



## Advancements and Challenges in Magnesium-Air Battery

Yang Yu<sup>1</sup>, Xiaohui Liu<sup>2</sup>, Xiaoen Shi<sup>3</sup>, Kaixuan Yang<sup>1</sup>, Yijia Huang<sup>1</sup>, Lin Hu<sup>1\*</sup>

<sup>1</sup>School of Materials Science and Engineering, East China Jiaotong University, Nanchang 330013, China

<sup>2</sup>Ningguo Economic and Technological Development Zone, Xuancheng 242000, China

<sup>3</sup>Ningguo Jiutian Chemical Co., Ltd, Xuancheng 242000, China

\*[hulin21@hotmail.com](mailto:hulin21@hotmail.com)

**Abstract:** The growing reliance on electronic devices has led to significant energy consumption and environmental challenges, such as air pollution and climate change. As a result, there is an urgent need for alternative energy sources and advanced energy storage solutions. Among these, metal-air fuel cells—particularly magnesium-air batteries—have garnered considerable attention due to their low cost, high theoretical voltage, and environmental benefits. Magnesium, as a promising alternative to lithium-ion batteries, is valued for its abundant reserves, low cost, high theoretical energy density, and relatively low reactivity. However, the development of magnesium-air batteries faces obstacles such as passivation, corrosion, and efficiency limitations. This paper reviews recent advancements in the development of magnesium and its alloys as anodes, with a particular focus on Mg-Al and Mg-Zn-Sn alloys, which have shown potential to reduce corrosion and enhance efficiency. On the cathode side, various catalysts and their different morphologies have demonstrated distinct advantages in improving battery voltage and discharge capacity. Innovations in electrolytes have introduced new combinations that enhance the physicochemical properties of the electrode-electrolyte interface, prevent the deposition of magnesium reaction products, and reduce interfacial impedance. These collective efforts have significantly improved the stability, durability, and efficiency of magnesium-air batteries. With ongoing technological advancements, magnesium-air batteries hold promising potential for applications in portable power supplies, electric vehicles, drones, and beyond.

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**Keywords:** Magnesium ion batteries; battery anode; metal-air batteries; corrosion resistance; electrolyte

### 1. Introduction

In the 21st century, the increasing use of electronic devices in households has brought convenience but also significantly raised energy consumption, making energy a crucial resource. However, the combustion of fossil fuels to meet this growing demand has led to the emission of greenhouse gases, resulting in adverse effects such as deteriorating air quality and global climate change (Chun 2017). This has driven the search for alternative energy sources and advanced energy storage solutions, which are now regarded as essential by society. Metal-air fuel cells have attracted significant research attention due to their low cost, high theoretical voltage, and environmentally friendly characteristics (Han, 2017).

Lithium-ion batteries, as advanced energy storage devices, offer benefits such as high working voltage, environmental friendliness, and a lack of memory effects (Jie, 2007). These batteries are widely used in various fields, including electric vehicles, consumer electronics, and aerospace (Xin Yang, 2011). However, their current energy density is insufficient to meet the demands of many key industries. To extend the range of electric vehicles and reduce costs, researchers are aiming for lithium-ion batteries to

achieve energy densities greater than 400 Wh/kg and costs of less than \$100 per kWh (Deivanayagam, 2019). Despite this, achieving these targets has proven challenging in common lithium-ion battery chemistries, such as LiCoO<sub>2</sub>, LiFePO<sub>4</sub>, and LiNiCoAlO<sub>2</sub> (Tutusaus, 2016).

During the charging process, issues such as crystal growth (Dongli, 2024) can cause the crystals to pierce the separator, leading to short circuits between the battery's electrodes (Youzhi, 2018), which may result in overheating and even explosions. The strong oxidizing agents formed in organic electrolyte systems can further exacerbate safety risks (Girishkumar, 2010). Additionally, rising lithium ore prices have made the development of alternative battery technologies even more urgent.

In recent years, various types of metal batteries, such as magnesium, sodium, zinc, and calcium, have gained significant attention in the field of new energy storage. Among these, magnesium-ion batteries are considered one of the most promising alternatives to lithium-ion batteries (Lan Luo, 2021. Maosheng, 2021). This is largely due to magnesium's abundant reserves, accounting for 2.1% of the Earth's crust, ranking eighth among all elements (Huihuang,

2022). Magnesium is also environmentally friendly, low-cost, and readily available. Additionally, magnesium is a vital element in the human body, contributing to physical development and regulating physiological functions, with excellent biocompatibility (Tao,2011) .

One of magnesium's key advantages is its high theoretical energy density (6.8 Wh/g), which is nearly double that of lithium. Its standard electrode potential is relatively low (-2.37 V), and it offers a theoretical discharge capacity of 2.2 Ah/g and a theoretical voltage of 3.09 V (Bo,2011). Moreover, magnesium's reactivity is relatively low, and it does not easily form dendritic deposits, a common issue in other battery chemistries (Chao,2020). This makes magnesium a safe and viable option for use as an anode material in new battery technologies. With its promising research prospects, magnesium-ion batteries are expected to find applications in portable power supplies, electric vehicles, drones, and exoskeleton technologies in the near future.

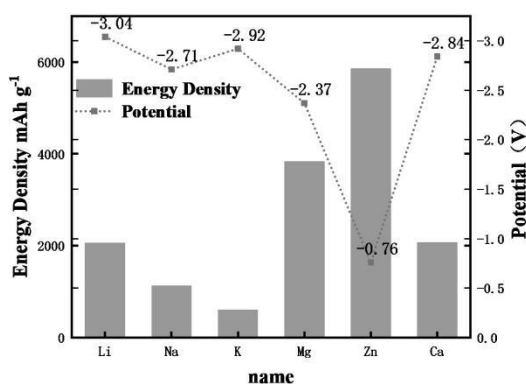


Figure 1. The comparison chart of the energy and potential of all kinds of metal theory.

However, the continued development of magnesium-ion batteries faces several significant challenges.

① Traditional electrolytes often lead to the formation of passivation films such as MgO, Mg(OH)<sub>2</sub>, MgS, and Mg<sub>3</sub>N<sub>2</sub> on the magnesium anode (Ma , 2022). These passive layers seriously hinder Mg<sup>2+</sup> ion movement and can damage the electrode, impeding reversible stripping and deposition processes, thereby reducing efficiency and shortening the cycle life.

② The hydrogen evolution reaction on the magnesium anode consumes magnesium and diminishes the efficiency and lifespan of the battery system (Kai, 2018).

③ During discharge, the peeling of the unconstructed matrix can cause a "block effect" that reduces battery efficiency (Zhuangzhuang 2023).

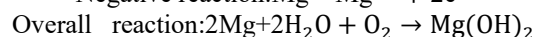
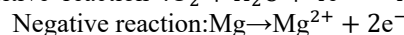
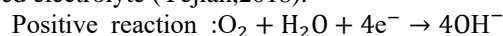
④ Magnesium-air batteries suffer from low negative electrode efficiency and slow oxidation-reduction response rates of the air electrode (Bo,2020).

To address these issues, researchers are exploring improvements in anode materials, cathode designs, and electrolytes.

## 2. Current progress in magnesium-Air battery

### 2.1. Magnesium batteries working Principle

Magnesium-air batteries are a type of metal-air battery, or metal fuel cell (MFC), which consists of a magnesium metal anode, an air cathode, and a water-based electrolyte (Yejian,2018).



### 2.2. Magnesium anode

The efficiency of magnesium-air batteries is often limited by the passivation and corrosion of Magnesium anode the magnesium anode, which prevents the realization of its theoretical capacity and energy. To address these issues, researchers are focusing on improving corrosion resistance and reducing oxidation. Studies indicate that certain magnesium alloys exhibit enhanced corrosion resistance under natural conditions (Bo,2020). Stronger magnesium alloys also demonstrate good corrosion resistance within the battery system (Yujia,2017), making alloying a crucial approach for enhancing anode performance (Xingrui,2024). Additionally, the  $\beta$ -phase of magnesium alloys offers better corrosion resistance compared to the alpha phase, and modifying the lattice structure of the anode material is another effective strategy(Bo,2011).

#### 2.2.1. Mg-Ge Alloy

The research team led by Xingrui Chen (Xingrui,2024) employed a vacuum melting and casting system to prepare ultra-high-purity Mg-0.5Ge alloy for use as the anode in magnesium-air batteries. The cathode used was a commercial air electrode with an MnO<sub>2</sub>/C catalyst layer, along with two waterproof gas diffusion layers and a nickel (Ni) net collector. The electrolyte was a 3.5 wt% NaCl solution with no additives. The battery achieved a significant high discharge voltage of 1.69 V at 0.5 mA/cm<sup>2</sup> and 2272 mWh/g at 20 mA/cm<sup>2</sup>. The researchers noted that:

① The observed battery voltage in magnesium-air batteries is influenced by the reduction in internal resistance (IR), which includes polarization, ohmic, and transport resistances. Higher current densities increase electron demand between the anode and cathode, necessitating efficient removal of

oxidation and discharge products to maintain high battery potential and performance.

② The high corrosion rate of magnesium and its alloys, a major issue in structural applications, is attributed to its active electrochemical potential and lack of protective film. During operation, the magnesium anode faces self-corrosion challenges, exacerbated by the presence of impurities which significantly affect its corrosion resistance.

#### 2.2.2. Mg-Re Alloy

The research team led by Bingjie Ma (Bingjie,2023) used intermediate compounds of  $Mg_3Re$  ( $Re = La, Ce, Pr, Nd$ ) as the anode material in magnesium-air batteries, which significantly enhanced the performance of high-current-density batteries. This approach led to higher battery voltages, power densities, and improved stability in both continuous and intermittent power outputs. Among these compounds,  $Mg_3Pr$  exhibited the best performance, achieving a high discharge voltage of 0.91 V at 60 mA/cm<sup>2</sup> and a peak power density of 54.4 mW/cm<sup>2</sup>.

In conventional Mg anodes, a thick passivation layer of  $Mg(OH)_2$  tends to accumulate due to the gradual build-up of small  $Mg(OH)_2$  particles, which severely restricts the active discharge area, resulting in uneven discharge and poor electrochemical performance. However, when the rare earth (RE) element is introduced,  $Mg_3Pr$  with its long-range ordered structure dissolves, generating both  $Mg^{2+}$  and  $Pr^{3+}$  simultaneously. The formation of  $Pr(OH)_3$ , which grows rapidly, helps separate the  $Mg(OH)_2$ , leading to the formation of a mixed oxide layer of  $Mg(OH)_2$  and  $Pr(OH)_3$  on the alloy surface.

This interface, composed of large crystal lattices of  $Pr(OH)_3$  and  $Mg_3Pr$ , becomes unstable and can easily be disrupted by  $H_2$  gas bubbles, causing the surface discharge products to peel away. This effectively mitigates passivation and promotes the continuous removal of discharge products, thereby maintaining high activity and stability in the  $Mg_3Re$  anode. The presence of RE elements in  $Mg_3Re$  alloys causes trivalent rare earth cations to participate in the metal/oxide interface, forming an unstable composite oxide layer composed of  $Mg(OH)_2$  and  $Re(OH)_3$ , which facilitates the removal of discharge products and helps preserve the anode's electrochemical activity.

#### 2.2.3. Mg-Al Alloy

The research team led by Danya Huang (Danyan,2022) investigated the impact of aluminum (Al) content on the performance of magnesium-air batteries. In their study, they observed that when discharging at 1 mA/cm<sup>2</sup> in a 3.5% NaCl solution, the battery voltage decreased as Al content increased, particularly from 20% to 40%. This decrease was attributed to the formation of a passivation film on the

surface of the anode, which significantly suppressed the sample's activity. The passivation film was primarily composed of  $Al_2O_3$  and  $MgO$ .

Despite this, the anode efficiency and capacity of the sample improved with increasing Al content. When the passivation film formed, it prevented  $Mg^{2+}$  ions from being directly exposed to water, thereby reducing the formation of hydrogen and enhancing anode efficiency. The dynamic formation and dissolution of the  $MgO/Mg(OH)_2$  membrane allowed  $Mg^{2+}$  to dissolve into the solution without generating hydrogen. Additionally, Al atoms in the alloy could effectively bond with  $Mg^{2+}$  ions, reducing their reactivity with water and further improving anode efficiency.

In contrast, the research team led by Jingling Ma (Jingling 2020) highlighted that corrosion resistance in magnesium alloys is significantly influenced by aluminum content and microstructure. Aluminum, as a major alloying element, enhances corrosion resistance by forming a dense  $Al_2O_3$  protective layer on the surface of the alloy. If the aluminum content exceeds the solid solubility limit in the  $\alpha$ -Mg matrix (which is 12.7 wt% at 437°C), it leads to the formation of the  $\beta$  phase ( $Mg_{17}Al_{12}$ ). The  $\beta$  phase plays a dual role: it accelerates corrosion of the  $\alpha$  matrix and serves as an anode barrier. The proportion of the  $\beta$  phase is crucial, as it can either enhance corrosion protection or act as a barrier to anode reactions, depending on its volume and distribution.

#### 2.2.4. Mg-Zn-Sn alloy

The research team led by Fanglei Tong (Fanglei,2021) investigated the effects of adding tin (Sn) and zinc (Zn) to the anode material of magnesium-air batteries, focusing on the microstructural, electrochemical, and discharge performance impacts. The addition of Sn alters the microstructure of the Mg-Zn alloy and leads to the formation of  $SnO$  or  $SnO_2$  films on the anode during discharge. This film formation significantly enhances battery performance at low current densities (<10 A/cm<sup>2</sup>). Sn also stimulates the electrochemical activity of the magnesium matrix, with  $Mg_2Sn$  exhibiting a stronger cathode effect compared to  $MgXZnY$ . As a result, the working voltage of Mg-Zn-Sn alloy anodes is notably higher than that of Mg-Zn anodes studied previously. Moreover, a small amount of Zn improves the corrosion resistance of the magnesium alloy by forming a protective film, which reduces the pH near the surface and accelerates the dissolution of the discharge product  $Mg(OH)_2$ .

#### 2.2.5. Mg-Zn alloy

Fanglei Tong (Fanglei,2021) discovered that as the Zn content in magnesium-air battery anodes increased, the anode efficiency and capacity decreased due to the growing volume fraction of metal intermetallic phases. The  $Mg_2Zn$  alloy exhibited the

best battery performance, achieving a utilization rate of 54.42% and a capacity of 1185.50 mAh/g. However, in Mg6Zn and Mg15Zn alloys, the large number of secondary phases accelerated the corrosion of the  $\alpha$ -Mg matrix when acting as a cathode, especially under high current density, leading to reduced anode efficiency.

The shape, size, quantity, and distribution of intermetallic compounds significantly affect the corrosion performance of magnesium alloys. Song et al. demonstrated that in AZ91 alloy, a fine and continuous Mg17Al12 phase can serve as a corrosion barrier, while a rough and discontinuous Mg17Al12 phase accelerates corrosion when acting as the current cathode. Similarly, in Mg-Zn alloys, the MgXZnY secondary phase can either act as a corrosion barrier or a cathode. When the Zn concentration is low (around 4 wt%), a small amount of metal phase is distributed within grains and along grain boundaries, enhancing the corrosion resistance of the Mg2Zn alloy. However, as Zn content increases to 6 wt% and 15 wt%, a large number of metal phases continuously form and accumulate along the grain boundaries, reducing the overall corrosion resistance and anode performance.

#### 2.2.6. Mg-Ca-Zn alloy

The research team led by Bowen Yu (Bowen,2023) proposed that calcium (Ca) can enhance the activity of magnesium anodes due to its more negative standard electrode potential (-2.87 V) compared to magnesium. This results in magnesium-calcium (Mg-Ca) anodes exhibiting high discharge voltage. When zinc (Zn) is added to Mg-Ca alloys, two types of secondary phases form within the  $\alpha$ -Mg matrix: Mg2Ca and Ca2Mg6Zn3. Both Ca and Zn can dissolve in the  $\alpha$ -Mg, which helps adjust the microstructure at high temperatures. Key findings include:

① In cast anodes, the secondary phases are primarily distributed within the grains and along the grain boundaries. In water-cooled (WC) anodes, most of these secondary phases dissolve into the matrix, leaving only small amounts of Ca2Mg6Zn3 at the triple junctions. In contrast, in furnace-cooled (FC) anodes, the Mg2Ca phase precipitates along with some Ca2Mg6Zn3, forming a semi-continuous network at the grain boundaries.

② The WC anode demonstrated excellent discharge capacity of 1388.9 mAh/g and an anode efficiency of 62.9% at 10 mA/cm<sup>2</sup>, with a peak energy density of 1893.67 mWh/g at 2 mA/cm<sup>2</sup>.

The uniform dispersion of the secondary phases in the casting anode helps create numerous initial discharge points, contributing to improved anode performance and discharge characteristics.

### 2.3. positive electrode

Most metal-air fuel cells rely on catalysts to enhance the oxidation and reduction reactions, which

play a crucial role in determining the energy conversion efficiency and overall cost of the fuel cell stack (Debe,2012). A good catalyst can significantly improve these reactions, making it a key factor in the performance of fuel cells. Traditionally, precious metal catalysts, such as platinum (Pt), are used due to their high activity and excellent selectivity. However, these catalysts are expensive, limiting their cost-effectiveness.

Recent research has focused on reducing the use of Pt and exploring non-precious metal electrocatalysts as low-cost alternatives. These alternatives include metal macrocyclic complexes, metal-N-C cluster catalysts, and metal-free carbon-based catalysts, which have shown promise in maintaining performance while reducing costs (Mu,2015). This shift toward more affordable and sustainable catalyst materials aims to make fuel cell technology more economically viable.

#### 2.3.1. PPcFe catalyst

The research team led by Zhong Fang Li (Tingwei,2020) developed a catalyst where the molecular skeleton of the polymer creates a continuous  $\pi$  (P) system, enhancing electron transfer and increasing the molecule's ability to gain or lose electrons. This type of catalyst demonstrates high activity and excellent durability. The PPcFe/C catalyst, used in a 10 wt% NaCl electrolyte for air electrodes, is inexpensive and easy to prepare.

Heating the catalyst to 400°C yields unsatisfactory results, but XPS analysis identifies FeN<sub>4</sub> within the phthalocyanine structure as the active center. The PPcFe/C catalyst achieves an oxygen reduction reaction (ORR) onset potential of 0.82 V vs. RHE at 20°C in saturated O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, predominantly facilitating the four-electron process. Electrochemical and FTIR tests confirm that PPcFe/C offers excellent durability and performance. When used in metal-air fuel cells (MAFCs), PPcFe/C shows significant advantages over traditional Pt/C catalysts, exhibiting similar high-current density properties and maintaining stable performance for over 11 hours with less than a 0.01 V voltage drop.

#### 2.3.2. CuMnO<sub>2</sub> Nano flakes

Xiaoyang Dong (Yangdong,2021) emphasizes that manganese (Mn) possesses several exceptional properties, including high theoretical capacitance, significant electrochemical oxidation activity, and its synergy with other metal ions. Compared to traditional precious metal catalysts, Mn-based catalysts offer lower costs, broader availability, and excellent stability, making them ideal for practical applications. Specifically, CuMnO<sub>2</sub>, a single diagonal structure of MnO<sub>2</sub>, features MnO<sub>6</sub> octahedra and Cu<sup>+</sup> cations at the layer edges. CuMnO<sub>2</sub> shows several advantages, such as good conductivity, excellent

oxygen absorption capacity, and environmental friendliness.

In alkaline electrolytes,  $\text{CuMnO}_2$  demonstrates better oxygen reduction reaction (ORR) activity than in neutral electrolytes. It also shows high stability, with the electron transfer number approaching the ideal four-electron pathway, indicating significant potential for use in magnesium-air batteries. After 5,000 CV cycles, the half-wave potential of the  $\text{CuMnO}_2$  catalyst only shifts by 22 mV, further demonstrating its outstanding stability and durability. The large surface area of  $\text{CuMnO}_2$ , which allows full contact with oxygen and electrolyte, contributes to its long-term stability. Additionally, the nanosheet structure exposes more active sites, and the unique crystal structure facilitates oxygen adsorption and enhances the ORR process.

In experiments, the open-circuit voltage (OCV) of the  $\text{CuMnO}_2$  catalyst starts at 1.78 V and remains stable at around 1.77 V after 30 minutes of operation, highlighting its excellent stability. During the initial discharge phase, a voltage drop occurs due to internal resistance, followed by a steady operating voltage until a sudden voltage drop, which is linked to the complete corrosion of the anode material. As discharge current density increases, the working voltage of magnesium-air batteries decreases accordingly.

#### 2.3.3. Carbon fiber felt/ PTFE base

Traditional gas diffusion electrodes (GDEs) are generally composed of carbon powder pressed onto both sides of a metal nickel mesh (Ailin, 2023), which serves as a physical support for electrical conduction and electrode stability. The nickel mesh also helps support the hydrophobic adhesive and catalyst layers, which facilitate oxygen reduction reactions. To improve the performance and lifespan of GDEs, recent research has focused on understanding how carbon loading and the type of carbon affect the performance of these double-layer GDEs (Han, 2000).

SeungWook Eom et al. (Eom, 2006) explored the electrochemical performance of GDE cathodes by using various types of activated carbon, such as Darco G 60N, Darco G 60 A, Norit SX Ultra, YP-17, and BP-20. Their findings showed that the ratio of macropores to mesopores, rather than the BET surface area, plays a critical role in GDE performance. The microporous structure of activated carbon does not significantly enhance cathode performance.

The research team led by Chaozhu Shu (Chaozhu, 2013) achieved the highest power density for magnesium-air fuel batteries using a cathode prepared with a carbon fiber felt gas diffusion layer (GDL). Under mild ambient pressure and a 10 wt% NaCl electrolyte, they attained a maximum power density of 116 mW/cm<sup>2</sup>. Compared to traditional magnesium-air fuel cell cathodes, the carbon fiber felt-

based electrode offers a more stable structure and lower resistivity. Additionally, under a current density of 30 mA/cm<sup>2</sup>, the carbon fiber felt-based magnesium-air fuel cell maintained cathode stability, achieving 1,100 hours of discharge during life testing. This stability highlights the durability and effectiveness of carbon fiber felt in enhancing magnesium-air battery performance.

#### 2.3.4. Restore glycyrrhene

Graphene, composed of a single layer of carbon atoms, is gaining attention as an electrocatalyst due to its high conductivity ( $10^3$ – $10^4$  S/m) and large surface area (2,630 m<sup>2</sup>/g) (Jian, 2019). Typically prepared through chemical methods, graphene can have numerous edges and defects that facilitate oxygen access (Jianguo, 2019).

Jingling Ma's team (Jingling, 2019) investigated the performance of magnesium-air batteries using a PSS/RGO (poly(sodium 4-styrenesulfonate/reduced graphene oxide)) and RGO/ $\text{MgN}_3\text{O}_4$  nanocomposite as the air electrode catalyst in a 3.5% NaCl electrolyte. Their study revealed that adding PSS/RGO to the NaCl solution enhances the electrochemical activity of the magnesium anode, increasing the negative potential from 1.548 V to 1.654 V and reducing the switching current density from 60.7 mA/cm<sup>2</sup> to 7.4 mA/cm<sup>2</sup>. The batteries with PSS/RGO and RGO/ $\text{MnO}_2$  nanocomposites achieved a maximum energy density of 1,620 Wh/kg and a high anode utilization rate of 82%. The improvement in electrochemical activity is attributed to the suspended PSS/RGO nanoparticles in the NaCl solution, which promote continuous electrochemical behavior.

#### 2.3.5. Multi-wall carbon nanotubes load binary PDSN nano-catalyst

The Chenchen Zhao's team uses borohydrodiamine immersion reduction method to prepare the PDSN dual metal nano catalyst at room temperature, and then perform heat treatment at different times in the H<sub>2</sub>/Ar restore atmosphere of 200°C. In the end, the H-24 hours showed a constant current discharge curve of 112.4 mW cm<sup>-2</sup> at the highest power density density of 112.4 mW cm<sup>-2</sup> at 40 mA cm<sup>-2</sup>. At the beginning of the discharge, the voltage of about 1.25 V was shown, and it did not decrease significantly.

#### 2.3.6. The two supports of $\alpha$ - $\text{MnO}_2$ are in three-dimensional graphene

The research team led by TingWei Zhang (Tingwei, 2020) highlights that  $\text{MnO}_2$  is extensively studied due to its high catalytic activity, oxidation-reduction stability, low cost, environmental friendliness, and abundant availability.  $\text{MnO}_2$  exists in

various polycrystalline forms, including  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\Delta$ -MnO<sub>2</sub>, with  $\alpha$ -MnO<sub>2</sub> demonstrating the highest catalytic activity in alkaline solutions. The one-dimensional nanostructure of MnO<sub>2</sub> nanorods provides high catalytic activity for the oxygen reduction reaction (ORR). Moreover, the nanorods form a skeletal structure, which enhances the active sites and facilitates oxygen transfer. However, the limited conductivity of MnO<sub>2</sub> nanorods hampers their electrochemical activity.

To address this issue, the use of carbon materials—such as carbon black (C), carbon nanotubes (CNT), graphene, and three-dimensional graphene (3D-G)—is beneficial in improving conductivity. Experimental durability tests show that  $\alpha$ -MnO<sub>2</sub>/3D-G exhibits better durability than the commonly used 20 wt% Pt/C catalyst. Magnesium-air fuel cells using  $\alpha$ -MnO<sub>2</sub>/3D-G in the air cathode achieved a peak power density of 106.2 mW/cm<sup>2</sup>, with continuous durability (maintaining discharge for 16 hours at 50 mA/cm<sup>2</sup>, with only a 7.6% voltage drop). These findings demonstrate that the  $\alpha$ -MnO<sub>2</sub>/3D-G catalyst, with its high activity and durability, is a highly promising electrocatalyst for magnesium-air fuel cells.

#### 2.3.7. PdCo/C Dual Metal Catalysts

Pd and Pd-based electrocatalysts have emerged as promising alternatives to traditional platinum (Pt) catalysts due to their comparable atomic sizes, high electrochemical activity, and lower costs (Minhua,2011). PdCo nano catalysts are particularly noteworthy because they exhibit exceptional oxygen reduction reaction (ORR) activity in both acidic and alkaline media (Calderon,2016). Research by Ghenchen Zhao's team (Chenchen,2018) revealed that these catalysts experience an inevitable degradation of 4.1%, with the voltage dropping from 1.22 V in the first cycle to 1.17 V by the 100th cycle. The charging voltage increased slightly from 2.01 V to 2.06 V over the first 10 cycles and then remained relatively stable throughout the next 90 cycles (2.06 V in the 11th cycle and 2.07 V in the 100th cycle). During discharge, the voltage remains stable for up to 8 hours until the anode AZ31 alloy is consumed. Replacing the magnesium alloy and NaCl electrolytes in the magnesium-air battery (MAB) restores the discharge voltage immediately.

#### 2.3.8. Three-Dimensional Graphene-Polypyrrole Hydrogel

Qijie Wu's team(Qijie,2024) found that the G-PPy gel delivers a voltage of 1.03 V at 500  $\mu$ A/cm<sup>2</sup> and achieves full discharge characteristics at 200  $\mu$ A/cm<sup>2</sup>, with a discharge capacity of 13.6 mAh/cm<sup>2</sup>. The G-PPy electrode demonstrates a high performance density of 5150 mW/m<sup>2</sup> (or 8.25 W/L). This improvement is attributed to the increase in active catalytic sites due to the incorporation of effective electrocatalysts like

polypyrrole (PPy). Additionally, the three-dimensional pore structure of the graphene gel enhances the electrochemical dynamics of PPy, as it facilitates easier ion and oxygen penetration and improves conductivity.

#### 2.3.9. $\alpha$ -MnO<sub>2</sub>'s 2-nano wire/graphene

The team led by Min Jiang (Min,2016) asserts that the one-dimensional (1-D) MnO<sub>2</sub> nanostructures offer high surface area and minimal size, which facilitate effective electronic transmission. However, due to the inherently slow electronic transfer rate,  $\alpha$ -MnO<sub>2</sub> nanowire/graphene ( $\alpha$ -MnO<sub>2</sub>-NWs/graphene) composites were synthesized using a straightforward hydrothermal method and evaluated in magnesium-air fuel cells. The  $\alpha$ -MnO<sub>2</sub>-NWs/graphene composite exhibits excellent oxygen reduction activity, approaching the performance of traditional Pt/C catalysts. This promising catalyst demonstrates significant potential for applications in Mg-air fuel cells. A large-area (5 cm  $\times$  5 cm) cathode was prepared and tested in a full battery setup. In real Mg-air fuel cell tests, the  $\alpha$ -MnO<sub>2</sub>-NWs/graphene composite cathode achieved a maximum power density of 96 mW/cm<sup>2</sup> at a current density of 140 mA/cm<sup>2</sup>, outperforming the commercial MnO<sub>2</sub> cathode.

#### 2.4. Electrolytes

The electrolyte acts as a charge carrier medium, facilitating electron transfer through free ions to sustain oxidation reactions and maintain voltage stability. Its composition is crucial for battery performance, making the development of advanced electrolytes a significant focus. Currently, the primary types of electrolytes used in magnesium-ion batteries (MIBs) include organic liquids, aqueous solutions, ionic liquids, and solid electrolytes (Deivanayagam, 2019). In 2008, Mizrahi et al. (Deivanayagam, 2019) introduced a novel electrolyte for MIBs—a phenyl compound electrolyte—capable of achieving highly reversible magnesium deposition and providing a wide voltage window. Since then, MIB electrolytes have diversified rapidly, aiming to enhance performance.

##### 2.4.1. Phosphoric Acid and Chlorides

YanChun Zhao's team (Yanchun,2018) highlights that pyrite and phosphate electrolytes are cost-effective, exhibit superior inhibitory effects, and maintain high magnesium alloy potential in NaCl solutions. They used 0.6 M NaCl + 0.02 M NaVO<sub>3</sub> and 0.6 M NaCl + 0.02 M Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O as electrolytes, with AZ31 as the working electrode, platinum as the counter electrode, and saturated calomel electrodes as reference electrodes. The addition of phosphates and pyrites significantly enhanced the corrosion resistance of the AZ31 alloy. Continuous discharge tests under constant current conditions revealed that the inclusion of phosphate and pyrite notably improved anode efficiency. While batteries using standard electrolytes had an anode efficiency of only 65.5%, those with

phosphate additives showed substantial performance gains.

#### 2.4.2. Na<sub>3</sub>PO<sub>4</sub> and SDBS

The Yaqiong Li (Yaqiong,2018) team suggests that SDBS can serve as an effective organic corrosion inhibitor. It is particularly useful for protecting AZ31 magnesium alloy in a 1% NaCl solution. The addition of SDBS improves the alloy's resistance to corrosion, enhancing its performance in corrosive environments.

Table 1. Chemical ingredients of different solutions.

	NaCl(wt%)	Na <sub>3</sub> PO <sub>4</sub> (g/L)	SDBS(g/L)
A	3.5		
B	3.5	0.5	
C	3.5		0.05
D	3.5	0.5	0.05

The following results were obtained by electrochemical testing.

Table 2. Combining data of polarization curves in different solutions.

	I(10 <sup>-4</sup> A/cm <sup>2</sup> )	E (V)	R (Ω)
A	2.887	-1.483	83.9
B	1.130	-1.567	234.6
C	2.085	-1.563	128.6
D	0.187	-1.574	888.0

It was observed that Solution D achieves a potential of -1.574 V, indicating that the addition of Na<sub>3</sub>PO<sub>4</sub> and SDBS enhances the potential of magnesium-air batteries. Additionally, Solution D exhibits a lower corrosion current density compared to Solution A, suggesting improved anode utilization. The corrosion current densities decrease in the following order: Solution A > Solution C > Solution B > Solution D, while the polarization resistance (R<sub>p</sub>) shows the reverse trend. The cathode polarization curves are similar across different solutions, indicating a consistent hydrogen reaction process.

The Hengli discharge test, conducted for 300 minutes at 20 mA/cm<sup>2</sup>, revealed that electrolytes with 3.5 wt% NaCl + 0.5 g/L SDBS and 3.5 wt% NaCl + 0.5 g/L SDBS + 0.5 g/L Na<sub>3</sub>PO<sub>4</sub> exhibit higher potential and anode utilization rates compared to 3.5 wt% NaCl alone. The enhanced potential is attributed to reduced accumulation of discharge products and fewer surface cracks. The higher anode utilization rate is due to a lower self-corrosion rate. Notably, magnesium-air batteries with a 3.5 wt% NaCl + 0.5 g/L Na<sub>3</sub>PO<sub>4</sub> solution maintain an average potential of 1.150 V at 20 mA/cm<sup>2</sup>, achieving an anode utilization rate of 49.1%.

#### 2.4.3. Acid Salt Dual Electrolyte

The Keewah Leong (Kee,2021) team explores a novel dual-electrolyte acid salt configuration for fixed, pump-free magnesium-air batteries.

#### 2.4.4. Organic Additives for Magnesium-Air Batteries

Hoche et al. (Daniel,2018) were pioneers in using organic additives to enhance the performance of magnesium-air batteries. These additives activate the magnesium anode surface and form soluble complexes with Mg<sup>2+</sup> ions, which prevents the formation of Mg(OH)<sub>2</sub>. This helps mitigate the decline in Ohmic resistance and improves the conductive potential of the Mg anode.

Bahram Vaghefinazari's team (Vaghefinazari, 2022) explored the use of ethylenediaminetetraacetic acid (EDTA) sodium salt as a water-based electrolyte additive in magnesium-air batteries using a commercial pure Mg anode. By varying the pH of the electrolyte, the effects of EDTA on the magnesium anode performance were investigated. The study found that EDTA improves discharge performance within a narrow pH range of 7.0–12.0 at low current densities (1 mA/cm<sup>2</sup>). However, as current density increases, the discharge potential improves less significantly and may even become unstable if the potential falls below that of the blank electrolyte. This instability at high current densities is attributed to the inability of EDTA to form soluble complexes with Mg<sup>2+</sup> ions in sufficient quantities, which may lead to the formation of denser Mg(OH)<sub>2</sub> layers that obstruct the Mg anode surface. Battery tests showed that the presence of EDTA in alkaline electrolytes with a pH of 11 could increase energy density by 1.5 times compared to conventional electrolytes. Across all tested pH levels, EDTA generally enhanced the power density of magnesium-air batteries.

#### 2.4.5. Organic and Inorganic Lithium Salt Additives

The team led by Haiyan Fan (Haiyan,2022) developed high-performance MgCl<sub>2</sub>-based electrolytes using a dual salt additive approach with LiHMDS and LiCl. In MgCl<sub>2</sub>/THF electrolytes, single salt additives act as a "double-edged sword": in small amounts, they form waterproof complexes with MgCl<sub>2</sub> (e.g., [Mg<sub>x</sub>L<sub>y</sub>HMDS<sub>z</sub>Cl<sub>2x+y-z</sub>·nTHF]), which helps reduce the Mg<sup>2+</sup> off-solvent energy. However, when the concentration of these additives increases, they begin to dissolve functional aggregates, potentially diminishing the benefits.

The opening voltage (OCV) obtained before starting discharge is 1.48 and 1.52V, respectively. Obviously, the OCV of the DG surfactant is higher than the control (blank). This indicates that the Dg surfactant has the effect of cathode inhibitors.

#### 2.4.6 6-dihydroxybenzoic acid choline Magnesium-Air Batteries

Ning Ling (Ning,2024) introduced a novel electrolyte additive, [CH][DHB], which enhances both

discharge potential and anode utilization efficiency in magnesium-air batteries. The electrolyte containing 0.2M [CH][DHB] demonstrated impressive performance with a half-cell discharge potential of HP-Mg reaching 1.64 VSCE and an anode utilization rate of 68.0%. The [CH]<sup>+</sup> cation and [DHB]<sup>-</sup> anion synergistically improve the discharge performance, with [DHB]<sup>-</sup> combining with Mg<sup>2+</sup> ions to promote Mg matrix dissolution while reducing corrosion. EIS, real-time hydrogen analysis, SEM, and EDS measurements confirmed these results. Full-cell tests showed that the electrolyte with 0.2M [CH][DHB] significantly enhanced the performance of magnesium-air batteries using different magnesium anodes. Specifically, at a discharge rate of 5 mA/cm<sup>2</sup>, the energy density increased by 67% (2093 Wh/kg) for HP-Mg, 15% (1788 Wh/kg) for AM50, 11% (1896 Wh/kg) for AZ31, and 28% (713 Wh/kg) for ZK61 compared to the reference electrolyte.

#### 2.4.7. 5-Sodium Salicylate Additive

The Yaqing Zhou (Yanchun,2018) team conducted an in-depth study on the effects of 5-sodium-based salicylate in 0.6M NaCl electrolyte on the corrosion and discharge performance of magnesium-air batteries. Their findings demonstrated significant improvements in magnesium corrosion resistance and battery discharge performance:

① The open-circuit potential (OCP) became more negative, and the average discharge voltage increased by 275–470 mV.

② The cathode activity of the magnesium electrode was significantly reduced, and impedance values stabilized after prolonged soaking.

③ Hydrogen evolution was reduced by a factor of four compared to blank electrolytes. At a current density of 0.5 mA/cm<sup>2</sup>, the discharge potential increased from approximately 1.58 V to 1.82 V. At the optimal inhibitor concentration of 0.1M, the battery life extended from around 12.5 hours to 80 hours, and the energy density doubled, significantly enhancing anode utilization efficiency.

These improvements indicate that 5-sodium-based salicylate is a promising corrosion inhibitor for magnesium-air batteries, contributing to better performance and longer battery life.

#### 2.4.8. 2,6-dihydroxybenzoate

Linqian Wang (Linqian,2022) explored the effects of 2,6-DHB in electrolytes for magnesium-air batteries. In their tests, Mg-0.15Ca showed a stable discharge potential of 1.56 V Ag/AgCl with 0.1M 2,6-DHB. For Mg-0.55Ca with 0.05M 2,6-DHB, the potential started at -1.62 V but stabilized at 1.54 V after 20 hours. The addition of 0.1M 2,6-DHB provided the best anode utilization efficiency, and 0.2M 2,6-DHB also offered high performance but did not surpass 0.1M

concentrations. Notably, 0.3M 2,6-DHB did not improve discharge potential and led to decreased efficiency. Full battery tests demonstrated that 0.2M 2,6-DHB enhanced discharge performance across various magnesium anodes. At low current densities, it improved battery voltage and power density, and at high current densities (e.g., 10 mA/cm<sup>2</sup>), it significantly outperformed the reference electrolyte (3.5% NaCl), with increases in energy density for AZ31 (8%), HP Mg (15.6%), and AM50 (50.5%) anodes.

#### 2.4.9. Sodium acetate for Magnesium-Air Batteries

The Jianxin Gao team (Jianxin,2023) compared the performance of magnesium-air batteries using NaCl and NAAC (sodium acetate, CH<sub>3</sub>COONa) electrolytes. Their tests revealed a significant reduction in corrosive current density from  $3.04 \times 10^{-2}$  to  $8.32 \times 10^{-3}$  mA when switching from NaCl to NAAC electrolytes. The charge transfer resistance (R<sub>ct</sub>) of the Mg anode in NaCl was 705 Ω cm<sup>2</sup>, whereas in NAAC, it increased to 1897 Ω cm<sup>2</sup>, indicating a much lower corrosion rate for the Mg anode in the NAAC electrolyte. This reduction in corrosion was confirmed by hydrogen evolution tests, which showed a significantly lower hydrogen evolution rate for the Mg anode in NAAC.

While the discharge voltage of the magnesium-air batteries in NAAC electrolytes was reduced by 100–200 mV, the overall anode efficiency improved, resulting in a significantly extended battery lifespan. The battery discharge continued until the magnesium anode was exhausted. Although the duration of magnesium-air batteries was longer in NaAc electrolytes compared to NaCl electrolytes, their energy density ratios were nearly identical at current densities of 1, 2, and 5 mA/cm<sup>2</sup>. However, at 10 mA/cm<sup>2</sup>, the energy density ratio of the NaAc electrolyte decreased due to the lower battery voltage.

Constant power tests demonstrated that the NaAc electrolyte substantially extended the discharge duration of magnesium-air batteries, increasing from 27 hours and 10 minutes to 32 hours and 21 minutes. Moreover, at 10 mA/cm<sup>2</sup>, the utilization efficiency of the Mg anode in NAAC electrolytes increased from 59% (in NaCl) to 84%, and the energy density improved from 1370 to 1770 Wh/kg. This indicates that NaAc electrolytes offer superior performance and prolonged battery life compared to traditional NaCl electrolytes.

#### 2.4.11. Glycine as an Additive in Magnesium-Air Batteries

The Bingjie Ma (Bingjie,2023) team explored the use of glycine as an additive to enhance the discharge performance of commercial AZ31 magnesium alloys. Their findings showed that AZ31 in a 0.1 M glycine solution maintained an average voltage of 0.81 V at 60 mA/cm<sup>2</sup>. This performance was notably better than that of other alloys under high current



conditions. The AZ31 alloy with 0.1 M glycine achieved a peak power density of 48.6 mW/cm<sup>2</sup> at 60 mA/cm<sup>2</sup>, which is about 42% higher compared to other reported alloys.

The addition of glycine, a neutral amino acid, to water-based electrolytes significantly improves battery performance, particularly at high current densities. At a concentration of 0.1 M, glycine effectively prevents the precipitation of discharge products, leading to optimal battery performance. The enhanced discharge performance is attributed to glycine's reaction with Mg<sup>2+</sup> ions, forming soluble amino acid complexes that reduce the obstruction of the anode surface and lower potential reduction. Furthermore, the AZ31 alloy in 0.1 M glycine exhibited high anode efficiency, reaching 64% at 60 mA/cm<sup>2</sup>. This efficiency is due to the uniform electrochemical dissolution of the magnesium base, which mitigates the blockage effects during discharge.

#### 2.4.12. Various electrolyte defects

The electrolyte for MIB (Magnesium-Ion Batteries) needs to be compatible with the magnesium anode, offering high Mg<sup>2+</sup> ion conductivity, good solubility, and sufficient mass of Mg salts in the solvent. It should also support efficient magnesium deposition and peeling (Yuhua, 2023). Additionally, the electrolyte must have a suitable electrochemical stability window while meeting the lowest safety and cost requirements.

Organic liquid electrolytes generally exhibit relatively high ionic conductivity and are widely used (Liang, 2023). However, common organic solvents tend to volatilize, posing potential toxicity risks. Moreover, certain organic solvents, such as nitriles and esters, can form non-conductive passivation layers, further reducing efficiency (Liang, 2023).

Water-based electrolytes have gained widespread attention due to their excellent safety, environmental friendliness, low cost, and ease of manufacturing, as these properties stem from the inherent characteristics of water as a solvent (Yuanhao, 2021). These electrolytes enhance the ion diffusion dynamics, promoting Mg<sup>2+</sup> movement within the battery system. However, the narrow stable potential window (1.23 V) of aqueous electrolytes limits the battery's capacity. Additionally, water-based batteries are prone to side reactions, such as hydrogen or oxygen evolution, which significantly affect the internal pH and damage the electrode structure.

Ionic liquids, which can act as sources of cations/anions and as non-flammable solvents for dissolving salts (Jianguo, 2019), are applicable for various Mg salts and can mitigate passivation issues. However, ionic liquids face challenges such as high cost and viscosity, though some researchers have

explored adding organic solvents to address these problems.

Solid electrolytes offer the potential to increase the energy density of magnesium-ion batteries by eliminating non-active electrochemical components. Furthermore, their limited reactivity and high stability with metal anodes make solid-state ion conductors an ideal choice for metal-based batteries (Deivanayagam, 2019). However, there is limited evidence supporting their use, and further research is needed to validate their long-term cycling performance.

### 3. Conclusion

The integration and optimization of battery systems will be a key focus of future research. For magnesium-air fuel cells, system integration must address the stability, durability, and efficiency of both charging and discharging. Researchers will need to explore new electrolytes, separators, and other materials while optimizing battery design to enhance power and energy density. Additionally, the battery management system requires improvements in status monitoring, fault diagnosis, and protection.

The application field of magnesium-air fuel cells is expected to broaden. Currently, they are primarily used in mobile power, drones, and electric vehicles. Future advancements will likely see their use expand into large-scale energy storage, household power supply, and marine energy applications. Magnesium-air fuel cells hold significant potential, especially for renewable energy storage and utilization.

The large-scale production and commercialization of magnesium-air fuel cells will be crucial for their future development. Presently, high production costs limit their commercial viability. However, advancements in technology, improvements in the industrial chain, and increased production capacity are expected to lower costs and enhance market competitiveness.

The environmental benefits of magnesium-air fuel cells are notable; they produce only water as a byproduct and have minimal environmental impact compared to traditional fossil fuels. As environmental awareness grows, magnesium-air fuel cells are likely to become a viable alternative to conventional energy sources. Overall, with their advantages of high energy density, safety, and low cost, magnesium-air fuel cells have promising prospects. Research into electrode materials, catalysts, system integration, and large-scale production will be critical in realizing their potential in renewable energy and sustainable development.

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### Corresponding Author:

Prof. Lin Hu, School of Materials Science and Engineering, East China Jiaotong University, Nanchang 330013, China

E-mail: [hulin21@hotmail.com](mailto:hulin21@hotmail.com)

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