Review Article

# Research Progress and Future Expectations in Anode of Secondary Zinc-Air Batteries: A Review

Chen Shunhong and Saroj Pullteap*
Department of Mechanical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University (Sanam Chandra Palace Campus), Nakhon Pathom, Thailand

Tang Mao
School of Mechanical Engineering, Chengdu University, Sichuan, China

* Corresponding author. E-mail: saroj@su.ac.th

**Abstract**
Zinc-air batteries have attracted widespread attention due to their advantages, including high safety, high theoretical energy density (1086 W·h/kg), low cost, etc. A zinc-air battery primarily consists of a metal anode, electrolyte, and air cathode. However, the anode, as the core component of zinc-air batteries, faces various challenges at the present stage, such as dendritic growth, anode deformation, surface passivation, hydrogen evolution corrosion, etc. These challenges limit the development of secondary zinc-air batteries. To address the challenges faced by the anode, researchers are committed to developing anode materials with long cycle life and high capacity. However, this is achieved through methods like alloying, surface coating, 3D structures, surface modification, and the addition of additives. Therefore, this article provides a comprehensive review of recent breakthroughs and progress in the research on zinc-based battery anodes in recent years. Furthermore, it offers a certain outlook on the future development direction of secondary zinc-air batteries.

**Keywords**: Secondary zinc-air batteries, Zinc anode, Dendritic growth, Alloying, Coating, 3D structure

## 1 Introduction

Nowadays, the increasing demand for energy and the consumption of non-renewable fossil fuels put tremendous pressure on humans [1]. This forces our human beings to be concerned, and also turn to the development of clean energy, such as wind energy, solar energy, hydro energy, tidal energy, fuel cells, biomass power, etc. [2]–[5]. However, clean energy sources are often unstable, therefore, the development of energy storage systems (ESSs) will help balance the production and demand of intermittent energy. At this stage, there are energy storage systems such as battery energy storage, thermal energy storage, pumped hydro energy storage, and chemical energy storage. Battery energy storage systems have been widely used in recent years because of their high power and ease of use [6], [7]. The escalating demand for energy storage is driving advancements in battery technology [2], [8], [9]. However, lithium-ion battery is a type of battery that has good characteristics such as high voltage, high energy density, high coulomb efficiency, low self-discharge, cycling stability, etc. [8], [10], [11]. Focus on such result, lithium-ion batteries have becoming to be the most commercially viable energy storage solution in recent decades [12]. Unfortunately, the high costs and unsafety issues contribute to their lack of competitiveness in a part of secondary energy storage applications [13], [14]. To eliminate a such problem, a series of metal-air batteries such as Li-air batteries, Na-air batteries, K-air batteries, Zn-air batteries, Mg-air batteries, Al-air batteries, and Iron-air batteries [15]–[21] have emerged. However, the metal-air batteries utilize oxygen from the air as the cathode,
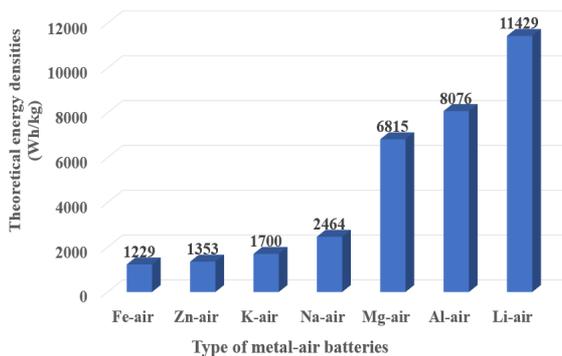
**Figure 1**: Theoretical energy densities of various types of metal-air batteries [23].

which not only reduces the weight of the battery but also enhances its energy density. This contributes largely to the improvement of battery energy density [22]. Among all of these batteries, the lithium-air battery has the highest theoretical energy density [23], as shown in Figure 1.

However, it also faces many challenges, for example, discharge by-products cause clogging of the cathode, resulting in incomplete discharge, etc. [15]. The charging over-point is much higher than the discharging over-point, resulting in low efficiency [24]. Thus, these issues make it difficult to apply. Comparably, the lower reduction potentials of magnesium and aluminium-air batteries result in severe self-discharge for both. Iron-air batteries have lower energy density (763 W·h/kg) and open circuit voltage (1.28 V). Such problems led to zinc-air batteries gaining widespread attention. Owing to their higher energy density (1086 W·h/kg) and high volumetric capacity (6163 W·h/L) [2].

As mentioned before, zinc-air batteries can be divided into two main types: primary zinc-air batteries and secondary zinc-air batteries, respectively [25]. After the commercialization of the first zinc-air battery in 1932, its influence rapidly expanded because of its high capacity. Currently, the primary zinc-air batteries are mainly used for powering hearing aids and cochlear implants [26]. In the late 20th century, it was, continuously, applied to electric Mercedes-Benz trucks [27] also the electric bus of Electric Fuel Ltd. [28], propelling the development of secondary zinc-air batteries to climax. Nevertheless, the flourishing trend of secondary zinc-air batteries was terminated by the emergence of lithium-ion batteries [29]. Until the 2010s, lithium-ion batteries faced limitations in capacity, expensive raw materials, and safety concerns. This created an opportunity for the development of secondary zinc-air batteries again. For secondary zinc-air batteries, the cathode material is unlimited atmospheric oxygen, therefore the actual energy density is normally related to the discharge capacity of the zinc anode [30]. However, there are many issues with the anode itself, i.e. dendrite growth, deformation, surface passivation, and hydrogen evolution. However, there are several researchers have conducted extensive studies on the aforementioned problems with the anode. By the way, Kadam *et al*. [31] use two anodes to improve the ability of anode. Dilshid et al. improve the anode through the adoption of a 3D structure [32]. Besides, Yuan *et al*. enhance the anode using the properties of alloying techniques [33]. Consequently, Mou *et al*. enhance the anode by employing surface coating [34]. All these methods did some improvement of the anode of zinc-air batteries.

In this work, the development of zinc-air batteries was first explored to highlight the importance of the development of the anode of the zinc-air batteries. Subsequently, through a summary of recent years' research, various methods for improving the energy density of zinc-air batteries by enhancing the anode are reviewed. The primary approaches for anode enhancement include alloying of the anode metal, addition of anode additives, improvement of the anode's 3D structure, and surface treatment and modification of the anode. Finally, viewpoints and suggestions regarding the future development of secondary zinc-air batteries are proposed. With the development of contemporary advanced technology and its application in the development of zinc air batteries, the development of high-capacity anode zinc air batteries is both necessary and possible. This will be an important part of the battery development history. Summarizing the development process of zinc-air batteries can further clarify the developmental direction of zinc-air batteries, aiding researchers in the expedited development of high-performance zinc-air batteries. At the same time, the cost of lithium-ion batteries is 3 times of zinc-air batteries. This means zinc-air batteries have high economic value for the application of battery energy storage technology.
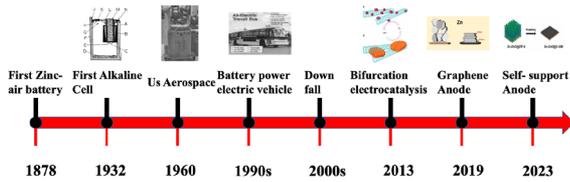
**Figure 2**: Development history of zinc-air batteries [35]–[39].

## 2 Brief History of Zinc-Air Battery

The development of zinc-air batteries is not like other batteries. It has undergone a prolonged period of development to date. The combination of metallic zinc and oxygen from the air to form a battery represents the arrival of the first milestone that belongs to the zinc-air battery era, as shown in Figure 2.

In 1878, the French engineer L. Maiche [40] disclosed a battery design featuring a porous air cathode, indicating the vast potential of zinc-air batteries and paving the way for the development of novel zinc-air batteries. In 1932, Heise and Schumacher [37] pioneered the first alkaline zinc-air battery using sodium hydroxide as the electrolyte, which weighed 116 kg and had an open-circuit voltage of 1.4–1.45V. The military demands of the 1960s became a significant driving force in the development of zinc-air batteries. Following the creation of magnesium-air (1960s) [38], lithium-air (1970s) [41], and aluminum-air (1970s) [42] batteries, the energy density of zinc-air batteries was elevated to 200Wh/kg in the 1980s [29]. Nonetheless, progress invariably experiences fluctuations. Starting in the late 1970s, with the introduction of the rocking chair concept for lithium batteries, the development of lithium-ion batteries faced certain constraints [43]. Particularly in the 1980s, the proposal of LixCoO$_2$ as a cathode material for lithium-ion batteries [44], incorporated with a theoretical energy density of up to 1100Wh/kg, greatly advanced the development of lithium-based energy storage technology. Electrode materials introduced in the late 1990s, such as LiFePO$_4$ [45] and LiMn$_2$O$_4$ [46], brought the energy density of lithium-based batteries to 300Wh/kg, far surpassing that of zinc-air batteries. Lithium-based energy storage technology gradually took the developmental lead during this period. Meanwhile, zinc-air batteries were primarily utilized in simple devices such as hearing aids and pagers [35].

Entering the 21$^{st}$ century, lithium-ion batteries have become the mainstay of development with diversified applications in everyday life. According to the International Energy Agency's data from 2020, lithium-ion batteries accounted for 93% of the new battery storage capacity added in that year, indicating their extensive development and application [29]. However, when the energy density of lithium-ion batteries reaches 400Wh/kg [47], they pose a risk of spontaneous combustion [48]. Furthermore, the high cost of lithium resources presents challenges for industrial production [49]. Additionally, the toxicity of the electrolyte leads to difficulties in subsequent processing [50]. This has led to a recognition of the need to develop an alternative to lithium-ion batteries. Zinc-air batteries have once again come to the forefront of development.

In 2013, Li *et al*. [36] achieved an increase in the energy density of zinc-air batteries to 700Wh/kg through the development of an innovative catalyst. A developed bifunctional oxygen electrocatalyst with a ΔE of approximately 0.63 V achieved 3,600 and 650 charge-discharge cycles at current densities of 10 mA/cm$^2$ and 50 mA/cm$^2$ respectively [51]. However, as the ability of ORR/OER catalysts continues to improve, a decline in battery performance has been observed. Given that the oxygen reactant for zinc-air batteries is sourced from the limitless atmosphere, the actual energy density is also related to the discharge capacity of the zinc anode [30]. The zinc anode faces complex challenges such as zinc stripping/deposition, dendrite growth, hydrogen evolution, and deformation. In 2019, Zheng *et al*. [39] developed a graphene-coated electrode, which showed superior performance through thousands of cycles with an epitaxial zinc anode. In 2023, Mou *et al*. [34] developed a highly ordered zinc anode array structure, achieving a capacity of 995.77 mAh for zinc-air batteries, with 1,200 effective cycles at a current density of 10 mA/cm$^2$. These developments have laid a solid foundation for the further advancement of zinc anodes.

From the aforementioned developmental history, we can observe that early zinc-air batteries had large volumes, low energy densities, and also low discharge efficiencies, etc. With the advancement of smart technology, the volume of zinc-air batteries is gradually decreasing, while their energy density, on the opposite ways, increased leading to increasingly widespread applications.
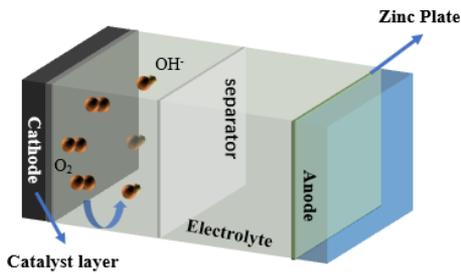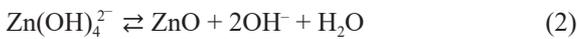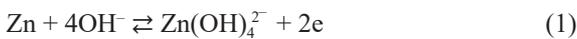
**Figure 3**: Schematic structural diagram of secondary zinc-air batteries.



**Figure 4**: Schematic structural diagram of lithium-ion battery.

## 3 Structure of Rechargeable Zinc-Air Battery

The structure of a rechargeable zinc-air battery is illustrated in Figure 3 [52], which comprises primarily a zinc anode, an air cathode, an electrolyte, and also a separator. Moreover, the chemical reactions during the charge and discharge processes of the rechargeable zinc-air battery are as follows Equations (1)–(4):
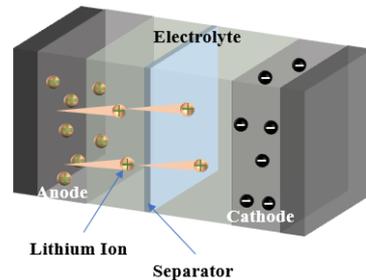
*Zinc Anode*:

$$Zn + 4OH^- \rightleftarrows Zn(OH)_4^{2-} + 2e \quad (1)$$

$$Zn(OH)_4^{2-} \rightleftarrows ZnO + 2OH^- + H_2O \quad (2)$$

*Air Cathode*:

$$O_2 + H_2O + 4e \rightleftarrows 4OH^- \quad (3)$$

*Overall Reaction*:

$$2Zn + O_2 \rightleftarrows 2ZnO \quad (4)$$

From the above reaction equations, it can be observed that during discharge, zinc at the anode is initially oxidized to $Zn(OH)_4^{2-}$. Also, when $Zn(OH)_4^{2-}$ reaches a certain saturation concentration in the electrolyte, it further undergoes deposition to form ZnO. Meanwhile, oxygen at the cathode is reduced to generate OH– ions. During charging, $Zn(OH)_4^{2-}$ in the electrolyte is reduced back to zinc, redepositing on the surface of the zinc anode.

The structure of Lithium-ion batteries is shown in Figure 4 [53]. As shown in Figures 3 and 4, the huge difference between zinc-air batteries and lithium batteries is that the cathode of zinc-air batteries is derived from oxygen in the air. This means that there is a constant supply of the cathode of zinc-air batteries. This is also one of the reasons why zinc-air batteries have the great potential to replace lithium-ion batteries.

## 4 Challenges for Anode of Zinc-Air Batteries

Currently, the widely used anode material in large-scale applications of rechargeable zinc-air batteries is a paste-like substance made from zinc powder [54]. This type of anode material has the advantage of ensuring sufficient contact between the active material and the electrolyte. However, its rechargeability is lacking, which hinders its broad use in rechargeable zinc-air batteries. For the rechargeable zinc-air batteries, the theoretical voltage should be 1.6V, but the actual discharge voltage is generally below 1.2V, and the charging voltage needs to be above 2V. This directly results in the lower Coulombic efficiency of rechargeable zinc-air batteries. These issues are mainly caused by dendritic growth, deformation, surface passivation, and hydrogen evolution corrosion in rechargeable zinc-air batteries [54], as illustrated in Figure 5.
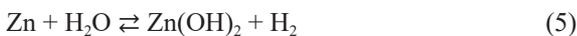
In ideal circumstances, the $Zn(OH)_4^{2-}$ on the surface of the anode should be uniformly distributed. However, in reality, due to various factors, $Zn(OH)_4^{2-}$ on the anode surface is rarely distributed uniformly. This uneven distribution leads to an uneven distribution of the deposited substances on the anode surface, forming a rough and uneven surface. Dendritic growth is inevitable because it is caused by the uneven distribution of ions near the zinc electrode, especially during repeated cycles, as given in detail in Figure 5(a) [34]. With repeated cycling, the extent of unevenness intensifies, ultimately causing continuous growth and
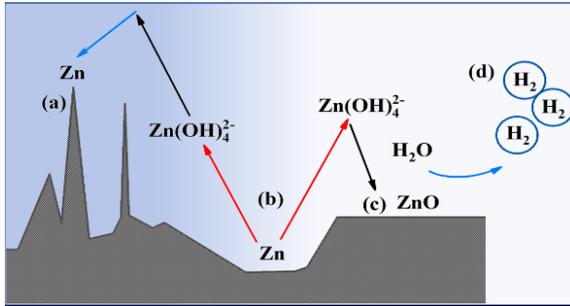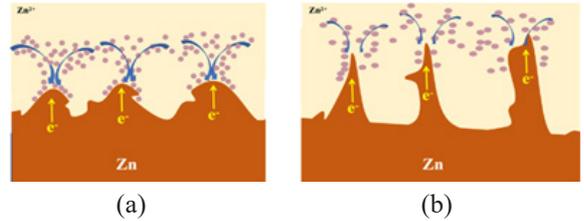
**Figure 5**: Possible phenomena in zinc anodes; (a) Dendrite growth; (b) Shape change; (c) Passivation; and (d) Hydrogen evolution.



**Figure 6**: Volume change and formation of dendrite of bare Zn [50].

extension of dendrites, resulting in dead zinc that cannot participate in the reaction. In extreme cases, large dendrites may pierce through the battery's separator, causing a short circuit and destroying the battery.

The deformation of the anode occurs because the zinc salt products obtained in reaction 1) are insufficient/ do not participate in a reaction 2), failing to form ZnO but instead depositing directly on the anode surface. After repeated charge and discharge cycles, a large amount of zinc salt accumulates leading to the deformation of the battery and a significant reduction in capacity, as shown in Figure 5(b). Besides the passivation of the anode surface is due to the formation of a dense layer of non-reactive ZnO during repeated charge and discharge cycles as displayed in Figure 5(c). By the way, this not only increases the internal resistance of the battery but also hinders direct contact between the anode and the electrolyte. With increased internal resistance, the battery requires a higher voltage during the charging process, while in the discharging process, it can only maintain a lower voltage. The lack of direct contact between the anode and the electrolyte leads to capacity decay in the battery. Furthermore, The hydrogen evolution reaction at the anode occurs in a battery during open-circuit conditions because the reduction potential of hydrogen is more positive than the reduction potential of zinc as addressed in Figure 5(d). Therefore, in the reaction process, a side reaction will take place first as shown in the calculation below:

$$Zn + H_2O \rightleftarrows Zn(OH)_2 + H_2 \qquad (5)$$

Besides, this reaction results in the unnecessary consumption of zinc, reducing the battery capacity, while the generated $Zn(OH)_2$ also increases the internal resistance of the battery, further decreasing its capacity.

The four mentioned situations interact and correlate with each other during the reaction process. A large amount of active material at the zinc anode is consumed, leading to a significant disparity between the actual capacity and theoretical capacity of the zinc-air batteries.

## 5 Modification Methods for Anode of Zinc-Air Secondary Batteries

To achieve better performance for the anode of zinc-air secondary batteries, researchers have developed various methods to enhance the anode. These methods, based on the extent of their application, mainly include 1) Alloying of the anode 2) Surface coating and treatment of the anode 3) Addition of the anode additives properties and 4) 3D structuring of the anode, respectively.

### 5.1 *Alloying of anode*

For the zinc metal anode, the single zinc metal anode exhibits a significant number of cracks and defects due to the substantial volume changes during the de-zincing and zinc plating processes, as illustrated in Figure 6 [55]. For Figure 6(a), during the plating or stripping of zinc, Zinc ions exhibit a preference for nucleation at dislocated sites, leading to the development of initial protuberances on the surface of zinc. Figure 6(b) displays the protuberances have higher potentials and consist of high-density low-coordination steps. Both of these contribute to the growth of dendrites. Alloying zinc with other metals can greatly improve the performance of zinc-air batteries. For example, conductivity is one of the important indicators of zinc-air batteries. The selected metal should possess a higher overpotential of the

evolution of hydrogen compared to zinc, effectively mitigating the corrosion caused by hydrogen evolution on the zinc anode altering its shape, and increasing its utilization. Commonly used metals for alloying include lead (Pb), cadmium (Cd), indium (In), tin (Sn), aluminum (Al), bismuth (Bi), nickel (Ni), etc [56]. Research has displayed that incorporating metals with zinc not only enhances the conductivity of the zinc anode but also serves as a substrate for the deposition of zinc during charging deeds, effectively improving the coulombic efficiency of zinc-air batteries. Due to the simplicity of the alloying process and its favorable outcomes, this method has been widely applied in past research studies.

Recently, Ning *et al*. [57] identified through orthogonal experimental methods that an alloy with the composition Zn-0.1% In-0.1% Bi-0.01 Ca exhibited optimal performance as an anode. The maximum power density of the anode was 169.7 mW/cm$^2$, and it could maintain a stable constant current discharge of 0.93V at 100mA/cm$^2$ for over 200 min. The addition of alloying elements increased the resistance of the anode's corrosion reaction, suppressing intermediate products and reducing zinc corrosion, enhancing the anode's performance. Peng *et al*. [58] prepared an integrated, dense Zn-Sn alloy plate electrode using powder sintering technology. Further, this alloy electrode significantly improved the electrochemical performance of zinc-air batteries. Besides, the fabricated alloy-based battery maintained excellent dendrite-free zinc peeling and plating performance even after 400 h of cycling. Yuan *et al*. [33] proposed a method to alloy the zinc anode with rare earth metal Ce and alkaline earth metal Yb to alleviate dendrite growth. This was achieved by changing the anisotropic modulus and strength at the zinc anode interface. However, the results indicate that an uniaxial modulus of six could achieve a 35% suppression of anisotropic modulus. The most effective way to inhibit dendrite growth was to use zinc anodes composed of Zn98%-Mg2% or Zn93.5%-Yb6.5%, and the addition of Ce expand the anode interface's anisotropic modulus, changing the direction of dendrite growth and reducing its height, while the addition of the Yb reduced the anisotropic strength of the interface, hindering dendrite growth. According to the above three methods, the anode performance of zinc-air batteries can indeed be improved through alloying.
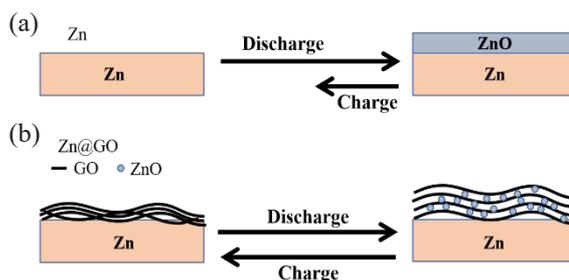


**Figure 7**: Schematic diagram of morphological changes of zinc anodes during electrochemical cycling [28].

## 5.2 *Surface coating and treatment of anode*

Surface coating of the anode can also play a significant role in improving the performance of the battery. Coating materials can isolate the electrolyte from the zinc anode, and confine $Zn(OH)_4$ ions within the anode, not only inhibiting hydrogen evolution corrosion and dendrite formation but also reducing the consumption of active material. The combination of these effects can enhance the battery's performance. Additionally, depending on the properties of the coating material, this can truly enhance conductivity, contributing to the improvement of the anode's performance. Common coating materials include $Al_2O_3$, $TiO_2$, $SiO_2$, $Ca(OH)_2$, carbon, etc. [59]–[62]. With further research, new types of coating materials are also being developed.

Zhou *et al*. [63] coated zinc mesh with graphene oxide, and after 200 cycles of testing, they found that the cumulative discharge capacity was about 128% of that of pure zinc. This is because graphene oxide can prevent zincate ions from passing through, while $H_2O$ and OH- can pass through. During the decomposition of zincate into ZnO, graphene oxide wraps around it, reducing the loss of active material, as shown in Figure 7. Focusing on Figure 7(a), it express that the ZnO passivation layer leads to low utilization of the Zn mesh anode. In addition, graphene oxide on the Zn surface makes it possible for electrons to move freely across the insulating ZnO and slows down the dissolution of Zn species. This concept has been illustrated in Figure 7(b). In addition, Ismail *et al*. [64] proposed a novel technique by coating cassava starch onto the surface of the zinc anode and found that the conductivity increased by 30% compared to a pure zinc anode. This improved conductivity resulted in better performance of the zinc anode. Sun *et al*. [65]

coated ZnO nanorods uniformly dispersed on three-dimensional graphene oxide as a chemical buffer layer on the zinc metal (CBL@Zn) anode. Due to the synergistic effect of the crystallization of ZnO nanorods and the adsorption affinity of graphene oxide, the assembled battery achieved an unusually long cycling performance of 450 h. On the other hand, surface modification treatment of the anode can also improve the battery's capability to a certain extent. For example, Wang *et al*. [66] used laser irradiation on the surface of the zinc anode to remove the surface oxide layer, increasing the contact area of the anode and thereby inhibiting dendrite growth. Han *et al*. [67] decorated the surface of zinc with dual-functional indium metal, serving as both a corrosion inhibitor and a nucleating agent. This effectively prevented corrosion and dendrite growth, and the assembled battery maintained over 1500 hours of electroplating/ stripping cycles. The above literature shows that both coating and surface treatment of anodes can increase the surface area or remove the oxide layer to improve anode performance.

### 5.3 *Anode additives*

When the anode in zinc-air batteries is pure zinc, the discharge product ZnO has a larger volume, 1.6 times that of pure Zn [68] This directly leads to severe electrode deformation during the cycling process. Additionally, because ZnO is a semiconductor, it can also lower the battery's performance. Adding additives to the anode can to some extent address these issues. Lee *et al*. [69] by using zinc and ZnO as or with the anode, found that the stability of the mixed anode was significantly improved compared to a pure zinc anode. This improvement was attributed to the smaller expansion coefficient, suppressing the deformation of the mixed anode. Stamm *et al*. [61] found that adding ZnO to the mixed anode, while reducing the initial discharge capacity, increased the rechargeable capacity and the cycle life of the zinc anode. This is because the added ZnO in pure zinc becomes a nucleating crystal, promoting the uniform deposition and dissolution of ZnO, thereby improving the capacity retention of zinc-air batteries. Park *et al*. [62] achieved a discharge capacity of 160 mAh/g by refining the size of added ZnO to the nanoscale. This makes the nano ZnO have a higher surface area, allowing for a faster reaction
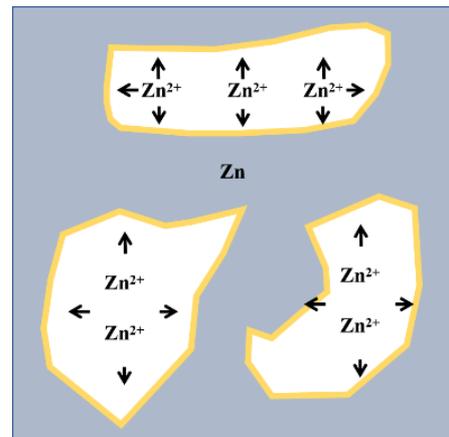


**Figure 8**: Employing a high surface area porous zinc structure [64].

with KOH solution, leading to quicker generation of zincate ions and thus enhancing battery performance.

If conductive agents, metal hydroxides, metal oxides, and other types of additives are introduced into the anode, the conductivity and cycling performance of the battery can be markedly improved. The addition of conductive agents such as graphite and carbon black facilitates rapid electron transfer between pure zinc and ZnO. This arises from these conductive additives enhancing the conductivity of the anode, slowing down the passivation of the anode, and improving battery performance. Masir *et al*. [60] by adding Super P carbon black to the zinc anode as an additive, achieved a 27% increase in the utilization of active materials compared to a pure zinc anode. However, this is attributed to Super P carbon black providing a pathway for electron transfer, allowing more active materials to participate in the cycling process. Both additives and conductive agents can enhance the cycling life of zinc-air batteries on one hand, while improving the performance of the negative electrode on the other hand.

### 5.4 *3D structure of anode*

Zinc materials with a 3D porous structure can not only increase the anode's specific surface area but also enhance the utilization of zinc, playing a beneficial role in promoting the complete reaction of zinc-air batteries. As shown in Figure 8 [70]. Moreover, the large surface area of a 3D porous structure allows for a uniform distribution of current across the entire

electrode during the effective reduction of zincate concentration. The porous structure also restricts the dissolution/precipitation process, effectively reducing dendrite growth in secondary zinc-air batteries [59], [64] thereby contributing to the improvement of the battery's performance.

Dilshad *et al*. [32] grew 3D zinc nanosheets with a high surface area on the surface of zinc through molecular modification. The assembled electrode with the modified material exhibited over 500 cycles of cycling performance under a condition of 5 mA/cm$^2$, with an operating time exceeding 83 h. This improvement is attributed to the increased contact area, promoting more complete reactions. Qu *et al*. [65] obtained a 3D structured zinc-coated foam anode by plating zinc on a copper foam substrate and assembled with a plated anode, PVA-TEAOH-KOH hydrogel, and carbon cloth, they created a flexible zinc-air battery that can bend at large angles without mechanical fracture. The fabricated battery achieved a high specific capacity of 566.7 mAh/g and completed 48 cycles, making significant contributions to the development of flexible zinc-air batteries. The 3D structure mainly improves anode performance by increasing the specific surface area. As mentioned, this manuscript summarises the main anode treatment methods and also their effects in Table 1.

**Table 1**: Different strategies and impacts of anode improvement

| Modification to Zinc Anode | Effects | Details of Methods/Technology | Result | Ref |
|---|---|---|---|---|
| Alloys with Sn, Bi, Ce, Yb, Mg, Al, etc. | Improve battery performance, reduce dendrite growth height, and inhibit hydrogen evolution corrosion | Sn | 0.5 mA/cm$^2$ current density for 400 h | [33] |
| | | Zn-0.1% In-0.1% Bi-0.01% Ca | 100 mA/cm$^2$ current density for 200 min | [57] |
| | | Ce and Yb | 35% inhibition efficiency of dendrite growth | [58] |
| Surface Coating with Garphen and Zno. The laser irradiates the anode surface. | Improve discharge capacity and achieve ultra-long cycle performance. Increase the anode contact area | Graphene oxide-modified | Improve its lifetime accumulated capacity by 28% | [63] |
| | | Femtosecond Laser Processing Structural Surfaces | The first discharge time of zinc anodes with surface structures of zinc-air batteries is about 10 times that of without processing. | [66] |
| | | Decorating the Zn surface with a dual-functional metallic indium (In) layer | 2A/g current density for 5000 cycle times | [67] |
| | | Chemical Buffer Layer of ZnO and graphene oxide | Symmetric coin cells could realize over 100 cycles | [71] |
| | | Cassava Starch Layer | Increment 30% of conductivity values from the original conductivity | [72] |
| Adding zinc oxide as an additive and refining the zinc oxide grain size Conductive agents, metal oxides, and hydroxides | Improve stability and battery capacity Enhance conductivity and improve battery performance | Carbon black as an additive | High specific discharge capacity (776 mAh/g) | [60] |
| | | ZnO as an additive | Improve the rechargeable capacity | [61] |
| | | The particle size of micronized ZnO was changed to nanosized ZnO | Nanosized ZnO showed a higher cycle capacity than microsized ZnO | [62] |
| Generate 3D nano-zinc flakes and three-dimensional structured Zn coatings | Increasing the contact area makes the reaction more complete, improving battery performance and cycle times. Successful development of flexible zinc-air batteries | Grow high-surface-area three-dimensional (3D) Zn nanoflakes on molecularly modified Zn surface | 0.5 mA/cm$^2$ current density for 100 cycles | [32] |
| | | Novel Cu foam substrate with uniform Ag nanoparticles deposited on the surface as a three-dimensional (3D) anode | High specific capacity of 676 mAh/g | [56] |
| | | A three-dimensional (3D) fibrous structure with a highly active surface and conductive pathway | Significantly reduce the charge transfer resistance after 200 cycles | [64] |
| | | Zn-coated foam anode with three-dimensional (3D) architecture | Specific capacity of 566.7 mAh/g | [65] |

# 6 Conclusions

This article gives a summary of the ways to modify the anode of a zinc-air battery. First, it introduces the importance of energy storage systems (ESSs). Due to the unstable of clean energy, ESSs are important not only in the industry but still also in our daily lives. Then, from a business perspective, we conclude that a zinc-air battery is a good choice for building ESSs. However, from a technical point of view, zinc-air batteries truly meet some problems. Additionally, the researchers did find some solutions to solve those problems. They are also listed in this manuscript. In summary, one of the main reasons why zinc-air batteries cannot be commercialized at the current stage and face slow development is the poor reversibility of the zinc anode. This is mainly attributed to the dendritic growth, deformation, passivation, and also hydrogen evolution corrosion of the zinc anode. To address this issue, researchers have taken various measures such as 1) alloying of the anode; 2) surface coating and treatment of the anode; 3) anode additives; and 4) 3D structure of the anode. These measures can to some extent increase the conductivity of the electrode, improve the utilization of active materials, reduce self-corrosion of the anode, and promote the uniform distribution of electronic currents on the electrode surface. However, on the other hand, other issues in the commercialization of secondary zinc-air batteries need to be considered, such as the electrode design and preparation process. The electrode design and preparation process directly settles the electrode's specific surface area, density, porosity, 3D structure, etc., which greatly influences the electrode's ability. Furthermore, the anode materials affect the ability of zinc-air batteries at the same time. So it is necessary to explore new materials or composites with enhanced electrochemical capabilities, reduced dendrite growth, and resistance to self-corrosion. Finally, a complete understanding of the reaction pathway of zinc-air batteries is required. After completing an exhaustive process, understanding the anode's reaction scheme, reaction kinetics, transport phenomena, developing more accurate models to predict and optimize ability, can enhance research efficiency. This manuscript sums up those methods in Table 2.

**Table 2**: Existing and prospective methods to improve the performance of zinc-air batteries

| Aspects | Methods |
|---|---|
| Anode | Alloying of the anode |
| | Surface coating and treatment |
| | Anode additives |
| | 3D structure of the anode |
| Electrode | Electrode design and preparation |
| | Exploration of new materials |
| Reaction mechanism | Comprehensive understanding |

## Author Contributions

Writing original draft preparation, C.SH.; Writing review and editing, S.P. All authors have read and agreed to the published version of the manuscript.

## Conflicts of Interest

The authors declare no conflict of interest.

## References

[1] L. Liu, Z. Wang, H. Zhang, and Y. Xue, "Solar energy development in China-A review," *Renewable and Sustainable Energy Reviews*, vol. 14, no. 1, 301–311, Jan. 2010.

[2] Y. Huang, Y. Wang, C. Tang, J. Wang, Q. Zhang, Y. Wang, and J. Zhang, "Atomic Modulation and structure design of carbons for bifunctional electrocatalysis in metal-air batteries," *Advanced Materials*, vol. 31, no. 13, 2019, Art. no. 1803800.

[3] P. Sapkota and H. Kim, "Zinc-air fuel cell, a potential candidate for alternative energy," *Journal of Industrial and Engineering Chemistry*, vol. 15, no. 4, 445–450, Jul. 2009.

[4] F. M. Guangul and G. T. Chala, "A comparative study between the seven types of fuel cells," *Applied Science and Engineering Progress*, vol. 13, no. 3, pp. 185–194, Apr. 2020, doi: 10.14416/j.asep.2020.04.007.

[5] A. Martsri, N. Yodpijit, M. Jongprasithporn, and

S. Junsupasen, "Energy, economic, and environmental (3E) analysis for sustainable development: A case study of a 9.9 MW biomass power plant in Thailand," *Applied Science and Engineering Progress*, vol. 14, no. 3, pp. 378–386, 2020, doi: 10.14416/j.asep.2020.07.002.

[6] J. Mitali, S. Dhinakaran, and A. A. Mohamad, "Energy storage systems: A review," *Energy Storage and Saving*, vol. 1, no. 3, pp. 166–216, Sep. 2022, doi: 10.1016/j.enss.2022.07.002.

[7] A. Z. A. Shaqsi, K. Sopian, and A. Al-Hinai, "Review of energy storage services, applications, limitations, and benefits," *Energy Reports*, vol. 6, pp. 288–306, Dec. 2020, doi: 10.1016/j.egyr.2020.07.028.

[8] X. Min, G. Xu, B. Xie, P. Guan, M. Sun, and G. Cui, "Challenges of prelithiation strategies for next generation high energy lithium-ion batteries," *Energy Storage Materials*, vol. 47, pp. 297–318, May 2022, doi: 10.1016/j.ensm.2022. 02.005.

[9] S. Agnew and P. Dargusch, "Effect of residential solar and storage on centralized electricity supply systems," *Nature Clim Change*, vol. 5, no. 4, pp. 315–318, Apr. 2015, doi: 10.1038/nclimate2523.

[10] T. Kim, W. Song, D.-Y. Son, L. K. Ono, and Y. Qi, "Lithium-ion batteries: outlook on present, future, and hybridized technologies," *Journal of Materials Chemistry A*, vol. 7, no. 7, pp. 2942–2964, Feb. 2019, doi: 10.1039/C8TA10513H.

[11] M. Armand and J.-M. Tarascon, "Building better batteries," *Nature*, vol. 451, pp. 652–657, Feb. 2008, doi: 10.1038/451652a.

[12] F. Zhao, J. Xue, W. Shao, H. Yu, W. Huang, and J. Xiao, "Toward high-sulfur-content, high-performance lithium-sulfur batteries: Review of materials and technologies," *Journal of Energy Chemistry*, vol. 80, pp. 625–657, May 2023, doi: 10.1016/j.jechem.2023.02.009.

[13] V. Soundharrajan, B. Sambandam, S. Kim, V. Mathew, J. Jo, S. Kim, J. Lee, S. Islam, K. Kim, Y.-K. Sun, and J. Kim, "Aqueous magnesium zinc hybrid battery: An advanced high-voltage and high-energy $MgMn_2O_4$ cathode," *ACS Energy Letters*, vol. 3, no. 8, pp. 1998–2004, Aug. 2018, doi: 10.1021/acsenergylett.8b01105.

[14] G. Fang, C. Zhu, M. Chen, J. Zhou, B. Tang, X. Cao, X. Zheng, A. Pan, and S. Liang, "Suppressing manganese dissolution in potassium manganate with rich oxygen defects engaged high-energy-density and durable aqueous zinc-ion battery," *Advanced Functional Materials*, vol. 29, no. 15, Apr. 2019, Art. no. 1808375, doi: 10.1002/adfm.201808375.

[15] A. Kraytsberg and Y. Ein-Eli, "Review on Li-air batteries-opportunities, limitations, and perspective," *Journal of Power Sources*, vol. 196, no. 3, pp. 886–893, Feb. 2011, doi: 10.1016/j.jpowsour.2010.09.031.

[16] Z. Khan, M. Vagin, and X. Crispin, "Can hybrid Na–air batteries outperform nonaqueous $Na-O_2$ batteries?," *Advanced Science*, vol. 7, no. 5, 2020, Art. no. 1902866, doi: 10.1002/advs.201902866.

[17] L. Qin, N. Xiao, S. Zhang, X. Chen, and Y. Wu, "From K-O2 to K-Air batteries: Realizing superoxide batteries on the basis of dry ambient air," *Angewandte Chemie International Edition*, vol. 59, no. 26, pp. 10498–10501, 2020, doi: 10.1002/anie.202003481.

[18] P. Chen, K. Zhang, D. Tang, W. Liu, F. Meng, Q. Huang, and J. Liu, "Recent progress in electrolytes for Zn–Air batteries," *Frontiers in Chemistry*, vol. 8, p. 372, 2020, doi: 10.3389/fchem.2020.00372.

[19] P. Jiang, D. Li, R. Hou, H. Yang, J. Yang, S. Zhu, L. Wang, and S. Guan, "A micro-alloyed Mg-Zn-Ge alloy as promising anode for primary Mg-air batteries," *Journal of Magnesium and Alloys*, 2023, doi: 10.1016/j.jma.2023.05.004.

[20] M. Wei, K. Wang, Y. Zuo, J. Liu, P. Zhang, P. Pei, S. Zhao, Y. Li, and J. Chen, "A high-performance Al-air fuel cell using a mesh-encapsulated anode via Al–Zn energy transfer," *iScience*, vol. 24, no. 11, 2021, doi: 10.1016/j.isci.2021.103259.

[21] B. Qian, Y. Zhang, X. Hou, D. Bu, K. Zhang, Y. Lan, Y. Li, S. Li, T. Ma, and X.-M. Song, "A dual photoelectrode photoassisted Fe–Air battery: The photo-electrocatalysis mechanism accounting for the improved oxygen evolution reaction and oxygen reduction reaction of air electrodes," *Small*, vol. 18, no. 7, 2022, Art. no. 2103933, doi: 10.1002/smll.202103933.

[22] Md. A. Rahman, X. Wang, and C. Wen, "High energy density metal-air batteries: A review," *Journal of The Electrochemical Society*, vol. 160, no. 10, pp. A1759–A1771,

2013, doi: 10.1149/2.062310jes.

[23] D. Ahuja, V. Kalpna, and P. K. Varshney, "Metal air battery: A sustainable and low-cost material for energy storage," *Journal of Physics: Conference Series*, vol. 1913, no. 1, May 2021, Art. no. 012065, doi: 10.1088/1742-6596/1913/1/012065.

[24] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, and N. Sammes, "A novel high energy density rechargeable lithium/air battery," *Chemical Communications*, vol. 46, no. 10, pp. 1661–1663, 2010, doi: 10.1039/B920012F.

[25] V. Caramia and B. Bozzini, "Materials science aspects of zinc-air batteries: A review," *Materials for Renewable and Sustainable Energy*, vol. 3, no. 2, p. 28, Apr. 2014, doi: 10.1007/s40243-014-0028-3.

[26] X. U. Neng-neng and Q. I. A. O. Jin-li, "Recent Progress in bifunctional catalysts for zinc-air," *Journal of Electrochemistry*, vol. 26, no. 4, pp. 531–562, 2020.

[27] J. R. Goldstein and B. Koretz, "Tests of a full-sized mechanically rechargeable zinc-air battery in an electric vehicle," *IEEE Aerospace and Electronic Systems Magazine*, vol. 8, no. 11, pp. 34–38, Nov. 1993, doi: 10.1109/62.242061.

[28] J. Goldstein, I. Brown, and B. Koretz, "New developments in the Electric Fuel Ltd. zinc/air system," *Journal of Power Sources*, vol. 80, no. 1, pp. 171–179, Jul. 1999, doi: 10.1016/S0378-7753(98)00260-2.

[29] J.-N. Liu, C.-X. Zhao, J. Wang, D. Ren, B.-Q. Li, and Q. Zhang, "A brief history of zinc–air batteries: 140 years of epic adventures," *Energy & Environmental Science*, vol. 15, no. 11, pp. 4542–4553, 2022, doi: 10.1039/D2EE02440C.

[30] P. Pei, K. Wang, and Z. Ma, "Technologies for extending zinc–air battery's cyclelife: A review," *Applied Energy*, vol. 128, pp. 315–324, Sep. 2014, doi: 10.1016/j.apenergy.2014.04.095.

[31] N. Kadam and A. Sarkar, "A high voltage zinc–air battery with two isolated electrolytes and moving auxiliary electrodes," *Applied Energy*, vol. 344, Aug. 2023, Art. no. 121309, doi: 10.1016/j.apenergy.2023.121309.

[32] K. A. J. Dilshad and M. K. Rabinal, "Rationally designed Zn-Anode and $Co_3O_4$-Cathode nanoelectrocatalysts for an efficient Zn-Air battery," *Energy and Fuels*, vol. 35, no. 15, pp. 12588–12598, 2021, doi: 10.1021/acs.energyfuels.1c01108.

[33] X. Yuan, C. He, J. Wang, X. You, Y. Chen, Q. Gou, N. Yang, G. Xie, Y. Hou, "Inhibition of zinc dendrite growth in zinc-air batteries by alloying the anode with Ce and Yb," *Journal of Alloys and Compounds*, vol. 970, 2024, doi: 10.1016/ j.jallcom.2023.172523.

[34] C. Mou, Y. Bai, C. Zhao, G. Wang, Y. Ren, Y. Liu, X. Wu, H. Wang, Y. Sun, "Construction of a self-supported dendrite-free zinc anode for high-performance zinc-air batteries," *Inorganic Chemistry Frontiers*, vol. 10, no. 10, pp. 3082–3090, 2023, doi: 10.1039/d3qi00279a.

[35] C. Sparkes and N. K. Lacey, "A study of mercuric oxide and zinc-air battery life in hearing aids," *The Journal of Laryngology & Otology*, vol. 111, no. 9, pp. 814–819, Sep. 1997, doi: 10.1017/S002221510013871X.

[36] Y. Li, M. Gong, Y. Liang, J. Feng, J.-E. Kim, H. Wang, G. Hong, B. Zhang, and H. Dai, "Advanced zinc-air batteries based on high-performance hybrid electrocatalysts," *Nature Communications*, vol. 4, no. 1, May 2013, Art. no. 1805, doi: 10.1038/ncomms2812.

[37] G. W. Heise and E. A. Schumacher, "An air-depolarized primary cell with caustic alkali electrolyte," *Transactions of The Electrochemical Society*, vol. 62, no. 1, p. 383, Jan. 1932, doi: 10.1149/1.3493794.

[38] R. P. Hamlen, E. C. Jerabek, J. C. Ruzzo, and E. G. Siwek, "Anodes for refuelable magnesium-air batteries," *Journal of the Electrochemical Society*, vol. 116, no. 11, p. 1588, Nov. 1969, doi: 10.1149/1.2411622.

[39] J. Zheng, Q. Zhao, T. Tang, J. Yin, C. D. Quilty, G. D. Renderos, X. Liu, Y. Deng, L. Wang, D. C. Bock, C. Jaye, D. Zhang, E. S. Takeuchi, K. J. Takeuchi, A. C. Marschilok, and L. A. Archer, "Reversible epitaxial electrodeposition of metals in battery anodes," *Science*, vol. 366, no. 6465, pp. 645–648, Nov. 2019, doi: 10.1126/science.aax6873.

[40] L. Maiche, French Patent 127069, 1878.

[41] J. Kolesar and S. Edward, "Thermoelectric cooling: Review and application. Aeromedical

review," Defense Technical Information Center, Fort Belvoir, VA, 1981.

[42] G. D. Brabson, J. Fannin, L. A. King, and D. W. Seegmiller, "Prototype high-power density aluminum-chlorine battery," in *Electrochemical Society*, May 1973, vol. 120, no. 3, Art. no. 7029560.

[43] B. Scrosati, "Lithium rocking chair batteries: An old concept?," *Journal of The Electrochemical Society*, vol. 139, no. 10, Oct. 1992, Art. no. 2776, doi: 10.1149/1.2068978.

[44] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, "LixCoO$_2$ $(0 < x < -1)$: A new cathode material for batteries of high energy density," *Materials Research Bulletin*, vol. 15, no. 6, pp. 783–789, Jun. 1980, doi: 10.1016/ 0025-5408(80)90012-4.

[45] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries," *Journal of The Electrochemical Society*, vol. 144, no. 4, Apr. 1997, Art. no. 1188, doi: 10.1149/1.1837571.

[46] M. M. Thackeray, "Manganese oxides for lithium batteries," *Progress in Solid State Chemistry*, vol. 25, no. 1, pp. 1–71, Jan. 1997, doi: 10.1016/ S0079-6786(97)81003-5.

[47] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B. Lestriez, P. Novák, M. Petranikova, W. Porcher, S. Trabesinger, M. Wohlfahrt-Mehrens, and H. Zhang, "Lithium-ion batteries – Current state of the art and anticipated developments," *Journal of Power Sources*, vol. 479, Dec. 2020, Art. no. 228708, doi: 10.1016/j.jpowsour.2020.228708.

[48] J, Duan, J, Zhao, X, Li, S, Panchal, J, Yuan, R, Fraser, and M, Fowler, "Modeling and analysis of heat dissipation for liquid cooling lithium-ion batteries," *Energies*, vol. 14, no. 14, Jul. 2021, Art. no. 4187, doi: 10.3390/en14144187.

[49] H. Tian, P. Qin, K. Li, and Z. Zhao, "A review of the state of health for lithium-ion batteries: Research status and suggestions," *Journal of Cleaner Production*, vol. 261, Jul. 2020, Art. no. 120813, doi: 10.1016/j.jclepro.2020.120813.

[50] M. S. H. Lipu, M. A. Hannan, A. Hussain, A. Ayob, M. H. M. Saad, T. F. Karim, and D. N. T. How, "Data-driven state of charge estimation of lithium-ion batteries: Algorithms, implementation factors, limitations and future trends," *Journal of Cleaner Production*, vol. 277, Dec. 2020, Art. no. 124110, doi: 10.1016/ j.jclepro.2020.124110.

[51] C.-X. Zhao, J.-N. Liu, J. Wang, D. Ren, J. Yu, X. Chen, B.-Q. Li, and Q. Zhang, "A $\Delta E = 0.63$ V bifunctional oxygen electrocatalyst enables high-rate and long-cycling zinc–air batteries," *Advanced Materials*, vol. 33, no. 15, 2021, Art. no. 2008606, doi: 10.1002/adma.202008606.

[52] X. Chen, Z. Zhou, H. E. Karahan, Q. Shao, L. Wei, and Y. Chen, "Recent advances in materials and design of electrochemically rechargeable zinc–air batteries," *Small*, vol. 14, no. 44, 2018, Art. no. 1801929, doi: 10.1002/smll. 201801929.

[53] J. B. Goodenough and K.-S. Park, "The Li-Ion rechargeable battery: A perspective," *Journal of the American Chemical Society*, vol. 135, no. 4, pp. 1167–1176, Jan. 2013, doi: 10.1021/ ja3091438.

[54] J. Pan, Y. Y. Xu, H. Yang, Z. Dong, H. Liu, and B. Y. Xia, "Advanced architectures and relatives of air electrodes in Zn–Air batteries," *Advanced Science*, vol. 5, no. 4, 2018, Art. no. 1700691, doi: 10.1002/advs.201700691.

[55] S.-B. Wang, Q. Ran, R.-Q. Yao, H. Shi, Z. Wen, M. Zhao, X.-Y. Lang, and Q. Jiang, "Lamella-nanostructured eutectic zinc–aluminum alloys as reversible and dendrite-free anodes for aqueous rechargeable batteries," *Nature Communications*, vol. 11, no. 1, Apr. 2020, Art. no. 1634, doi: 10.1038/s41467-020-15478-4.

[56] Y. Li and H. Dai, "Recent advances in zinc–air batteries," *Chemical Society Reviews*, vol. 43, no. 15, pp. 5257–5275, 2014, doi: 10.1039/C4CS000 15C.

[57] Q. Ning, L. He, X. Wang, H. Liu, and S. Gao, "Effects of alloying elements on electrochemical performance of zinc-air battery anode," *Journal of Central South University (Science and Technology)*, vol. 52, no. 10, pp. 3389–3396, 2021, doi: 10.11817/j.issn.1672-7207.2021.10.002.

[58] Y. Peng, C. Lai, M. Zhang, X. Liu, Y. Yin, Y. Li, and Z. Wu, "Zn–Sn alloy anode with repressible dendrite grown and meliorative corrosion resistance for Zn-air battery," *Journal of Power Sources*, vol. 526, 2022, Art. no. 231173, doi: 10.1016/j.jpowsour.2022.231173.

[59] J. Yu, F. Chen, Q. Tang, T. T. Gebremariam, J. Wang, X. Gong, and X. Wang, "Ag-modified Cu foams as three-dimensional anodes for rechargeable zinc-air batteries," *ACS Applied Nano Materials*, vol. 2, no. 5, pp. 2679–2688, 2019, doi: 10.1021/acsanm.9b00156.

[60] M. N. Masri and A. A. Mohamad, "Effect of adding carbon black to a porous zinc anode in a zinc-air battery," *Journal of the Electrochemical Society*, vol. 160, no. 4, pp. A715–A721, 2013, doi: 10.1149/2.007306jes.

[61] J. Stamm, A. Varzi, A. Latz, and B. Horstmann, "Modeling nucleation and growth of zinc oxide during discharge of primary zinc-air batteries," *Journal of Power Sources*, vol. 360, pp. 136–149, 2017, doi: 10.1016/j.jpowsour.2017.05.073.

[62] D. J. Park, W. G. Yang, H. W. Jeong, and K. S. Ryu, "Study of zinc compounds for improving the reversibility of the zinc anode in zinc–air secondary batteries," *Bulletin of the Korean Chemical Society*, vol. 38, no. 7, pp. 706–710, 2017, doi: 10.1002/bkcs.11157.

[63] Z. Zhou, Y. Zhang, P. Chen, Y. Wu, H. Yang, H. Ding, Y. Zhang, Z. Wang, X. Du, and N. Liu, "Graphene oxide-modified zinc anode for rechargeable aqueous batteries," *Chemical Engineering Science*, vol. 194, pp. 142–147, 2019, doi: 10.1016/j.ces. 2018.06.048.

[64] R. Khezri, K. Jirasattayaporn, A. Abbasi, T. Maiyalagan, A. Mohamad, and S. Kheawhom, "Three-dimensional fibrous iron as anode current collector for rechargeable zinc-air batteries," *Energies*, vol. 13, no. 6, Mar. 2020, Art. no. 1429, doi: 10.3390/en13061429.

[65] S. Qu, B. Liu, X. Fan, X. Liu, J. Liu, J. Ding, X. Han, Y. Deng, W. Hu, and C. Zhong, "3D foam anode and hydrogel electrolyte for high-performance and stable flexible zinc–air battery," *ChemistrySelect*, vol. 5, no. 27, pp. 8305–8310, 2020, doi: 10.1002/ slct.202002573.

[66] C. Wang, Y. Yuan, J. Chen, D. Li, J. Wu, and K. Zhang, "Femtosecond laser processing structural surfaces of zinc anodes for rechargeable zinc-air battery," in *E3S Web of Conferences*, 2021, vol. 261, Art. no. 02078, doi: 10.1051/e3sconf/202126102078.

[67] D. Han, S. Wu, S. Zhang, Y. Deng, C. Cui, L. Zhang, Y. Long, H. Li, Y. Tao, Z. Weng, Q.-H. Yang, and F. Kang, "A corrosion-resistant and dendrite-free zinc metal anode in aqueous systems," *Small*, vol. 16, no. 29, Jul. 2020, Art. no. e2001736, doi: 10.1002/smll.202001736.

[68] T. Arlt, D. Schröder, U. Krewer, and I. Manke, "In operando monitoring of the state of charge and species distribution in zinc air batteries using X-ray tomography and model-based simulations," *Physical Chemistry Chemical Physics*, vol. 16, no. 40, pp. 22273–22280, 2014, doi: 10.1039/C4CP02878C.

[69] C. W. Lee, S. W. Eom, K. Sathiyanarayanan, and M. S. Yun, "Preliminary comparative studies of zinc and zinc oxide electrodes on corrosion reaction and reversible reaction for zinc/air fuel cells," *Electrochimica Acta*, vol. 52, no. 4, pp. 1588–1591, Dec. 2006, doi: 10.1016/j.electacta.2006.02.063.

[70] J. Fu, R. Liang, G. Liu, A. Yu, Z. Bai, L. Yang, and Z. Chen, "Recent progress in electrically rechargeable zinc–air batteries," *Advanced Materials*, vol. 31, no. 31, doi: 10.1002/adma.201805230, Art. no. 1805230, 2019.

[71] W. Sun, M. Ma, M. Zhu, K. Xu, T. Xu, Y. Zhu, and Y. Qian, "Chemical buffer layer enabled highly reversible Zn anode for deeply discharging and long-life Zn–air battery," *Small*, vol. 18, no. 9, 2022, doi: 10.1002/ smll.202106604.

[72] W. M. I. W. Ismail, M. N. Masri, and H. K. Adli, "Study of cassava starch layer on zinc anode by electrochemistry method for zinc-air fuel cell system," in *IOP Conference Series: Earth and Environmental Science*, 2020, vol. 596, Art. no. 012004, doi: 10.1088/1755-1315/596/1/012004.