

Edited by
Zongping Shao and Xiaomin Xu

Zinc–Air Batteries

Introduction, Design Principles, and
Emerging Technologies



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Preface

Electrochemical energy storage and conversion technologies, which can mitigate the gaps between supply and demand of electricity, will continue to play a critical role in humanity's pursuit of a green and sustainable energy future. One extraordinary example is battery technologies, among which Li-ion batteries are the best known and have transformed portable electronic devices and dominated the consumer market ever since their introduction in the 1990s. Regrettably, the maximum energy density of the currently available Li-ion batteries is still not sufficient to meet the demands of emerging markets, such as electric vehicles. Very recently, metal-air batteries are receiving a great deal of interest as an alternative option because they show extremely high energy densities that far exceed the best that can be offered by Li-ion batteries. In particular, zinc-air batteries (ZABs) have attracted growing attention, which, compared with Li-ion batteries, feature additional advantages such as lower cost, higher safety, and better environmental friendliness. While the past decades have witnessed significant research efforts in developing advanced ZABs with improved performance in terms of energy efficiency, cost reduction, and durability, challenges hindering the wider-scale deployment of the ZAB technology still remain. With respect to this, a specified book contribution on the fundamentals and applications of ZABs, which is currently not seen, should be highly useful to facilitate the research and development of the ZAB technology in the long run.

This book provides a comprehensive and up-to-date introduction to ZABs, covering past, present, and future developments and spanning both fundamental and applied research. In particular, design principles regarding the key components of ZABs ranging from air cathode to zinc anode and to electrolyte are emphasized. A special focus is given to the recent advances in the cathode catalysts achieved by cutting-edge materials, engineering processes, and technologies. Furthermore, industrial developments of ZABs are overviewed and emerging new design of ZABs is also introduced. We hope that this book could serve as a handy tool for students, researchers, and instructors working in battery technologies, materials science, and electrochemistry, and for industry and government representatives for decision making associated with energy and transportation. We also hope that this book will stimulate wider general interest and promote further development in electrochemical energy storage and conversion technologies.

We express our sincere gratitude to all the contributors to this book who are actively engaged in research at the forefront of ZABs. We are also very grateful to the Wiley-VCH editorial staff and extend special thanks to Shaoyu Qian and Katherine Wong for their professional assistance and strong support during the preparation of this book. Finally, we welcome any constructive comments for further improvements to this book.

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Zongping Shao
Xiaomin Xu

1

Introduction to Zinc–Air Batteries

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1.1 Introduction

With the rapid development of society, people's dependence on energy sources is increased continually in terms of daily life and transportation [1]. Up to now, nonrenewable energies, such as fossil energy (oil, natural gas, and coal) and nuclear energy, account for 80% of energy consumption, thus inevitably causing serious environmental pollution (green-house gas, SO₂, and NO_x) and rapid consumption of reserve resources [2]. Therefore, it is urgent to develop renewable clean energy, including solar energy, tidal energy, wind energy, and hydropower, to substitute for traditional fossil energy in power grid [3, 4]. Generally, this renewable energy is regarded as intermittent energy, which is highly dependent on resource conditions, such as season, climate, and region; so, we should pay more attention to efficient energy storage and conversion technology to achieve continuous energy output.

Among the numerous energy storage and conversion devices, electrochemical storage and conversion systems, such as Li-ion/nickel-metal hydride (NIMH)/lead–acid battery, Li–sulfur battery, and metal–air battery, show the advantages of high-energy-conversion efficiency and high-energy density [5]. Devices using Li-ion/NIMH/lead–acid batteries as power sources can be seen everywhere in daily life, including mobile phones, laptops, unmanned aerial vehicles, wireless headphones, and even electronic vehicles. Given the great impact of Li-ion batteries on the whole society, the 2019 Nobel Prize in chemistry was awarded to three pioneers, including John B Goodenough, M. Stanley Whittingham, and Akira Yoshino, owing to their great achievement in rechargeable Li-ion batteries [6]. Although Li-ion battery has achieved great success, the low-energy-storage density, high cost, limited reserves of lithium, and insufficient safety for the usage of volatile organic electrolyte remain the biggest headaches in the field of electric vehicles or other

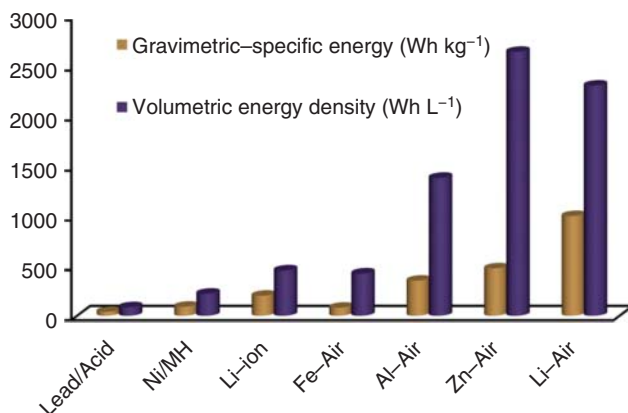


Figure 1.1 The gravimetric and volumetric energy density of various types of secondary batteries. Source: Lee et al. [11]/Reproduced with permission of Royal Society of Chemistry.

portable devices [7, 8]. Therefore, it is imperative to develop other rechargeable batteries with safety, high-specific-energy density, and cost-efficient, such as Li–sulfur battery, metal–air battery, and solid-state Li–metal battery. Among these batteries, metal–air battery is regarded as the next-generation energy-storage system owing to the low cost and high-energy density, while Li–sulfur battery and solid-state Li–metal battery just exhibit the advantage of high-energy density [9, 10]. As shown in Figure 1.1, the gravimetric and volumetric energy density of metal–air batteries, including lithium (Li), zinc (Zn), aluminum (Al), and iron (Fe), are significantly higher than other conventional rechargeable batteries [11, 12]. Although Li–air battery shows the highest theoretical energy density of 3458 Wh kg^{-1} , unfortunately, the volatilization of organic electrolyte and instability of lithium metal, when exposed to oxygen or water, were encountered for Li–air battery with open system, thus causing poor cycle stability [13]. For Fe–air and Al–air batteries, its actual specific energy and energy density are considerably lower than the theoretical value owing to large polarization voltage, its rechargeability is relatively poor in alkaline conditions, and rapid self-discharge through hydrogen-evolution reaction is encountered in alkaline conditions [14, 15]. In contrast, Zn–air battery shows obvious advantages for practical application [16], including (i) actual energy density reaching up to $500\text{--}600 \text{ Wh kg}^{-1}$ (theoretical energy density of 1086 Wh kg^{-1}), which is twofold of advanced lithium-ion batteries; (ii) the discharge platform is extremely stable, which could achieve stable output voltage; (iii) the battery with aqueous electrolyte is safe and environment-friendly; (iv) the cost of Zn–air batteries was decreased by using the zinc metal which is abundant reserves and low cost [16]. Up to now, Zn–air battery has been successfully applied to hearing aid, urban sightseeing vehicles, and postal vehicles. To accelerate and standardize the application of Zn–air batteries in electric vehicles, the Ministry of Industry and Information Technology of China has also approved the “The industry standard of Zn–air battery for electric vehicles” (GB/T 18333.2-2015).

1.2 History of Zn–Air Batteries

The first battery with zinc metal as the anode was developed by Volta in 1796 [17]. In the early nineteenth century, the zinc metal and MnO_2 were applied as the anode and cathode for zinc–manganese dry battery, respectively, with the shape of beaker, while the hybrid NH_4Cl and ZnCl_2 were served as the electrolyte [18]. Based on this, Maiche developed the first primary model of Zn–air battery in 1878 by replacing the MnO_2 with platinum-loaded porous carbon, indicating the first appearance of zinc–air battery [19]. Owing to the usage of weak acid NH_4Cl aqueous solution as electrolyte, the output-discharge current density for this primary zinc–air battery is just 0.3 mA cm^{-2} . Few years later, a Walker–Wilkins battery with first reported gas-diffusion layer consisting of porous carbon black was further designed [20]. In the Walker–Wilkins battery, aqueous potassium hydroxide and nickel were employed as electrolyte and current collectors of the gas-diffusion layer, respectively. At that time, the atmospheric oxygen was identified as the reactant for oxygen-reduction reaction (ORR). In 1932, Heise and Schumadcher redesign a waterproof porous carbon as the air cathode and a NaOH aqueous solution with 20% concentration as the electrolyte [21]. As a result, this Zn–air battery could achieve high-discharge current density of 10 mA cm^{-2} , which marks its practical commercial applications in many fields, including railway signaling equipment and lighthouse. Since the 1970s, the primary coin-type Zn–air battery with low-power density is widely applied in hearing aids, revealing the Zn–air battery entered into our daily life [22]. With rapid development of high-efficient gas-diffusion layer, Zn–air batteries have made great progress in discharge current density reaching up to 1000 mA cm^{-2} in pure oxygen atmosphere, while the electrode thickness was just 0.12–0.5 mm [23]. The high-power density of Zn–air batteries shows application prospects in the field of electric vehicles.

When operating in air atmosphere, the alkaline electrolyte would react with CO_2 to form the solid K_2CO_3 , which could block the gas-diffusion layer [24]. Different from alkaline electrolyte, neutral solution with NH_4Cl as the solute could avoid the direct reaction between alkaline and CO_2 in air to form the carbonates. Until 1973, Jindra et al. found that 5 M NH_4Cl aqueous solution could serve as a quasi-neutral electrolyte to achieve sufficient buffering capacity for primary Zn–air battery [25]. However, the ionic conductivity of neutral electrolyte is relatively poor, thus the Zn–air battery with neutral electrolyte shows low-power density. Alkaline electrolytes (e.g. KOH , NaOH , and LiOH aqueous solutions), which are widely applied in commercial primary Zn–air batteries, are the essential component to achieve high-energy density and power density owing to their high ionic conductivity and high catalytic activity of ORR [26]. For example, the KOH aqueous solution with mass concentration of 35% shows high ionic conductivity of 0.55 S cm^{-1} and low viscosity of 2.2339 mPa s at 25°C , which could provide excellent electrochemical kinetics and mass transfer for Zn–air battery [27]. More importantly, the catalytic activities of ORR and oxygen-evolution reaction (OER) in alkaline electrolytes is evidently better than that in neutral electrolytes.

Above researches about pristine Zn–air batteries just focus on the discharge performance. From 1997 onwards, rechargeable Zn–air batteries with alkaline electrolytes came into sight by researchers [28]. Commonly, 6 M KOH mixed with 0.2 M $\text{ZnCl}_2/\text{Zn}(\text{CH}_3\text{COO})_2$ was widely applied as the electrolyte for rechargeable Zn–air batteries [12]. In 2000s, the flexible rechargeable Zn–air batteries with polymer electrolytes consisting of polymer and KOH were proposed to satisfy the demands for flexible electronics [29]. The researches on polymer with the ability to bind water have been intensely explored to achieve long lifespan [30]. Recently, a large number of researches about bifunctional electrocatalysts involving both the ORR and OER, including single-atom catalysts, carbon materials, perovskite oxide, spinel oxide, and transition-metal compounds, have been proposed for reducing the potential gap between charge and discharge of Zn–air batteries, thus achieving high-energy efficiency [31–33]. With the emergence of high-efficient bifunctional oxygen electrocatalysts, the commercialization process of rechargeable Zn–air batteries has been accelerated. The timeline of the development of Zn–air batteries is shown in Figure 1.2.

Up to now, the rechargeable Zn–air batteries have made great progress in the field of electric vehicles. The Electric Fuel company in Israel developed a mechanically rechargeable Zn–air battery for electric buses, showing an energy density of 200 Wh kg^{-1} , which is reaching up to the advanced Li-ion batteries at present [34, 35]. In addition, the Mercedes Benz cars with mechanically rechargeable Zn–air batteries could be able to drive up to 425 km on one charge [36]. The key technology for mechanical rechargeable Zn–air battery is the recovery of zinc anode after deep discharge. To overcome the issues of zinc replacement, a zinc paste circulating Zn–air battery with specific energy density of 228 Wh kg^{-1} was designed by Metallic Power Inc., while the spent zinc paste was reduced to fresh zinc paste outside the battery [37]. Other companies, including EOS Energy Storage, ZincNyx Energy Solutions, and Fluidic Energy, also contributed to the development of

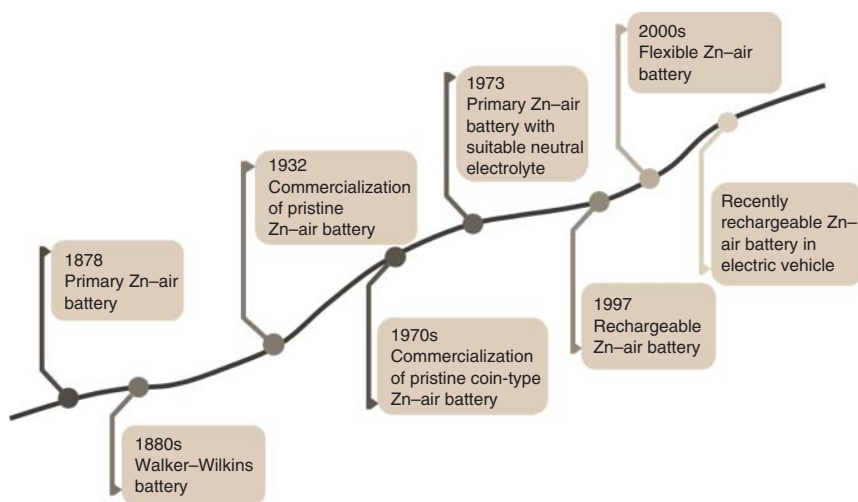


Figure 1.2 Timeline of the development of Zn–air batteries.

Zn–air batteries in practical applications [38]. In addition to electric vehicles, the Zn–air battery could also be applied in wearable devices, unmanned aerial vehicles, communication base stations, electric bicycles, etc.

1.3 Structure and Principle of Zn–Air Batteries

Generally, Zn–air battery is regarded as an alkaline fuel cell, which is composed of three main components—air electrode as cathode involving catalytic active layer and gas-diffusion layer, zinc metal as the anode, and porous separator immersed with alkaline electrolytes, such as 6 M KOH mixed with 0.2 M $\text{ZnCl}_2/\text{Zn}(\text{CH}_3\text{COO})_2$ aqueous solution [39, 40]. In detail, a porous separator is also provided to build a physical barrier between cathode and anode to avoid short circuits, while the electrolyte acts as the medium for the transmission of OH^- between anode and cathode [41]. In addition, the gas-diffusion layer is applied to improve the transfer rate of oxygen to catalysts surface, while the catalytic active layer could facilitate the reaction rate between oxygen and OH^- [42]. During electrochemical discharge process, the reduction of oxygen molecules to OH^- occurs by ORR, while reversible OER occurs during OER process [43]. For zinc anode, which served as the counter electrode, the spontaneous chemical reaction between zinc and OH^- occurs to produce ZnO during discharge process, while the ZnO is decomposed to zinc and OH^- during charge process [43]. In general, zinc metal is regarded as the main active species to achieve electric energy output for pristine Zn–air battery, also called Zn–air fuel cell. For the air electrodes with different catalysts, there are three types of Zn–air batteries models, including pristine Zn–air batteries, two-electrode rechargeable Zn–air batteries, and three-electrode rechargeable Zn–air batteries [44], as shown in Figure 1.3. The sandwich structure of cathode/separator/anode for these three typical batteries are same, while the component of catalytic active layer in air cathode is different.

For pristine Zn–air battery, only ORR occurs on air electrode (Figure 1.3a) [45]. The ORR in alkaline electrolyte is a complex reaction process with multielectron-involved elementary reactions. During the ORR process, molecular oxygen, adsorbed on catalysts surface via the bidentate configuration, is reduced to OH^- through a 4-electron pathway (see Eq. (1.1)) [46]. Otherwise, molecular oxygen, adsorbed on catalysts surface via the end-on one oxygen atom coordination mode, is reduced to HO_2^- through a 2-electron pathway (see Eq. (1.2)) [47]. In general, the 2-electron oxygen-reduction pathway, which is usually applied to produce the hydrogen peroxide (H_2O_2), is regarded as the side reaction for 4-electron oxygen-reduction pathway. The 2-electron pathway may cause tremendous energy loss and inferior discharge durability for Zn–air batteries [48]. Therefore, it is desirable to develop ORR catalysts with 4-electron pathway regarding the activity and stability. When evaluating ORR performance, the electron-transfer number also needs to be calculated with the exception of limiting current and half-wave potential [49]. From the 4-electron ORR equation, the consumption of H_2O and production of OH^- occur for the electrolyte, thus causing the increase of local pH values on cathode surface. The equilibrium potential of 4-electron ORR is

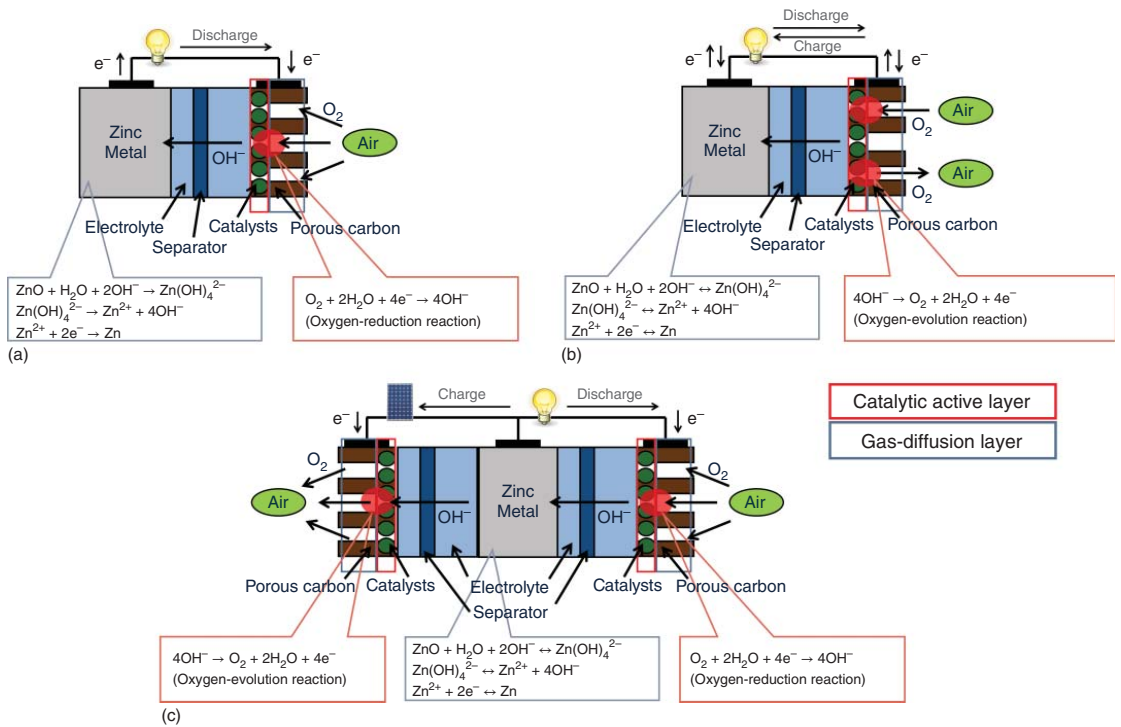
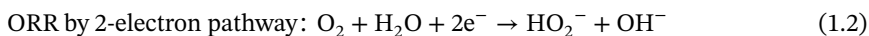
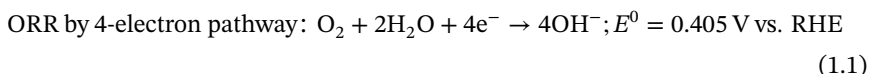


Figure 1.3 Working principle of (a) pristine Zn-air batteries, (b) two-electrode, and (c) three-electrode rechargeable Zn-air batteries. Source: Lee et al. [45]/Reproduced with permission of John Wiley & Sons.

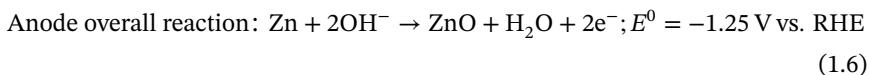
calculated to 0.405 V vs. reversible hydrogen electrode (RHE) based on the redox pair O_2/O^{2-} [50].

Cathode reaction:

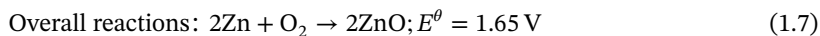


During discharge process, the zinc metal first loses two electrons to form the Zn^{2+} , which is further combined with OH^- to form the soluble $Zn(OH)_4^{2-}$ (see Eqs. (1.3) and (1.4)). Finally, the formed $Zn(OH)_4^{2-}$ is decomposed into H_2O , OH^- , and insoluble ZnO at supersaturated $Zn(OH)_4^{2-}$ concentrations on anode surface (see Eq. (1.5)) [51]. When a load is connected to the battery, the generated electron on anode side transfers to air cathode through external circuit, and the 4-electron ORR on air cathode further occurs. From the anode overall reaction equation (see Eq. (1.6)), the consumption of OH^- and production of H_2O occur for the electrolyte [51]. Combined with above cathode reaction, the OH^- would spontaneously transfer from cathode to anode surface during discharge process to overcome the concentration polarization. Therefore, alkaline electrolyte with high ionic conductivity is chosen as the commercial electrolyte. In addition, the distance between cathode and anode is also an important parameter for discharge performance [52]. Based on the redox pair Zn/Zn^{2+} , the equilibrium potential of anode reaction is calculated to be -1.25 V vs. RHE [53].

Anode reaction:



Combining the anode and cathode reaction, the theoretical open-circuit voltage of Zn–air battery should be 1.65 V, where $E^0 = E^0_{\text{cathode}} - E^0_{\text{anode}}$. Generally, the actual open-circuit voltage of Zn–air battery is just 1.4–1.5 V owing to the existence of polarization potential under working conditions [54]. The overall discharge reactions of Zn–air battery is actually the reaction between zinc and oxygen to generate the ZnO (see Eq. (1.7)). In other words, there is just consumption of zinc metal during discharge process. If sufficient zinc metal is provided and the durability of ORR catalysts is excellent, the pristine Zn–air battery could continuously discharge for a long term [55]. Therefore, the mechanical replacement of zinc metal after deep-discharge process with fresh zinc metal could achieve the rechargeability of pristine Zn–air battery. This mechanically rechargeable Zn–air battery has been proved to be a desirable choice for application in electric vehicles [56, 57], and this is discussed in detail later.



For electrochemically rechargeable Zn–air battery, there are two configurations involving two-electrode (Figure 1.3b) and three-electrode (Figure 1.3c) [58]. Generally, two-electrode rechargeable Zn–air battery shows similar configuration to the pristine Zn–air battery. For two-electrode rechargeable Zn–air battery, its catalytic active layer in air cathode mainly consists of bifunctional ORR/OER electrocatalyst, while that of just ORR electrocatalyst for pristine Zn–air battery [59]. Therefore, screening the bifunctional electrocatalysts with both high-efficient ORR and OER activities is necessary for these rechargeable batteries. To assess the bifunctional activity, the potential gap (ΔE) between half-wave potential of ORR and overpotential of OER at 10 mA cm^{-2} is proposed, which is an important parameter for evaluating the bifunctional electrocatalysts [60–62]. In general, lower ΔE value implies higher bifunctional activity [49]. The anodic and cathodic reactions during discharge process are same as that of pristine Zn–air battery mentioned above. During charge process, the OH^- is converted to O_2 on air cathode and the surface ZnO is subsequently reduced to zinc metal on anode. Similarly, the OH^- produced on anode side transfers to cathode side to make up its consumption of OH^- . The generated O_2 is finally transmitted outside through the gas diffusion layer to accomplish the whole discharge/charge process [63]. Unfortunately, the uneven deposition of soluble $\text{Zn}(\text{OH})_4^{2-}$ on zinc anode is observed during charge process, thus inevitably causing the growth of zinc dendrite [64]. In addition to the stability of bifunctional electrocatalyst, zinc dendrite is also a key factor for the cycle life of Zn–air battery [65]. The discussion about the adverse impact of zinc dendrite in Section 1.5.3 is continued.

In general, it is hard to design a bifunctional electrocatalyst with both excellent ORR and OER activities owing to the completely reversible reaction process [55]. The high-efficient ORR or OER catalysts have been developed intensely in the past few years [66, 67]. Although the bifunctional catalysts could be achieved by physical mixing of ORR catalysts with OER catalysts, the random stack of two type of catalysts would affect the actual discharge/charge performance [55]. In addition, numerous ORR catalysts, such as carbon materials, may be decomposed during OER process with high-charging potential [63, 68]. For example, the Zn–air battery with heteroatom-doped carbon materials exhibited excellent discharge performance, including high-power density and high-discharge voltage; however, the power density and discharge voltage are rapidly decreased after first charge process owing to the decomposition of low-crystalline carbon catalyst under high-charge voltage [69]. In addition, the electrolyte turned from clear to yellowish-brown, revealing the electrochemical degradation of carbon-based catalysts [63, 68]. The three-electrode Zn–air battery consisting of air-discharge electrode, air-charge electrode, and zinc anode is proposed to overcome above issues for two-electrode Zn–air battery (Figure 1.3c) [15]. When assembling the three-electrode Zn–air battery, the ORR catalysts and OER catalysts are dropped on gas-diffusion layer to obtain two air electrodes, respectively [70]. Then the two air electrodes form a sandwich structure with zinc metal, while two separators are also inserted between two cathodes and one anode. The air electrode with ORR catalysts and OER catalysts are served as the cathode during discharge and charge process, respectively, and the principle of

discharge and charge for three-electrode Zn–air battery is same as the two-electrode Zn–air battery. During the charge process, the air electrode with ORR catalysts is inoperative, thus avoiding the adverse impact on subsequent discharge performance after charging operation [44]. Although three-electrode Zn–air battery is superior to the two-electrode battery in cycling performance, the tedious configuration would increase the overall weight and volume of Zn–air batteries, which is unfavorable for the gravimetric and volumetric energy density.

As revealed by the overall reactions of Zn–air battery, zinc anode is the main active species to achieve the electric energy output. In many commercial zinc-based dry cells, the gelled mixture of zinc pellets in range of 50–200 mesh is served as the anode [71]. The size of zinc pellets has been proved to be a key factor for Zn–air battery in view of inter-particle contact and reaction activity [72]. In principle, high surface area of zinc pellets means better electrochemical activity. However, the small zinc pellets with high surface energy are easily corroded by the alkaline electrolyte, thus causing serious self-discharge [72]. Dai et al. revealed that the zinc particles with grain size of above 200 mesh show the highest rate capacity owing to the low internal electrical resistance in anode pack [17]. Meanwhile, Metallic Power Inc. reported an electrolytic technique to prepare small dense zinc pellets with size of 0.5–0.6 mm for mechanically rechargeable Zn–air battery, while the spent zinc pellets could be electrochemically reduced to fresh one for further discharge cycles on-site [73]. The zinc pellets are dispersed on alkaline electrolyte to form the liquid electric fuel, which is pumped into the anode side of cell. Moreover, the morphology of zinc metal is also an important influence factor for the discharge energy density of Zn–air batteries [74–76]. For example, the Zn–air battery with fibrous form of zinc shows higher discharge capacity and voltage than commercial zinc particles [77]. For the usage of these zinc powder in Zn–air batteries, the zinc particles or zinc fibers are processed into the rod and plate to form zinc anode for pristine or rechargeable cylindrical and prismatic Zn–air batteries, as shown in Figure 1.4 [77]. This zinc anode always exhibits abundant pore structure for the permeation of alkaline electrolyte, thus achieving fast-discharge reaction. For rechargeable Zn–air battery, after converting the zinc metal to ZnO under desirable depth of discharge

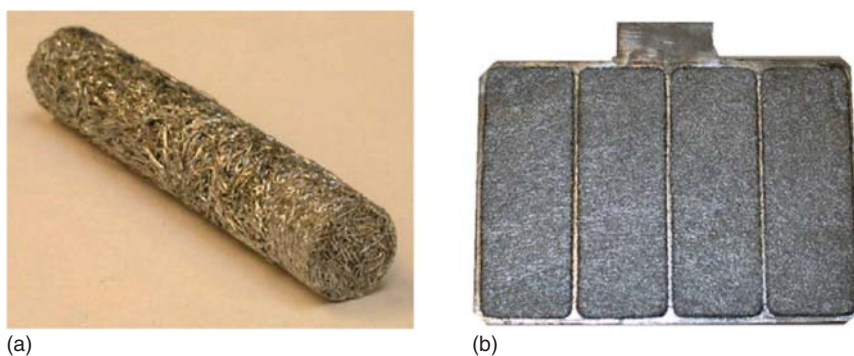


Figure 1.4 The digital photographs of (a) rod form and (b) plate form zinc anode for zinc–air batteries. Source: Zhang [77]/Reproduced with permission of Elsevier.

(DOD), electrochemically reducing the ZnO to fresh zinc electrode is an efficient strategy to realize the rechargeability of Zn–air battery [78].

Aqueous electrolytes, especially alkaline electrolytes, have been widely applied in commercial Zn–air batteries [79]. The alkaline electrolytes show high conductivity, high catalytic activity for both air cathode and zinc anode, and excellent low-temperature activity than neutral electrolyte. The alkaline concentration is an important parameter for Zn–air battery to determine the ionic conductivity [80]. When the alkaline concentration is relatively low, the poor reaction activity and high ion-transfer impedance of electrolyte would be observed, while high-alkaline concentration would also block the ion-transport rate owing to high viscosity of electrolyte [81]. Therefore, there exists optimal alkaline concentration to achieve the highest ionic conductivity. More importantly, KOH electrolyte shows higher ionic conductivity, lower viscosity, and higher oxygen-diffusion coefficients than NaOH and LiOH electrolytes, which have been widely applied in Zn-based batteries [82]. As shown in Figure 1.5a, the 30 wt% KOH electrolyte (about 7 M) shows the highest conductivity of 0.64 S cm^{-1} at room temperature, and the conductivity increases with the temperature [56, 83]. Fortunately, the 30 wt% KOH electrolyte also achieves fairly high conductivity of 0.22 S cm^{-1} when the temperature decreases to -15°C , revealing that the Zn–air battery with alkaline electrolyte could operate in a wide temperature range. In addition to aqueous electrolytes, polymer electrolytes, which

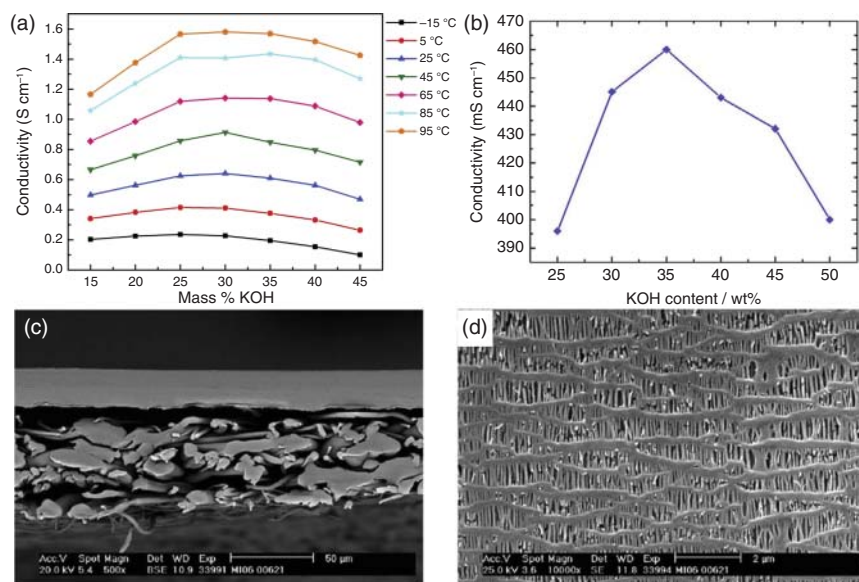


Figure 1.5 (a) The conductivity of alkaline electrolyte under different KOH concentrations and temperatures, Source: See and White [83]/Reproduced with permission of Elsevier., (b) the conductivity of gel polymer electrolyte under different KOH concentrations. Source: Zhang et al. [84]/Reproduced with permission of Elsevier., and the (c) cross section and (d) top-view images of nonwoven separator for Zn–air battery. Source: Kritzer and Cook [85]/Reproduced with permission of IOP Publishing.

are formed by conducting salts and polymers, are designed to eliminate the air cathode flooding for aqueous batteries. In general, the conducting salts is mainly KOH and polymers consists of polyvinyl alcohol (PVA) [86], poly(acrylic acid) (PAA) [87], poly(ethylene glycol) (PEG) [88], polyacrylamide (PAM) [89], and polyacrylate [87]. The ionic conductivity mechanism of polymer is the ionic motion in the chain segment, therefore, constructing the amorphous phase in the polymer above the glass transition temperature (T_g) is beneficial for the ionic conductivity of polymer electrolyte [90]. In addition, PAA-based polymer electrolyte with 35 wt% KOH exhibits high conductivity of 0.46 S cm^{-1} at room temperature (Figure 1.5b) [84], which is even comparable to the aqueous electrolytes. As reported, the polymer electrolyte is a desirable choice for flexible Zn–air batteries owing to its superior flexibility and mechanical strength [79].

The separator, as an electrochemically inactive component in Zn–air battery, is applied to physically isolate the cathode and anode. In general, separator is a critical component for Zn–air battery, which should satisfy the criteria of low ionic and high electrical resistance to allow fast ion transfer between cathode and anode [91, 92]. Moreover, separator should have low-contact angle with aqueous electrolytes, high chemical stability toward the corrosion and oxidation of electrolytes, and high mechanical strength to resist the zinc dendrite attack [13, 92]. Only the separator meeting above requirements can effectively improve the performance of Zn–air battery, including high security, high-discharge capacity, and long-term durability. Nonwoven polymers, such as polypropylene (PP), polyethylene (PE), polyamide (PA), and PVA, have been widely applied as the separator for traditional aqueous alkaline Zn–air batteries [85]. These nonwoven separators always show high porosity of 75%, which could achieve high electrolyte retention and low ionic resistance [85]. At present, laminated nonwoven separators, such as Celgard 5550, with a trilayer structure (PP/PE/PP) as shown in Figure 1.5c,d, while PP and PE layers are respectively applied to maintain the integrity of separator and shut down the battery when thermal runaway, is typically used in commercial coin type of Zn–air batteries [85]. When battery is short circuited, the PE layer would melt under high temperature and further closes the pores to shut down the battery, thus realizing safe operation. Given that the separator is an inactive component for Zn–air battery, its thickness and weight should be exactly controlled when applied for commercial application.

Owing to the low solubility of oxygen in the aqueous electrolyte, the active oxygen mainly diffuses in through the gas-diffusion layer during discharge process, and transfers out through the gas-diffusion layer during charge process to achieve the oxygen exchange between catalyst surface and external atmosphere, not the liquid electrolyte [93]. The charge and discharge reactions mainly occur at the three-phase interface between electrolyte, electrode, and oxygen (Figure 1.6) [39, 43, 94]. During discharge process, the oxygen is first diffused to catalysts surface to form the O_2^* and further reduced to OH^* at the catalysts surface, and then, the OH^- is desorbed from the catalysts surface and diffused to electrolyte, while the electrons required for surface reaction from O_2^* to OH^* are provided by external conductive skeleton [94, 95]. Therefore, porous carbon black is needed in catalytic active layer

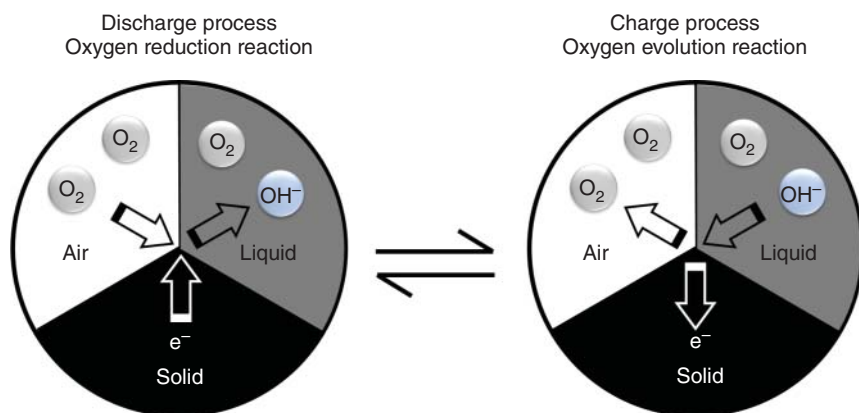
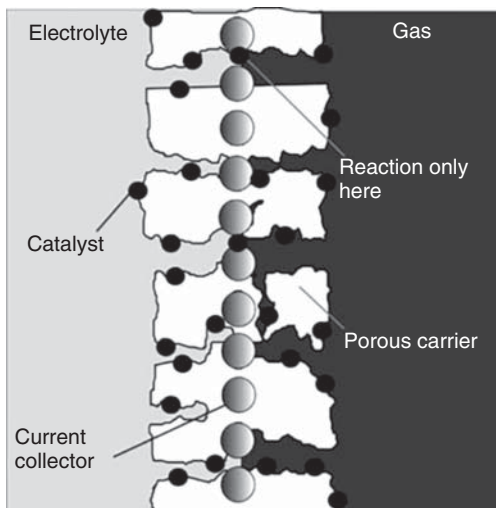


Figure 1.6 Schematic illustration of three-phase interface reaction for discharge and charge process.

considering the electron transfer and oxygen diffusion. The charge process is opposite to the discharge process, in detail, the OH^- absorbed from electrolyte is converted to oxygen through the OER catalysts and the oxygen is diffused outside through the gas-diffusion layer, while the generated electron is transferred from catalysts surface to zinc anode through external conductive skeleton [96]. The distribution of electrolyte and oxygen inside the air cathode determines the transmission distance of reactant and internal resistance, and the area of three-phase interfaces directly determines the active catalytic areas for ORR and OER inside the air cathode. Therefore, the formation of abundant efficient three-phase interfaces inside the air electrode is beneficial for the overall utilization rate of the electrocatalyst, thus improving the charge/discharge performance. If the three-phase interface is damaged, the discharge performance would seriously be decreased owing to trace oxygen in electrolyte is not sufficient to maintain the reaction [40, 97]; in addition, the generated oxygen could not be diffused outside and adhered to on catalysts surface, which isolates the catalysts from direct contact with the electrolyte, thus decreasing the charge performance owing to the catalytic active site is covered [96]. Therefore, maintaining the stability of the three-phase interface during charge/discharge process has also a direct impact on the cycle stability of Zn–air battery.

Based on above discussion about three-phase interface, the structural design of high-efficient air electrode, which accounts for the transfer of oxygen gas, has a great influence on its charge/discharge performance. In general, the hydrophobic air electrode is applied for Zn–air battery to build three-phase transfer interface, as shown in Figure 1.7 [20]. There is a hydrophobic region in air electrode for gas diffusion, and this porous region could serve as the carrier to store the oxygen gas [98]. Owing to the hydrophobic features of the porous carrier, electrolyte cannot fill the unpressurized gas chamber. At present, porous carbon, including carbon fiber, carbon-woven cloth, nonwoven fabric, activated carbon, and acetylene black, and polytetrafluoroethylene (PTFE) are first mixed, and further rolled and hot-pressed into a gas-diffusion layer, in which porous carbon provides gas chamber and PTFE

Figure 1.7 Schematic diagram of air electrode. Source: Harting et al. [20]/Reproduced with permission of Walter de Gruyter GmbH.



guarantees the hydrophobicity [99, 100]. The gas resistance is proposed to evaluate the performance of gas-diffusion layer owing to the oxygen being the critical active species during discharge process [101]. Generally, low gas resistance means fast oxygen-transfer rate during discharge process, which could ensure high-discharge rate performance. In addition, the mechanical strength of gas-diffusion layer should be considered owing to the repeated charge and discharge operations that could damage its inner structure [102]. For the catalytic active layer, the catalysts are hydrophilic to form the electrolyte film on catalysts surface, while the film serves as the depletion layer to achieve the OH^- exchange between catalysts and electrolytes [103]. The core of catalytic active layer is the bifunctional electrocatalyst, which could determine the overall performance of Zn–air battery [16]. In addition, the current collector, such as metal foam and mesh, is introduced between gas-diffusion layer and catalytic active layer to ensure the efficient transfer rate of electrons to or from external circuit [104]. A zigzag structure between the contact faces of gas-diffusion layer and catalytic active layer is formed to achieve continuous transmission network. At the contact interface, the high-efficient air electrode must meet the condition that there is a large amount of gas within the chamber, and building an interconnected channel between the thin electrolyte film and gas chamber is necessary [104]. Therefore, the air electrode must be a thin porous electrode with different hydrophobicity on both sides, in which the hydrophobic side should possess sufficient air holes for the transfer of oxygen to catalysts surface and the hydrophilic side should build enough electrolyte permeation channel for the species exchange between electrolyte and catalysts.

The emergence of miniaturized electronic devices, such as hearing aids, urges researchers to develop long-lasting energy supply. Zn–air batteries with high-energy density, low cost, and stable output voltage show obvious advantages in these electronic devices [105]. Up to now, the coin type of pristine Zn–air battery has been successfully applied as the power supply for hearing aids. As shown in Figure 1.8, coin type of batteries generally consists of the following components—air cathode,

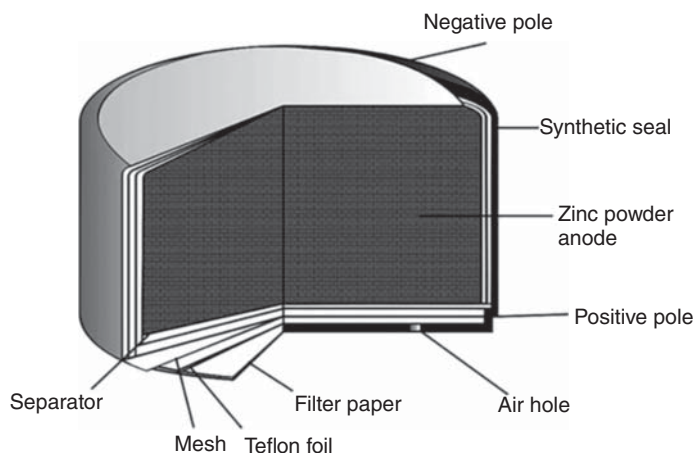


Figure 1.8 Schematic diagram of the coin type of Zn–air battery. Source: Harting et al. [20]/Reproduced with permission of Walter de Gruyter GmbH.

zinc anode, separator, electrolyte, insulating ring, and packaging shell. As previously described, air cathode is composed of catalytic active layer, gas-diffusion layer, and current collector [20]. In this coin type of battery, the waterproof layer (Teflon foil) serves as the gas-diffusion layer to prevent the electrolyte leakage. It is noteworthy that the volume and mass of air cathode could be ignored, while the zinc anode is the main component for this commercial battery owing to the zinc metal being the only consumptive active species, which also determines the discharge capacity of Zn–air battery. In addition, zinc powder rather than zinc foil is used as the anode owing to its large contact area with electrolyte. This type of Zn–air battery just discharges for a long time under low-current density, thus it can only be used in miniaturized electronic devices. To prevent battery aging, the air hole is always sealed by tape, and the tape needs to be removed before use. If the sealing tape is removed, the coin type of battery must be discharged until complete consumption of zinc anode owing to the adverse influence of CO_2 in atmosphere, and the detailed information is discussed in section of 1.5.2.

For electrochemically rechargeable Zn–air battery, the commercialization process has been impeded by the large charging overpotential owing to the inferior catalytic activities for OER electrocatalysts, and its energy efficiency is generally lower than 65% as laboratory reported [31]. In general, low-energy efficiency means low-energy utilization, while the side reactions, such as water electrolysis, would be occurred. Therefore, the high-efficient bifunctional electrocatalysts need further exploration to promote the commercial electrochemically rechargeable Zn–air battery. As previously mentioned, the mechanically rechargeable Zn–air battery is a desirable choice for electric vehicles [106]. Electric Fuel Ltd. has developed a mechanically rechargeable Zn–air battery for electric vehicles from the targets of price, safety, performance, and quick refueling [107]. As shown in Figure 1.9a, a static replaceable anode cassette containing the slurry of zinc particles is covered by isomorphic separator envelope and further embedded into a current collection

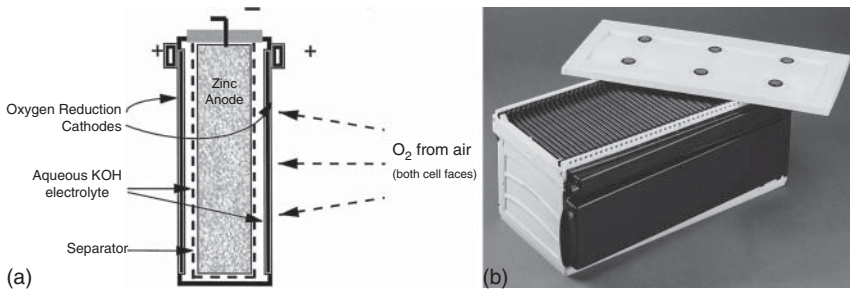


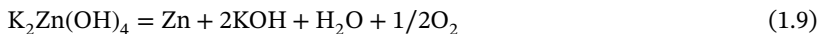
Figure 1.9 (a) Schematic diagram of mechanically rechargeable Zn–air battery by Electric Fuel Ltd. Source: Goldstein et al. [107]/Reproduced with permission of Elsevier. (b) the battery module containing 47 individual Zn–air batteries. Source: Goldstein et al. [107]/Reproduced with permission of Elsevier.

frame which is modified with high-efficient oxygen-reduction catalysts flanked on two sides, while the gap between catalyst layer and anode cassette was filled with potassium hydroxide solution [107]. As discussed above, zinc metal serves as the only electric fuel during discharge process, while exchanging spent electric fuel after deep discharge with fresh electric fuel could achieve charging performance of Zn–air battery, and this process is called refuel or mechanically recharge. Within the anode cassettes, zinc particle with high surface area and high-tapped density is tightly compacted onto a current collector to achieve a robust anode. The high surface area of zinc particles is beneficial for the discharge performance, however, the small zinc particles with high activity would react with electrolyte, thus inevitably causing negative self-discharge. Therefore, the corrosion rate of zinc particles should be controlled by the electrolyte additive to lower the self-discharge rates [108]. The time of refueling process for this type of Zn–air battery is comparable to that of gasoline refueling for fuel vehicle, revealing it could be applied in the field of electric vehicles.

After deep discharge at 80% DOD, the zinc metal is completely oxidized to ZnO based on the overall discharge reaction. The spent electric fuel could be electrochemically recharged outside the Zn–air battery to achieve the regeneration of zinc anode in zinc electrowinning cells. As reported, suitable morphology and size of zinc particles could be obtained at the electrowinning current density of 100–200 mA cm⁻² within the voltage of 2.2 V, which could achieve high-energy efficiency for cycled Zn–air batteries [107]. To achieve regeneration of zinc anode, the residual solid ZnO, which is collected from the dead Zn–air battery after deep discharge, is first dissolved in a KOH solution to obtain the soluble K₂Zn(OH)₄ as following Eq. (1.8):



Then, the soluble K₂Zn(OH)₄ is electrolyzed in a zinc electrowinning cell to regenerate the zinc particles as following Eq. (1.9):



After electrowinning process, the zinc particles are collected and recompact into the current collector frame. Finally, the recycled anode cassettes are inserted into a

fresh separator envelope, and further embedded into the previous current collection frame with original catalysts flanked on two sides, thus realizing a mechanically charging cycle. To achieve the application in electric vehicle, 47 individual Zn–air batteries are constructed into a basic module, as shown in Figure 1.9b [107], while a simple air-cooled thermal management system is inserted in the module casing.

The static ZnO particles would block the contact channels between the remainder of fresh zinc particles and electrolyte, thus preventing further discharge reaction. Therefore, the spent zinc particles and other side products should be cleaned up in time to allow direct contact between fresh zinc metal and electrolyte. Recently, flowing bed is proposed to achieve the regeneration of zinc particles [109], however, the parallel bipolar plate cannot well solve the problem of blocking spent zinc particles. Therefore, a tapered-end structural Zn–air battery with unparallel bipolar plate is designed, while air cathode covered with separator is tightly compacted onto the vertical plate, and its front and side sectional views are exhibited in Figure 1.10 [110]. During discharge process, alkaline electrolyte containing zinc pellets continuously falls to the hopper through a narrow opening (<3 mm), and further flows from the top of cell to bottom. The catalytic active region is on the top of cell, while it mainly serves as the reservoir for the zinc pellets. When reacted with oxygen, the zinc pellets continuously decreased in size and meanwhile flowed downwards by their own gravity. After deep discharge, the mixture of solid ZnO, side product, unreacted zinc metal, and electrolyte flowed out from bottom of the cell. Significantly, replacing the spent electrolyte mixture with the fresh electric fuel containing electrolyte and zinc pellets could be accomplished by pump to achieve refueling.

The spent electrolyte is pumped to a storage tank for further regeneration by applying a combined electrochemical and mechanical treatment. In detail, slight mossy zinc metal is electrochemically deposited on a porous nickel substrate under a constant current density and flow speed. Most regenerated zinc particles (about 80%) could not be adhered to the porous substrate owing to their own weight [110]. These regenerated zinc particles are further collected at the bottom of the electrolysis. Subsequently, the collected zinc particle is mechanically pressed into a cylindrical pellet, which is mixed with alkaline electrolyte and readded into

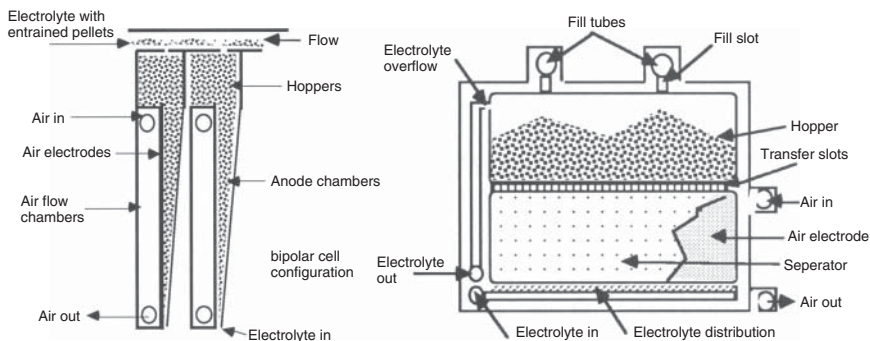


Figure 1.10 Schematic diagram of Zn–air battery with a tapered-end structure. Source: Cooper et al. [110]/Reproduced with permission of SAE International.