-situ* spectroscopy (infrared adsorption spectroscopy (IRAS), Raman spectroscopy (RS), X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, etc.) can also be used to better understand structure-property relationships by measuring local reaction environments and reaction intermediate distributions on catalyst surfaces. Moreover, deeper insights into the geometric configuration and electronic structure of catalysts are required, such as the local coordination environment of centrally active metal sites (e.g. coordination numbers, distances and adjacent atomic species), which can guide the design of metal anodes, air cathodes and MAB systems in terms of optimizing the conditions/parameters of electrode composition, thickness and fabrication as well as the morphology of electrocatalysts and catalyst supports.

(2) The creation of innovative methods to synthesize carbon or composite materials for advanced catalysts. For example, carbon materials doped with heteroatoms can play a central role in the formation of composite catalysts through strong interactions

between one or more dopants and carbon to produce synergistic effects.[246] Composite catalysts can also be optimized through careful material selection and innovative design. Moreover, the synergistic effects produced by different components can provide positive effects to counteract the shortcomings of individual components and generate more ORR active sites. Therefore, the understanding and establishment of morphology-controlled synthesis methods to obtain high surface areas, suitable pore sizes and distributions are necessary to enhance the activity and stability of ORR catalysts. In addition, the control of porous structures depends to a large extent on charge transfer and reactant transport. In recent years, metal organic frameworks (MOF) and MOF-derived materials have also attracted widespread attention. The 3D ordered crystal structures of MOF and MOF-derivatives can be constructed modularly using bridged metal ions/clusters and functionalized organic ligands so as to ensure that ORR mainly occurs at the three-phase boundary in which the active material electrode (solid) is close to the oxygen molecule and ion conductive electrolyte (liquid).

(3) Because advanced structures and related air cathode components play a vital role in battery performance, the innovative design and optimization of catalyst-based CLs and air cathodes based on multi-physics modelling and experimental characterization are needed to achieve high performance MABs for practical applications.

Overall, these research directions and related strategies must be integrated to develop comprehensive and effective methods for the design and enhancement of MAB systems.

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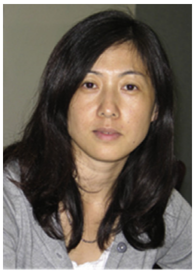

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