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Fundamentals, Materials, and Design

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Contents

Preface

Rapid economic development has increased the demand for traditional fossil energy sources (e.g. coal, oil, and natural gas), which has induced a series of serious global problems such as acid rain pollution, greenhouse effect, and land desertification. Fossil energy is formed by the natural deposition of ancient organisms over billions of years and cannot be recovered in the short term. To escape from the dilemma of energy depletion, sustainable and environmentally friendly renewable energy sources (e.g. solar, wind, and tidal) have attracted widespread attention in the past two decades. However, there is a critical scientific problem that needs to be solved in practical applications; that is, renewable energy is susceptible to weather and seasonal influences, and its power generation process is discontinuous and uncontrollable. Therefore, an effective energy storage system is needed as a medium device to coordinate the power input and output in the grid, thus improving the tolerance of the grid to renewable energy generation.

In recent years, electrochemical energy storage technology has developed rapidly and is evolving from a miniaturized application for portable electronic devices to an integrated application for large-scale energy storage systems and smart grids. Electrochemical energy storage is less affected by terrain and can store or release electrical energy directly through reversible chemical reactions, which is a very promising energy storage technology with the advantages of high energy density and high energy conversion efficiency. Lithium-ion batteries using organic electrolytes are one of the most widely used electrochemical energy storage systems. However, lithium-ion batteries have met big challenges in large-scale energy storage systems that are more focused on low cost, high stability, and high safety due to the limited lithium resources and the use of unsafe organic solvents. Compared with organic electrolytes, aqueous electrolytes are inexpensive and safe, and their ionic conductivity is greater, enabling the operation of batteries with large loads and high power. Aqueous batteries can completely meet the requirements of large-scale energy storage systems. In recent years, aqueous zinc-ion batteries have developed rapidly due to their high theoretical capacity ($820\ \mathrm{mAh\,g^{-1}}$), low electrochemical potential ($-0.76\ \mathrm{V}$ vs. standard hydrogen electrodes), and high natural abundance of zinc resources, which are currently a research hotspot for the application of large-scale energy storage systems.

This book systematically illustrates the basic theory and frontier development of electrochemical theory, key materials, and battery devices for aqueous zinc-ion batteries. Chapter 1 provides a general review of the history of zinc-ion batteries and also provides an overview of the main challenges of cathodes, anodes, separators, electrolytes, and battery devices. Chapter 2 discusses the theoretical fundamentals of aqueous zinc-ion batteries, including the electrochemical reaction mechanism of cathodes and the deposition/dissolution mechanism of zinc anodes. Chapter 3 lists all the promising cathode materials and summarizes their current problems and corresponding optimization strategies. Chapter 4 is a general overview of the development and modification strategy of the zinc anode in aqueous zinc-ion batteries. Chapter 5 introduces the research progress, key problems, and solutions in the design of aqueous electrolyte for aqueous zinc-ion batteries. Chapter 6 illustrates the properties and characteristic parameters of the separator and the strategy to construct high-performance separators for aqueous zinc-ion batteries. Chapter 7 presents the progress in the structure and packaging of full aqueous zinc-ion batteries from the perspective of practical application. Chapter 8 provides advanced characterization tools and theoretical research methods for aqueous zinc-ion batteries. Chapter 9 summarizes the current challenges of aqueous zinc-ion batteries and proposes some future directions for their further development. Thanks to Prof. Yougen Tang, Dr. Qi Zhang, and Dr. Yixin Li, we wrote this book together. Also, many thanks to my group members, Dr. Chao Hu, Zefang Yang, Chunlin Xie, Qi Wang, Yihu Li, Wenbin Li, Huimin Ji, Tingqing Wu, Hao Wang, and Zhiwen Cai, for their participation in the compilation of each chapter. All the above colleagues have been engaged in scientific research in aqueous zinc-ion batteries and have made hard efforts to ensure the quality of this book.

This book aims to provide a comprehensive overview of aqueous zinc-ion batteries in terms of basic theory, frontier science, current status, and development trends of practical applications, which can be used as a reference for science and technology workers engaged in scientific research and technology development in the field of electrochemical energy storage materials and devices. There are inevitably omissions in this book since aqueous zinc-ion batteries are still developing rapidly and new knowledge and research advances are emerging. We hope that experts will offer valuable comments on the additions and revisions.

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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_2, Zn–Ni, Zn–C, Zn–Ag, and Zn–Air were developed successively [1]. Among them, alkaline Zn–MnO_2 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^{2+} 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 ($Zn + 4OH^- \leftrightarrow Zn(OH)_4{}^{-2} + 2e^- \leftrightarrow ZnO + 2OH^- + H_2O + 2e^-$) 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 $Zn|ZnSO_4|MnO_2$ 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^{2+} storage cathode, and a Zn^{2+}-salt electrolyte, operating via the reversible Zn^{2+} 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

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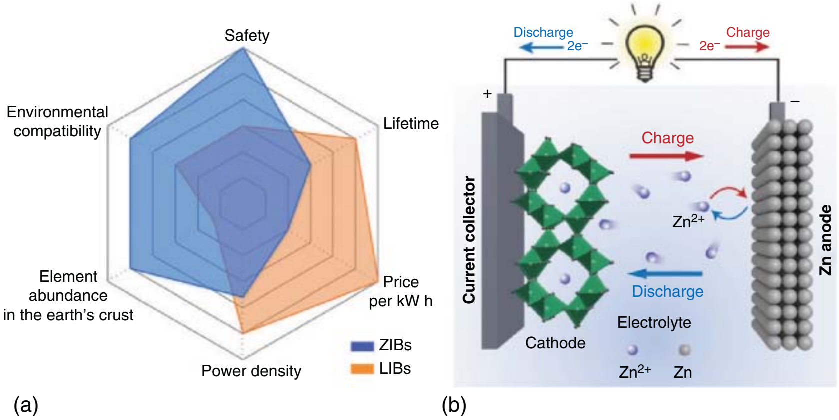

Figure 1.1 (a) Multi-angle comparison of zinc-ion and lithium-ion batteries. (b) Schematic illustration of the working principle of rechargeable zinc-ion batteries. Source: Zhang et al. [4]/Royal Society of Chemistry.

as the inhibition of zinc dendrite growth and the occurrence of side reactions. In terms of electrolytes, in addition to $ZnSO_4$, electrolytes with $ZnCl_2$, $Zn(CF_3SO_3)_2$, and $Zn(CH_3COO)_2$ 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

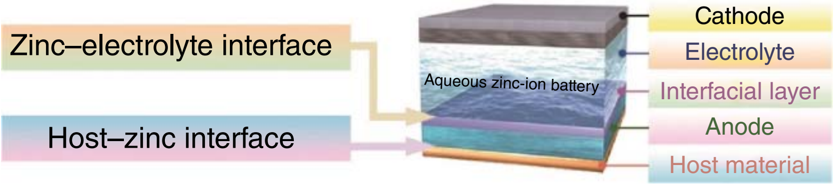

Figure 1.2 The configuration of AZIBs. Source: Zhang et al. [6]/John Wiley & Sons.

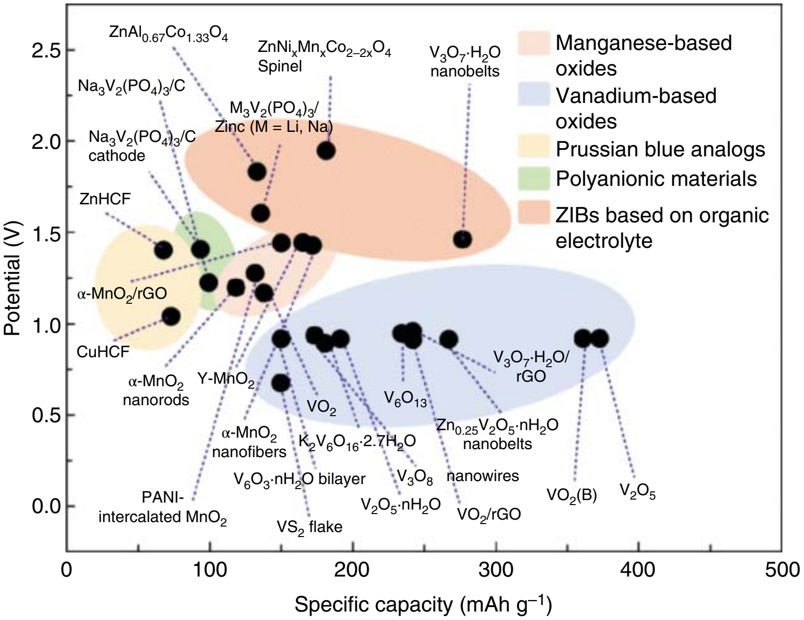

Figure 1.3 Operating voltage vs. specific capacity of various cathode materials currently used for AZIBs. Source: Xu and Wang [7]/Springer Nature/Licensed under CC BY 4.0.

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

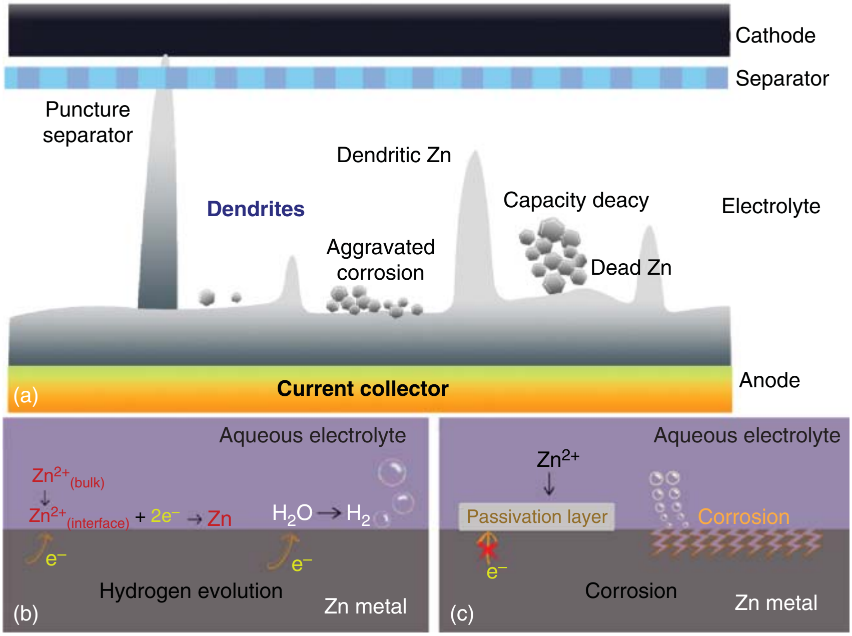

Figure 1.4 The dendrites (a), hydrogen evolution (b), and corrosion (c) of zinc metal anodes. Source: Xie et al. [8]/John Wiley & Sons/Licensed under CC BY 4.0.

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

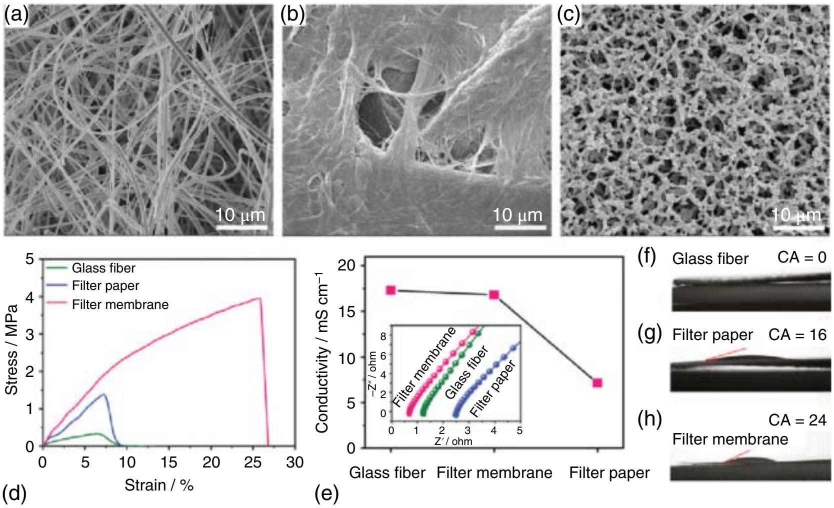

Figure 1.5 Relevant physical properties of the separators. SEM images of (a) glass fiber, (b) filter paper, and (c) filter membrane, (d) stress–strain curves, (e) ionic conductivities (the insert panel is corresponding to EIS curves), (f–h) and water contact angles. Source: Qin et al. [9]/John Wiley & 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 $0.1\,\mathrm{S\,cm^{-1}}$) is much higher than that of organic electrolytes ($1–10\,\mathrm{mS\,cm^{-1}}$). 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 °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

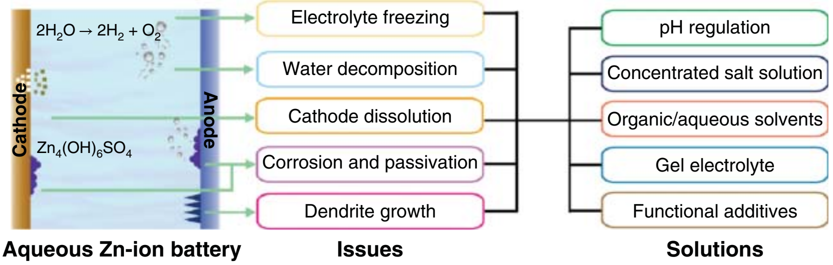

Figure 1.6 The challenges and solutions for AZIB electrolytes. Source: Zhang et al. [10]/ John Wiley & Sons/Licensed under CC BY 4.0.

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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2

Theoretical Fundamentals of Aqueous Zinc-Ion Batteries

2.1 Electrochemical Reaction Mechanism of Cathodes

The energy-storage mechanism of cathode materials remains complicated and controversial in aqueous zinc-ion batteries (AZIBs). To date, the recognized energy-storage mechanisms of zinc batteries are broadly classified into three categories: (i) Zn^{2+}-insertion/extraction mechanism, (ii) co-insertion mechanism, and (iii) chemical conversion reaction mechanism [1]. A brief account of these mechanisms is provided in this section, and readers may refer to other literature for an in-depth mechanistic understanding of charge storage in AZIB.

2.1.1 Zn^{2+}-Insertion/Extraction Mechanism

Among the three mechanisms, the insertion/extraction of Zn^{2+} in the host materials is the most essential mechanism in the AZIBs system, similar to that of the traditional rechargeable lithium-ion batteries (LIBs). In the discharge process, the Zn^{2+} in the electrolyte is inserted into the cathode, and the Zn in the anode loses electrons to produce Zn^{2+}, which maintains the charge balance of the electrolyte. When charging, Zn^{2+} is extracted from the cathode to the electrolyte. It migrates to the anode and collects electrons at the interface, finally diffusing inward in the form of atoms [2]. The cathode materials of the tunnel/layer structure store Zn^{2+} through this mechanism. Reversible Zn^{2+}-insertion/extraction was first proposed to explain the energy-storage mechanisms of ZIBs. Kang and coworkers first reported mild aqueous rechargeable ZIBs [3].

Meanwhile, they proposed that Zn^{2+} can be reversibly inserted into or extracted from α-MnO_2 cathode during discharge/charge processes (Figure 2.1a). And the Zn anode gets dissolving/depositing at the same time. Subsequently, it was proven that the Zn^{2+}-insertion/extraction mechanism would occur in β-MnO_2, γ-MnO_2, and λ-MnO_2 [4]. In addition to reversible Zn^{2+}-insertion/extraction, a reversible phase transition from the tunneled structure (α-MnO_2) to layered polymorphs was observed. This transition is initiated by the dissolution of manganese from α-MnO_2 during the discharge process to form layered Zn-birnessite (Figure 2.1b) [5].

Vanadium-based compounds are mainly layered/tunnel frameworks with a large void space favoring Zn^{2+}-insertion. In a milestone study, a reversible Zn^{2+}-insertion

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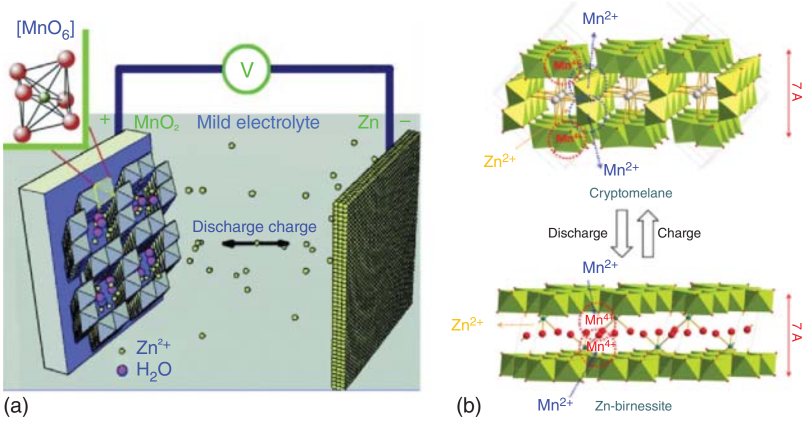

Figure 2.1 (a) Schematics of the chemistry of the zinc ion battery. Source: Xu et al. [3]/John Wiley & Sons. (b) Schematic illustrating the mechanism of zinc intercalation into α-MnO_2. Source: Lee et al. [4]/Springer Nature.

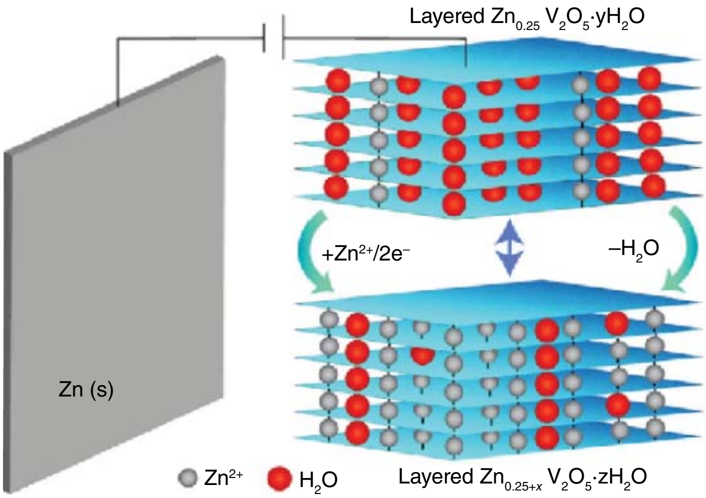

Figure 2.2 Rechargeable $Zn_{0.25}V_2O_5 \cdot nH_2O$ system. Source: Kundu et al. [6]/Springer Nature.

mechanism of $Zn_{0.25}V_2O_5 \cdot nH_2O$ was revealed by combining operando X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses [6]. This corresponds to the following equations (Figure 2.2):

Anode:

$$1.1Zn \leftrightarrow 1.1Zn^{2+} + 2.2e^{-} \tag{2.1}$$

Cathode:

$$1.1Zn^{2+} + 2.2e^{-} + Zn_{0.25}V_2O_5 \cdot nH_2O \leftrightarrow Zn_{1.35}V_2O_5 \cdot nH_2O \tag{2.2}$$

Overall:

$$1.1\text{Zn} + \text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O} \leftrightarrow \text{Zn}_{1.35}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O} \tag{2.3}$$

Alshareef and coworkers reported a simple microwave to synthesize layered metal pyrovanadate nanowires ($Zn_3V_2O_7(OH)_2{\cdot}2H_2O$) with a porous crystal framework [7]. The electrochemical energy storage mechanism can be described by the following equation:

$$\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O} + 1.9\text{Zn}^{2+}3.8\text{e}^- \leftrightarrow \text{Zn}_{4.9}\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O} \tag{2.4}$$

Similar Zn^{2+}-(de)intercalation storage processes have been demonstrated in most of the reported vanadium-based cathodes, such as VO_2, $V_5O_{12}{\cdot}6H_2O$, $Na_2V_6O_{16}{\cdot}3H_2O$, $Li_xV_2O_5{\cdot}nH_2O$, and $Ca_{0.25}V_2O_5{\cdot}nH_2O$ [8]. Vanadium-based compounds evolve from V^{5+} to V^{4+} or even V^{3+} through the evolution of the V oxidation state, adapt to the intercalation of Zn^{2+}, and maintain a stable crystal framework. Irreversible phase transitions were also observed in examples of NaV_3O_8-type compounds like $Na_5V_{12}O_{32}$, which experienced structural destruction, phase transition, and thus capacity degradation [9].

2.1.2 Co-Insertion/Extraction Mechanism

The Zn^{2+} insertion/extraction mechanism is the most ideal and acceptable, so the Zn/MnO_2 battery was developed based on the migration of Zn^{2+} ions between the cathode and anode, which was very early reported in 2012. It was found that not only zinc ions but also other ions were involved in the co-insertion/extraction mechanism. Because of the sluggish Zn^{2+} and the strong electrostatic repulsion, other ions or molecules (including H^+, Li^+, and H_2O) in the electrolyte can also be embedded and released when the insertion and extraction of zinc ions are happening in cathode during the process of charge and discharge [10, 11].

2.1.2.1 H^+ and Zn^{2+} Insertion/Extraction Mechanism

For manganese-based cathode materials, Sun et al. [12] first proposed the co-insertion mechanism of H^+ and Zn^{2+} in $Zn/\varepsilon\text{-}MnO_2$ batteries, and the insertion of H^+ and Zn^{2+} corresponds to the sloped plateau from 1.8 to 1.35 V in region I and the flat plateau at 1.3 V in region II, respectively (Figure 2.1a). Similar mechanisms of the difference crystallographic (α, δ, and β) are observed in these experiments. The joint charge storage of H^+ and Zn^{2+} delivers high-rate performance and long cycle life in the $Zn\text{-}\delta\text{-}MnO_2$ batteries [13]. The first step in fast charge storage is non-diffusion-controlled Zn^{2+}-ion-storage mechanism in bulk $\delta\text{-}MnO_2$ without significant phase transition. In contrast, the following step reaction is proven to be the diffusion-controlled H^+ conversion reaction in $Zn(TFSI)_2$-based electrolyte (Figure 2.1b). In addition, as evidenced by Gao et al., H^+-insertion can boost the $\alpha\text{-}MnO_2$ electrode [14]. They find that the capacity fading during cycling process is mainly due to the decay of second discharge plateau, which is ascribed to Zn^{2+} insertion (Figure 2.3a). An increased amount of irreversible $ZnMn_2O_4$ is observed on the surface of $\alpha\text{-}MnO_2$, which is less reversible than that of H^+. $\beta\text{-}MnO_2$

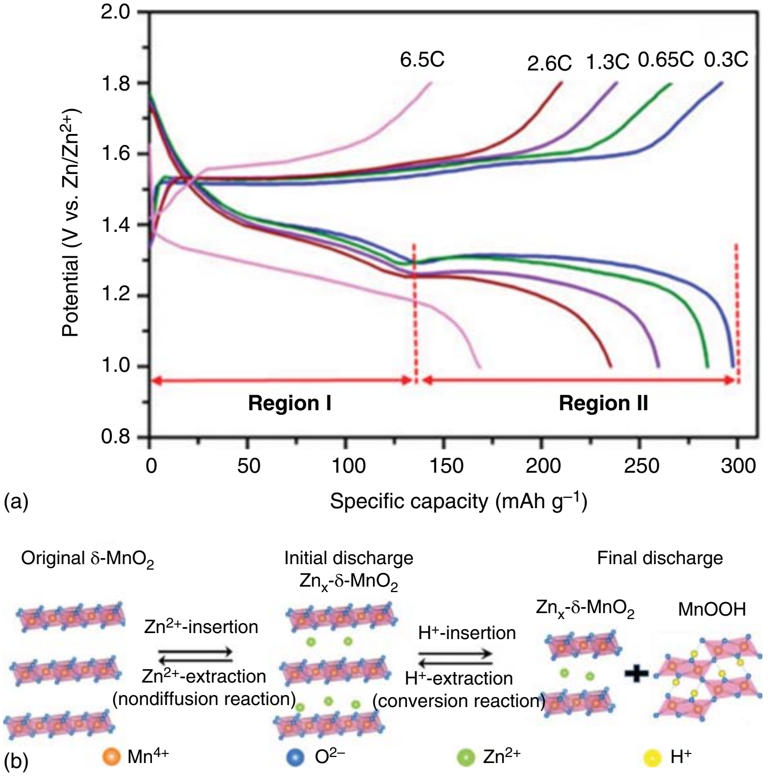

Figure 2.3 (a) Charge/discharge curves at different rates in the first cycle and two discharge regions. (b) Joint non-diffusion-controlled Zn^{2+}-intercalation and H^+-insertion/extraction in δ-MnO_2.

possessing oxygen defects also allows the insertion of H^+, and density functional theory (DFT) computation shows that the β-MnO_2 host structure is much easier for H^+ insertion rather than Zn^{2+} [15] (Figure 2.4).

For Zn/vanadium-based batteries, Wan et al. [16] reported that sodium vanadate hydrate experienced a simultaneous H^+ and Zn^{2+} insertion/extraction process as a cathode, which was mainly responsible for their excellent performance with a capacity of 380 mAh g^{-1} at 4 A g^{-1} (a capacity retention of 82% after 1000 cycles). Furthermore, as shown in Figure 2.1b, Wang and coworkers [17] verified the sequential insertion of H^+ and Zn^{2+} at 1.1–0.71 and 0.71–0.32 V plateaus in Zn/V_2C@CNT battery. Similar co-insertion mechanisms of H^+ and Zn^{2+} are also observed in other vanadium-based battery materials, such as $V_{10}O_{24}\cdot 12H_2O$ [18], $Zn_{0.3}V_2O_5\cdot 1.5H_2O$ [19], and (Ni)VO_2 [20].

2.1.2.2 Zn^{2+}/H_2O Co-Insertion/Extraction Mechanism

Zn^{2+}/H_2O co-insertion/extraction mechanisms usually exist in vanadium-based cathodes because the tunnel structure or layered structure of the cathode is

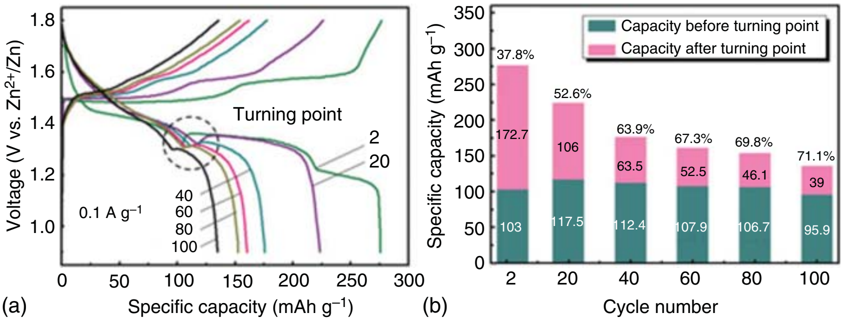

Figure 2.4 (a) Turning point in charge/discharge profiles. (b) Capacity statistics of two discharge plateaus after different cycles.

beneficial to the insertion/extraction of H_2O. Sometimes, the water in such layers of vanadium-based materials provides a pillar effect for stabilizing structures [21, 22].

Kundu et al. [6] reported that a single-crystal layered structure of $Zn_{0.25}V_2O_5 \cdot nH_2O$ nanobelt possesses two-electron redox containing intercalated divalent cations and water. Interlayer metal ions Zn^{2+} and/or structural water in this layered oxide act as pillars stabilizing the structure (Figure 2.5), providing a capacity retention of more than 80% after 1000 cycles. The water molecules expanding and contracting the layered galleries of $Zn_{0.25}V_2O_5$, allow Zn^{2+}-insertion/extraction in a highly reversible manner, and promise high-rate performance with a capacity of 220 mAh g^{-1} at a 15 C rate.

When used as cathode for AZIBs [23], porous V_2O_3@C material exhibits a capacity of 350 mAh g^{-1} at 100 mAh g^{-1} and capacity retention of 90% after 4000 cycles at 5 A g^{-1}. It is worth noting that the Raman spectra and ex situ XPS demonstrate the co-intercalation of Zn^{2+} and water, and the electrochemical reaction in the Zn//V_2O_3 can therefore be illustrated in Figure 2.6.

2.1.2.3 Li^+- and Zn^{2+}-Insertion/Extraction Mechanism

An aqueous Zn/V_2O_5 rechargeable battery with a Li^+/Zn^{2+} co-insertion mechanism was reported. By XRD, voltammetric, and Raman spectroscopy, it was elucidated that exclusive Li^+-insertion into V_2O_5 occurs up to mid-discharge. Still, the co-insertion of a few zinc ions is likely involved in the second part of the reduction. Besides, Zn^{2+} acts as pillar species, preventing important structural change and hindering the formation of the distorted δ-LiV_2O_5 phase [24].

Except for vanadium-based materials, Prussian blue analogs, for example, iron hexacyanoferrate (FeHCF), can also store and release Zn^{2+} and Li^+ [25]. It is found that Zn^{2+}- and Li^+-insertion/extraction cause crystalline distortion and the reduction of interlayer spacing, respectively (Figure 2.7).

2.1.3 Chemical Conversion of Cathodes

Compared with Zn^{2+} insertion/extraction and co-insertion/extraction mechanisms, the conversion reactions in the battery would tend to provide higher capacity due

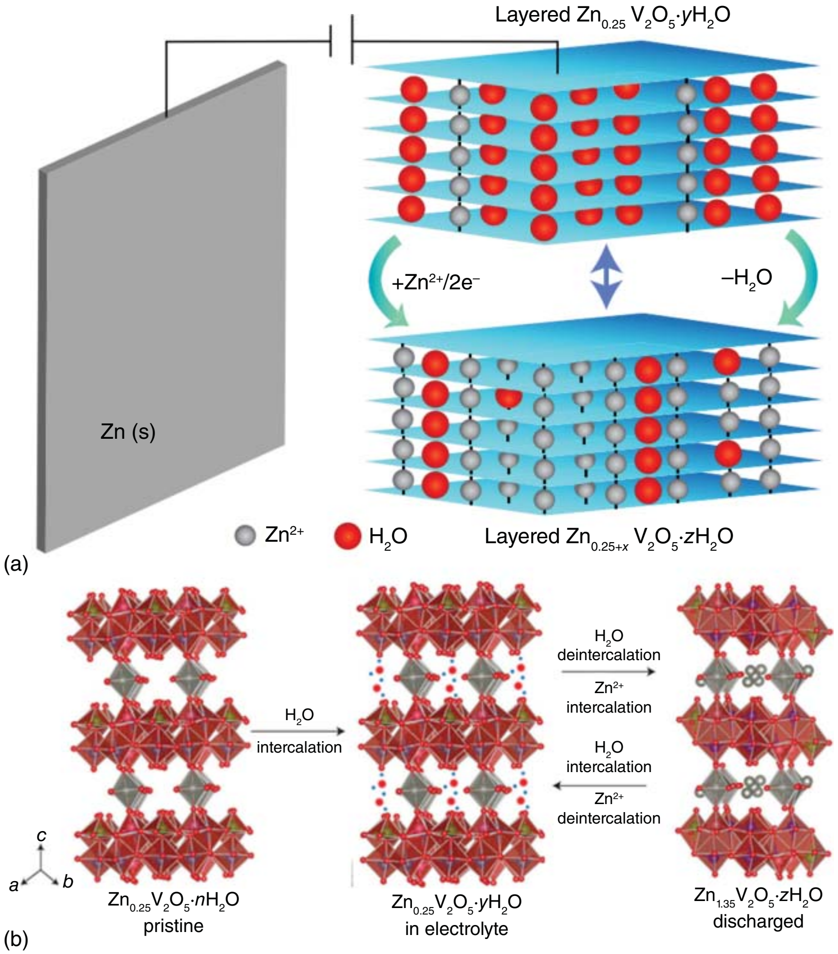

Figure 2.5 (a) Schematic of the Zn metal/$Zn_{0.25}V_2O_5$ battery and the expanded interlayer arrangement of $Zn_{0.25}V_2O_5$. (b) Scheme showing reversible water intercalation into $Zn_{0.25}V_2O_5 \cdot nH_2O$ and the intercalation or deintercalation of the water and Zn^{2+} during discharge/charge.

to direct charge transfer. Hence, it is very promising and effective to develop and design cathode materials with highly reversible conversion mechanisms [11]. Pan et al. [26]. first proved the role of the chemical conversion mechanism in charge storage of MnO_2-based cathodes. During the discharge process, α-MnO_2 reacted with H^+ to form MnOOH. To keep the charge constant in the system, the subsequent OH^- reacts with $ZnSO_4$ and H_2O to form lamellar $ZnSO_4[Zn(OH)_2]_3 \cdot xH_2O$ (ZHS). After charging, the aforementioned products are reduced to the original α-MnO_2, indicating that MnO_2 has reversible electrochemical behavior with MnOOH/ZHS, which can be expressed as follows:

Cathode:

$$H_2O \leftrightarrow H^+ + OH^- \tag{2.5}$$

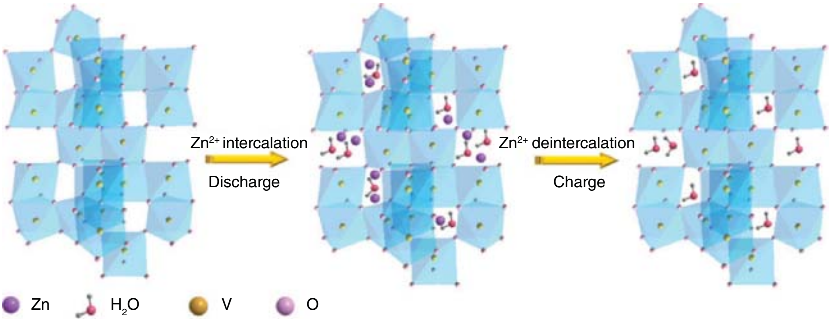

Figure 2.6 Schematic illustrations of Zn^{2+} and H_2O co-insertion mechanisms of V_2O_3 cathode.

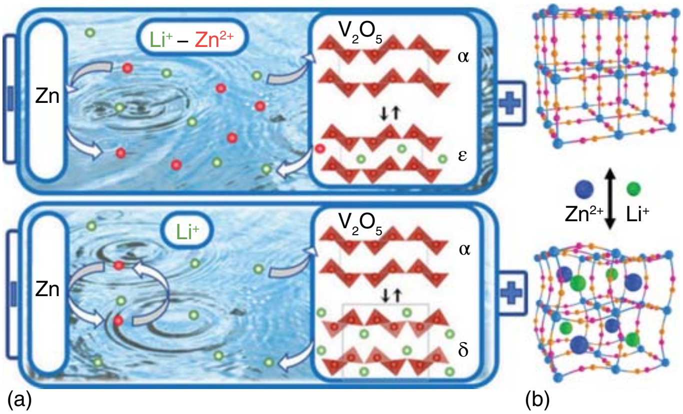

Figure 2.7 (a) Schematic diagram of Zn/V_2O_5 battery with Li^+/Zn^{2+} and Li^+ electrolyte. (b) Schematic illustration of the crystalline structure evolution under the insertion/extraction of Zn^{2+} and Li^+.

$$MnO_2 + H^+ + e^- \leftrightarrow MnOOH \tag{2.6}$$

$$\frac{1}{2}Zn^{2+} + OH^- + \frac{1}{6}ZnSO_4 + \frac{x}{6}H_2O \leftrightarrow \frac{1}{6}ZnSO_4[Zn(OH_2)]_3 \cdot xH_2O \tag{2.7}$$

Anode:

$$\frac{1}{2}Zn \leftrightarrow \frac{1}{2}Zn^{2+} + e^- \tag{2.8}$$

Overall:

$$MnO_2 + \frac{1}{2}Zn + \frac{x}{6}H_2O + \frac{1}{6}ZnSO_4 \leftrightarrow MnOOH + \frac{1}{6}ZnSO_4[Zn(OH_2)]_3 \cdot xH_2O \tag{2.9}$$

Similar to the co-insertion mechanism, the H^+ required for the chemical conversion reaction is generated by water decomposition, and the corresponding generated OH^- leads to the formation of ZHS [27]. There is another explanation for the formation of ZHS and the energy storage of MnO_2 in the charge/discharge process of the battery [28]. During the discharge process, the cathode manganese dioxide is electrochemically reduced to soluble Mn^{2+}, and OH^- is generated at the same time, increasing the pH of the electrolyte (Eq. (2.10)). Thus, Zn^{2+} reacts with the electrolyte to form ZHS and deposits on the electrode surface (Eq. (2.11)). Combining the aforementioned two equations, the total cathodic reaction equations can be obtained (Eq. (2.12)). The corresponding anodic reaction on the negative electrode during the discharge is a typical stripping reaction of zinc metal into the electrolyte (Eq. (2.13)). So, the total electrochemical reaction mechanism equation of α-MnO_2/Zn battery can be described as a reaction equation (Eq. (2.14)). Atomic absorption spectroscopy (AAS) and in situ pH measurement was used to analyze the concentration of manganese and zinc ions in the electrolyte at various stages of the charge–discharge process. Combined with in situ XRD analysis, the key role of pH change in the reaction mechanism of the battery system was further confirmed. Figure 2.8 shows the schematic diagram of the Zn/α-MnO_2 battery discharge process in the $ZnSO_4$ electrolyte.

$$MnO_2 + 2H_2O + 2e^- \rightarrow Mn^{2+} + 4OH^- \tag{2.10}$$

$$4Zn^{2+} + 6OH^- + SO_4^{2-} + 5H_2O \leftrightarrow Zn_4(OH)_6(SO_4) \cdot 5H_2O \downarrow \tag{2.11}$$

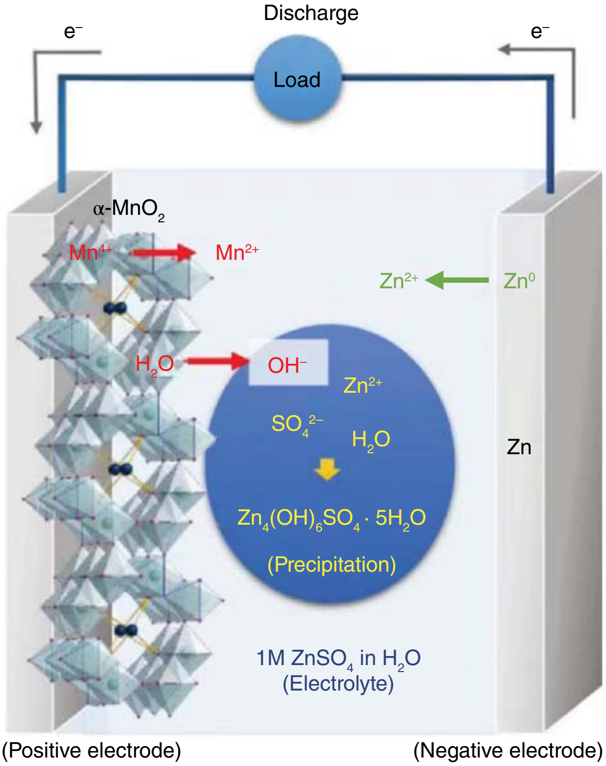

Figure 2.8 Schematic diagram of the conversion reaction energy-storage mechanism for the aqueous Zn/α-MnO_2 battery system. Source: Adapted from Lee et al. [28].