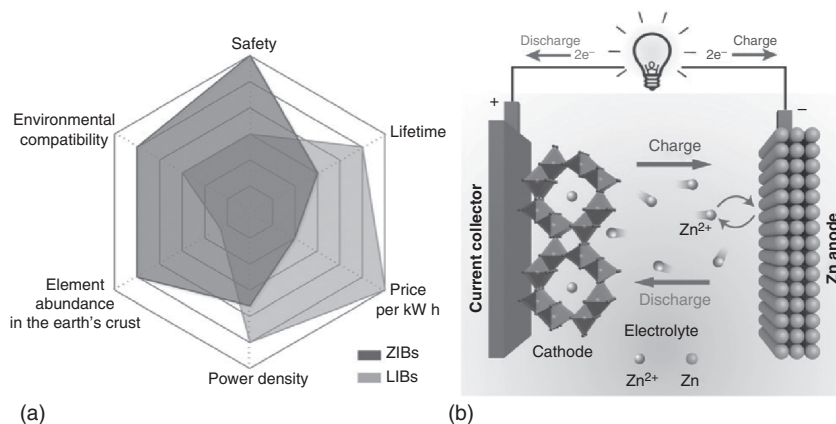


## 1

## Introduction for Aqueous Zinc-Ion Batteries

### 1.1 History of Aqueous Zinc-Ion Batteries

Aqueous zinc-based batteries can be traced as far back as the voltaic battery, which first used zinc metal as the negative electrode. Subsequently, alkaline zinc-based batteries such as alkaline Zn–MnO<sub>2</sub>, Zn–Ni, Zn–C, Zn–Ag, and Zn–Air were developed successively [1]. Among them, alkaline Zn–MnO<sub>2</sub> batteries have dominated the primary battery market since their commercialization. Earlier attempts to develop rechargeable Zn-based batteries were plagued by fast capacity fading and poor coulombic efficiency, mainly due to the uncontrollable growth of Zn dendrites and the formation of insulating, irreversible by-products (e.g. ZnO) in alkaline electrolytes (e.g. concentrated KOH solution). However, these batteries mentioned above cannot be called aqueous Zn-ion batteries (AZIBs) because the reaction mechanism of AZIBs is the plating/stripping of Zn<sup>2+</sup> at the anode and the intercalation/deintercalation at the cathode in an aqueous solution. The AZIBs differ from the traditional alkaline Zn battery that is based on dissolution/precipitation reactions at the Zn anode ( $\text{Zn} + 4\text{OH}^- \leftrightarrow \text{Zn}(\text{OH})_4^{2-} + 2\text{e}^- \leftrightarrow \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} + 2\text{e}^-$ ) and distinguished from other batteries with a Zn anode but no intercalation of Zn ions in cathode reactions [2]. The early investigations of AZIBs date back to 1986, when Yamamoto and Shoji first replaced the alkaline electrolyte with a zinc sulfate electrolyte and tested the electrochemical behavior of rechargeable Zn|ZnSO<sub>4</sub>|MnO<sub>2</sub> batteries [3]. But its research boom was overshadowed by lithium-ion batteries due to lower energy density and poor cycle stability (Figure 1.1a). Studies on rechargeable AZIBs slowed down until 2012, when Kang and coworkers revisited zinc-ion battery chemistries with mildly acidic aqueous electrolytes [5]. As shown in Figure 1.1b, a rechargeable AZIB generally consists of a metallic Zn anode, a Zn<sup>2+</sup> storage cathode, and a Zn<sup>2+</sup>-salt electrolyte, operating via the reversible Zn<sup>2+</sup> intercalation/deintercalation (cathode) and Zn plating/stripping (anode) upon discharging/charging [4]. AZIBs have been intensively investigated as potential energy storage devices on account of their low cost, environmental benignity, and intrinsically safe merits. With the exploitation of high-performance cathode materials, electrolyte systems, and in-depth mechanism investigation, the electrochemical performances of ZIBs have been greatly enhanced. For example, much work has been done on the modification of zinc anodes, and it mainly focuses on issues such



**Figure 1.1** (a) Multi-angle comparison of zinc-ion and lithium-ion batteries. (b) Schematic illustration of the working principle of rechargeable zinc-ion batteries. Source: Zhang et al. [4]/Royal Society of Chemistry.

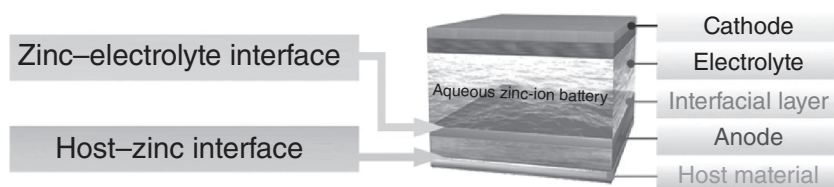
as the inhibition of zinc dendrite growth and the occurrence of side reactions. In terms of electrolytes, in addition to  $\text{ZnSO}_4$ , electrolytes with  $\text{ZnCl}_2$ ,  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ , and  $\text{Zn}(\text{CH}_3\text{COO})_2$  as the main salts have been developed, while much work has been done in optimizing electrolytes, such as solvents, additives, and concentrations. Cathode materials have also been expanded from the earliest manganese-based materials to vanadium-based materials, Prussian blue and analogs, and conductive polymer materials. The main purpose of these modification strategies is to improve the cycle stability and energy density of AZIBs, which has greatly promoted the development of AZIBs.

## 1.2 Main Challenges for Aqueous Zinc-Ion Batteries

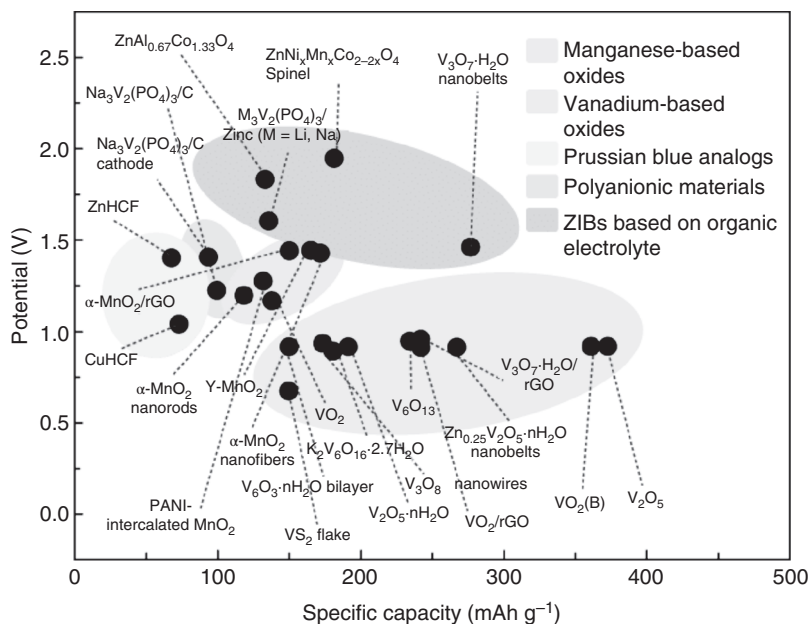
Recently, AZIBs have attracted much attention due to their advantages of large theoretical capacity, low cost, and environmental friendliness. The research on each component of AZIBs has increased significantly over the past decade [6]. However, the AZIBs have not been widely industrialized because their overall performance is not comparable to that of commercial lithium-ion and lead-acid batteries. The main reason is that the key materials involved in AZIBs, such as electrolytes, separators, anode materials, cathode materials, and current collector materials, cannot meet the cycle life and energy density requirements of practical batteries (Figure 1.2). Herein, the challenges and perspectives for the further development of AZIBs are reviewed, which are instructive for the research toward next-generation batteries for household appliances, electric vehicles, and large-scale energy storage systems.

### 1.2.1 Cathode

It is important to develop promising cathode materials with excellent electrochemical performance since the overall performance of AZIBs is determined by the



**Figure 1.2** The configuration of AZIBs. Source: Zhang et al. [6]/John Wiley & Sons.

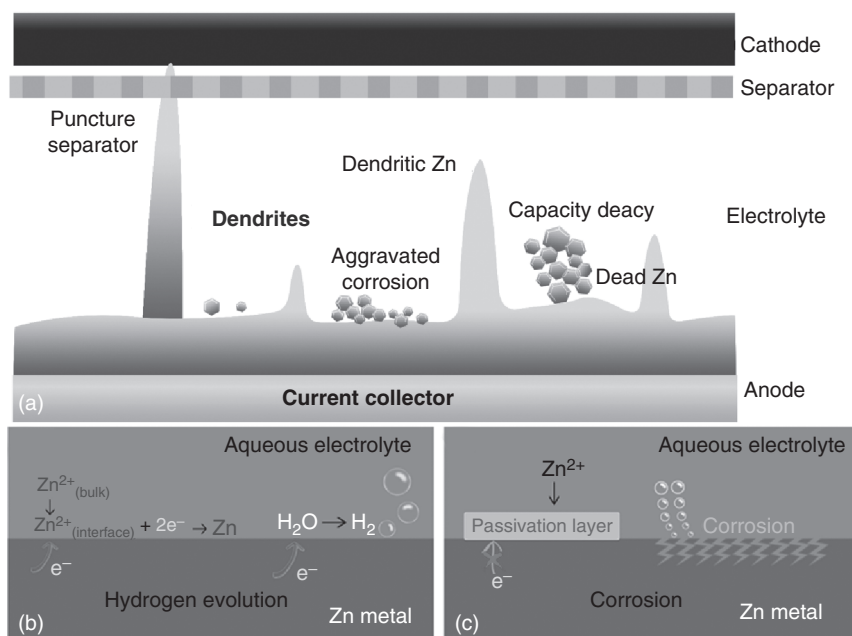


**Figure 1.3** Operating voltage vs. specific capacity of various cathode materials currently used for AZIBs. Source: Xu and Wang [7]/Springer Nature/Licensed under CC BY 4.0.

cathode materials. Manganese-based, vanadium-based, and polyanionic materials are the common cathodes applied in AZIB systems (Figure 1.3) [7]. However, these cathode materials exhibit low specific capacity and low-voltage platforms, and their wide application is limited due to the rapid capacity fading caused by cation dissolution, irreversible phase transition, and by-product generation. In addition, the current cathode materials usually cannot meet the requirement of some advanced features for practical AZIBs such as low-temperature performance, low cost, and nonbiotoxicity. Therefore, researchers have attempted to explore the large-scale preparation of commercial cathode materials with outstanding performance to solve the above problems using inexpensive modification strategies.

### 1.2.2 Anode

Zinc foil is the most common anode material used in AZIBs. However, the electrochemical performances of zinc foils are not sufficient for large-scale applications

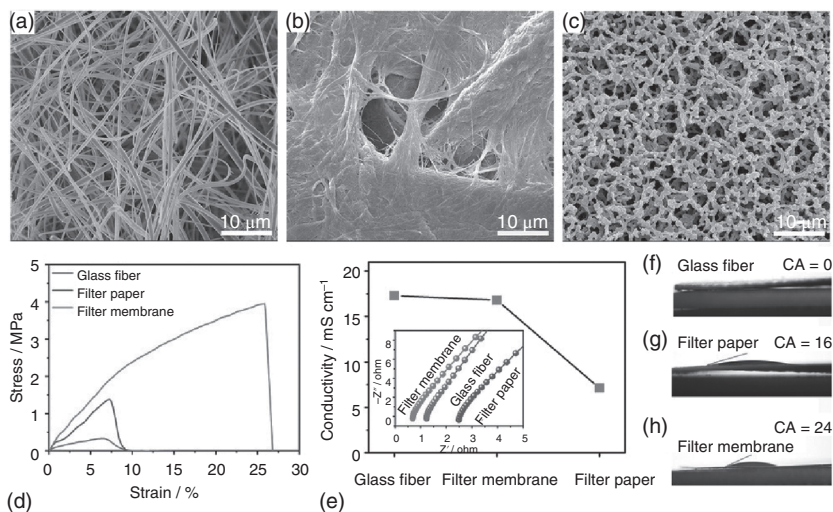


**Figure 1.4** The dendrites (a), hydrogen evolution (b), and corrosion (c) of zinc metal anodes. Source: Xie et al. [8]/John Wiley & Sons/Licensed under CC BY 4.0.

due to the severe dendrite growth, corrosion, and hydrogen evolution reaction (HER) (Figure 1.4) [8]. The corrosion and HER on the anode surface in AZIBs generally occur in neutral or mildly acid electrolytes, which give rise to decreased capacity, increased impedance, and electrolyte leakage. The by-products generated from corrosion and HER will hinder the uniformity of ion transmission to induce more dendrites and further exacerbate the corrosion and HER due to the increased specific area of zinc anodes. The zinc foil anode suffers from electrode perforation and joint detachment during the deep charge and discharge processes, which also limits its wide application.

### 1.2.3 Separator

Glass fibers are widely used as the separator in AZIBs due to their low price, large liquid absorption, and low ion transmission impedance. Glass fibers can significantly improve the ion transport of the cathode material for AZIBs. However, zinc dendrites are easily generated on the zinc anode due to their low strength, irregular pore size distribution, and high zinc affinity (Figure 1.5) [9]. Therefore, the glass fiber is not completely suitable for AZIBs. A large number of studies suggested that Nafion films, nonwoven fabrics, cellulose films, and coating-modified glass fibers can be considered substitutes for glass fibers. However, as there are still some problems with liquid absorption, pore size distribution, strength, and the high cost of these separators, they are not suitable for wide application in AZIBs. In addition, most of

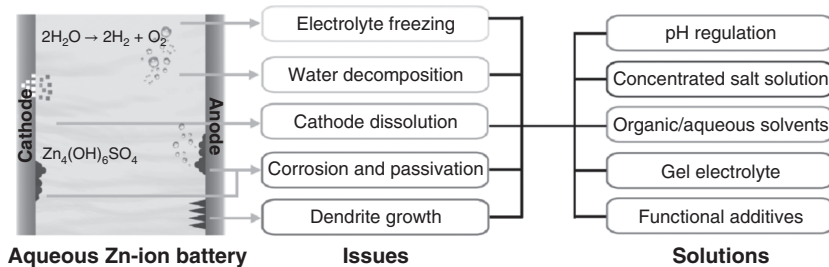


**Figure 1.5** Relevant physical properties of the separators. SEM images of (a) glass fiber, (b) filter paper, and (c) filter membrane, (d) stress–strain curves, (e) ionic conductivities (the insert panel is corresponding to EIS curves), (f–h) and water contact angles. Source: Qin et al. [9]/John Wiley & Sons.

the performance evaluations of separators are only carried out in button batteries, and these evaluation results may not be used as test indicators for practical batteries (such as soft pack and box batteries), caused by separators that should possess the strength, wettability, and pore size distribution of the separator, environmental protection, and low cost.

#### 1.2.4 Electrolyte

The design of electrolytes is an important method to improve the performance of aqueous batteries (Figure 1.6) [10]. Therefore, deepening the basic understanding of the solvation structure and interfacial chemistry of electrolytes is of great significance to promote the practical application of ZIBs. Compared with the traditional organic electrolyte battery, the aqueous battery possesses the following advantages, such as avoiding fire disasters caused by battery short circuits and lower cost. Meanwhile, aqueous batteries can be assembled and disassembled in the environment because their components are insensitive to air, which is beneficial to battery manufacturing and recycling. In addition, aqueous electrolytes display higher rate capability and power density than organic electrolytes because the ionic conductivity of aqueous electrolytes (about  $0.1 \text{ S cm}^{-1}$ ) is much higher than that of organic electrolytes ( $1\text{--}10 \text{ mS cm}^{-1}$ ). However, the presence of water makes the electrochemical window of the common electrolyte only 1.23 V (the organic system has more than 3 V), and the freezing point is high (about  $-10^\circ\text{C}$ ), which results in lower energy density, obvious battery self-discharge, and poor low-temperature performance for AZIBs. Therefore, it is of great significance to design electrolytes



**Figure 1.6** The challenges and solutions for AZIB electrolytes. Source: Zhang et al. [10]/ John Wiley & Sons/Licensed under CC BY 4.0.

with low cost, high safety, wide electrochemical window, low freezing point, fast ion transport speed, and good compatibility with electrode materials.

### 1.2.5 Full Battery Assembly and Practical Application

AZIBs have gradually shown a trend of widespread application due to their low cost, environmental friendliness, intrinsic safety, and relatively high energy and power densities. However, since the energy density, cycle stability, self-discharge behavior, and operating temperature range of AZIBs have not been uniformly optimized, assembling such batteries into commercial batteries still faces serious challenges [11]. The actual energy density of the battery is significantly lower than the theoretical energy density because the coin cells assembled in the laboratory rarely consider the capacity matching of cathode/anode electrodes and the loading of cathode active materials. The problems of low coulombic efficiency, poor cycle stability, and poor low-temperature performance in full cells have not been completely solved. Meanwhile, the widespread application of AZIBs requires a structural design that incorporates the essential characteristics of the battery. For example, aqueous batteries are not sensitive to air, so they can be designed as open batteries, which can replenish electrolytes in time to avoid battery failure caused by gas production and irreversible consumption of electrolytes. The choice of current collectors also has a critical impact on the performance and energy density of AZIBs. The carbon-based and self-supporting electrodes seem to be only suitable for small-scale AZIB devices due to their high price and difficulty in large-scale fabrication and battery assembly. Ni-based and Ti-based metal current collectors are not suitable for wide application due to their high price. Therefore, it is of great significance to develop current collectors (such as special copper foil and foamed stainless steel) that are cheap, show excellent performance, and are suitable for assembling large batteries.

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