Microstructural Engineering of Cathode Materials for Advanced Zinc-Ion Aqueous Batteries

Mei Er Pam, Dong Yan, Juezhi Yu, Daliang Fang, Lu Guo, Xue Liang Li, Tian Chen Li, Xunyu Lu, Lay Kee Ang, Rose Amal, Zhaojun Han,* and Hui Ying Yang*

Zinc-ion batteries (ZIBs) have attracted intensive attention due to the low cost, high safety, and abundant resources. However, up to date, challenges still exist in searching for cathode materials with high working potential, excellent electrochemical activity, and good structural stability. To address these challenges, microstructure engineering has been widely investigated to modulate the physical properties of cathode materials, and thus boosts the electrochemical performances of ZIBs. Here, the recent research efforts on the microstructural engineering of various ZIB cathode materials are mainly focused upon, including composition and crystal structure selection, crystal defect engineering, interlayer engineering, and morphology design. The dependency of cathode performance on aqueous electrolyte for ZIB is further discussed. Finally, future perspectives and challenges on microstructure engineering of cathode materials for ZIBs are provided. It is aimed to provide a deep understanding of the microstructure engineering effect on Zn$^{2+}$ storage performance.

1. Introduction

The expanding global demand for potential renewable energy such as wind and solar energy has stimulated the development of efficient and low-cost electrical energy storage systems. In the 1990s, rechargeable lithium-ion batteries (LIBs) have been introduced, and gradually dominated the portable electronics and electric vehicle industries.[1–3] However, limited lithium resources, long-term potential safety issues, and high cost have greatly impeded the future development of LIBs.[1,4–6] Owing to the low cost and high safety, aqueous rechargeable batteries have become one of the promising next-generation energy storage systems for the rapidly growing markets of portable electronics and electric vehicles.[7–9] In addition to that, aqueous batteries with water-based electrolytes exhibit much higher ionic conductivity as compared to that of nonaqueous electrolytes, further enabling high rate capability.[10–12]

Among the various aqueous-based batteries, zinc-ion batteries (ZIBs) with mild neutral pH or slightly acidic electrolyte have attracted intensive attention owing to their low redox potential, high theoretical volumetric energy density, and good stability in water.[10,13,14] Besides, high capacity and energy density can be achieved in ZIBs due to the involvement of two electron transfer in the electrochemical reaction of divalent Zn$^{2+}$.[15] To date, intensive efforts have been done to explore suitable cathode materials for aqueous ZIBs.[9,10,14,16] However, the high polarization property of Zn$^{2+}$ induces a strong electrostatic interaction between Zn$^{2+}$ and cathode hosts, leading to difficulty in Zn$^{2+}$ diffusion and insertion/extraction.[9,10] As a consequence, the well-investigated insertion/extraction hosts for Li$^+$ and Na$^+$ generally demonstrate a low capacity and poor cycling performance in ZIBs. Moreover, the fundamental understanding of the reaction mechanisms for cathode materials in aqueous ZIBs remains controversial, imposing great challenges to motivate the full potential of aqueous ZIBs.[10,14,16]

To solve the abovementioned challenges, microstructure engineering of cathode materials has received a lot of interest in pursuing suitable cathode materials for ZIBs.[9,10,13,16] Microstructure engineering of materials, taking the material composition/crystal structure, crystal defect, interlayer spacing, and morphology into account, is an effective way to boost electrochemical
performances of cathode materials. More specifically, intensive studies have revealed that the crystallographic forms of cathode materials play an important role in governing the reaction mechanism in aqueous ZIBs \cite{1,10,13,14}. For example, various reaction mechanisms such as $\mathrm{Zn}^{2+}$ insertion/extraction, conversion reaction, and $\mathrm{Zn}^{2+}/\mathrm{H}^+$ coinsertion/extraction are observed for manganese dioxide (MnO$_2$) polymorphs with different tunneled, layered, or 3D structures \cite{9,10,14,16}. Furthermore, defect engineering has recently been reported as an effective approach to promote the $\mathrm{Zn}^{2+}$ insertion/extraction ability in the current existing cathode materials by fine-tuning of the active sites and $\mathrm{Zn}^{2+}$ interactions \cite{17–20}. Besides, interlayer engineering is another important approach for tuning interlayer properties in layered materials, which modulates their $\mathrm{Zn}^{2+}$ insertion/extraction abilities \cite{21,22}. Specifically, interlayer expansion can effectively promote diffusion kinetics by reducing the diffusion barrier, thereby converting intrinsically inactive insertion/extraction host into efficient $\mathrm{Zn}^{2+}$ storage materials. Moreover, morphology engineering has been devoted to functionalizing a cathode material in terms of superior rate capability, long cycling performance, and high specific capacity for ZIBs \cite{23–26}. The integration of active materials into functionalized microstructure morphology will surely benefit to unlock new material functionalities in typical cathode materials for governing their electrochemical performances, owing to the synergy effects from each design structure advantages.

While the above examples indicate that microstructure engineering plays an important role in modulating properties and improving performance, up to date, a comprehensive review on the microstructure engineering of cathode materials to improve their electrochemical performance in aqueous ZIBs is still lacking. In this review, we mainly focus on the recent significant advances in the microstructure engineering of cathode materials for advanced aqueous ZIBs. We will first briefly highlight the current issues of cathode materials for aqueous ZIBs, including the lack of suitable $\mathrm{Zn}^{2+}$ insertion/extraction materials and the involvement of complex and controversial energy storage mechanisms. The microstructure engineering approaches of cathode materials for achieving high electrochemical performance in aqueous ZIBs are then discussed, including composition and crystal structure selection, crystal defect engineering, interlayer engineering, and morphology design (Figure 1). The electrolytes and their effects on the zinc storage mechanism will also be discussed since they play a critical role in achieving high-performance aqueous ZIBs.

**Figure 1.** Schematic illustration of microstructure engineering for the cathode in ZIBs.
Finally, a brief conclusion and perspective on the microstructure engineering of cathode materials for further research efforts in aqueous ZIBs will be presented.

2. Current Issues of Cathode

2.1. The Lack of Suitable Zn$^{2+}$ Insertion/Extraction Cathode Materials

The lack of suitable Zn$^{2+}$ insertion/extraction cathode materials with high reversible capacity, excellent cycling performance, and adequate operating voltage is a critical issue in aqueous ZIBs. Although the ionic size of Zn$^{2+}$ (139 pm) is smaller than that of Li$^+$ (182 pm) and Na$^+$ (227 pm), the high polarization property of Zn$^{2+}$ has induced a strong interaction with water molecules, resulting in the formation of a large clathrate structure with a size of 5.5 Å in aqueous electrolyte.\(^{27}\) The formation of the large clathrate structure will further induce difficulty in Zn$^{2+}$ diffusion and storage, leading to the accumulation of Zn$^{2+}$ clathrate structure will further induce difficulty in Zn$^{2+}$ insertion/extraction.

In aqueous ZIBs, the reaction mechanisms of aqueous ZIBs are complicated and debatable. According to the alkali-metal-ion-based working mechanisms, the mechanisms in ZIBs with low capacity:\(^{27,28}\) Manganese oxide and vanadium oxide have been widely studied as potential Zn$^{2+}$ insertion/extraction hosts, but the cathode dissolution and the formation of irreversible discharged-by-product associated with the structural transformation and disproportional reaction during cycling, greatly degrade the cycling stability.\(^{7,29–31}\) The gradual precipitation/dissolution during cycling may further result in a low active material utilization efficiency, inhibition of the ion transportation, and high electrochemical impedance.\(^{32}\) Therefore, it is crucial to explore the novel design of new cathode materials with high electrochemical activity in ZIBs, excellent structural integrity, little side reaction, and high electrical conductivity simultaneously for boosting the electrochemical performances of ZIBs.

2.2. Complex and Controversial Reaction Mechanisms

While there has been much significant progress in the advancement of ZIB performance over the past few years, the reaction mechanisms of various cathodes in aqueous ZIBs are not fully understood and established. Different from the monovalent-alkali-metal-ion-based working mechanisms, the mechanisms in aqueous ZIBs are complicated and debatable. According to the literature, the reaction mechanisms of aqueous ZIBs are mainly categorized into Zn$^{2+}$ insertion/extraction mechanism, conversion reaction, and H$^+$ and Zn$^{2+}$ cointercalation/extraction.\(^{10,11,14}\)

In addition to the aforementioned energy storage mechanisms, surface redox reactions and phase transition are also observed in aqueous ZIBs and contribute additional capacity during cycling.\(^{34,35}\)

Owing to the small ionic radius of Zn$^{2+}$ (0.74 Å), various compounds with tunnelled and layered structures allow the insertion/extraction of Zn$^{2+}$. For example, Kang and co-workers proposed the electrochemical reaction mechanism in the aqueous Zn/$\alpha$-MnO$_2$ system was based on the reversible insertion/extraction of Zn$^{2+}$ as below:\(^{7}\)

\[
\text{Cathode : } \text{Zn}^{2+} + 2e^- + 2\alpha - \text{MnO}_2 \leftrightarrow \text{ZnMn}_2\text{O}_4
\]

\[
\text{Anode : } \text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e^-
\]

Their following works further demonstrated that the main charge/discharge mechanism for other tunnelled-structure MnO$_2$ such as $\beta$-, $\gamma$-, and $\delta$-type MnO$_2$ was based on the reversible Zn$^{2+}$ insertion/extraction.\(^{36}\) It is worth noting that some studies have revealed the phase transformation in $\alpha$-MnO$_2$ during insertion/extraction of Zn$^{2+}$.\(^{37,38}\) For example, Lee et al. reported a phase transition from tunnelled MnO$_2$ to layered Znbuserite, instead of spinel ZnMn$_3$O$_4$. Later, Kim and co-workers further proposed a complex multiphase transformation during the insertion of Zn$^{2+}$ in $\gamma$-MnO$_2$ for an aqueous Zn/$\gamma$-MnO$_2$ cell, involving spinel-type ZnMnO$_4$, tunnel-type Zn$_2$Mn$_3$O$_7$, and a layered-type Zn$_2$Mn$_6$O$_9$.\(^{39}\) It is worth noting that the Zn$^{2+}$ insertion behaviors in aqueous ZIBs are different among MnO$_2$ polymorphs such as $\gamma$-, $\alpha$-, and $\beta$-MnO$_2$.\(^{38–41}\) The different Zn$^{2+}$ insertion/extraction behaviors of Zn$^{2+}$ in MnO$_2$ polymorphs may have corresponded to the differences in their microstructure properties such as crystal structure arrangements that modulate the ion insertion/extraction thermodynamics and kinetics.\(^{42}\)

Other materials such as V$_2$O$_5$ and MoS$_2$ with layered structure have also been investigated to undergo the Zn$^{2+}$ insertion/extraction reaction mechanism.\(^{27,43}\) For example, Liang et al. reported a layered oxygen-incorporated MoS$_2$ ($\text{O-MoS}_2$) cathode, which enables high reversibility for hydrated Zn$^{2+}$ insertion/extraction into/from the layered host accompanied by the reversible 2H to 1T MoS$_2$ phase transition.\(^{27}\) It is worth to note that the reversible surface Mo$^{4+}$/Mo$^{6+}$ redox reaction also contributes to the capacity. Owing to their open framework, Prussian blue analogs (PBAs)\(^{44,45}\) and polyion-based\(^{46,47}\) materials have been reported to allow the insertion/extraction of Zn$^{2+}$. For example, Zhang et al. reported the energy storage mechanisms of the Zn/zinc hexacyanoferrate system involving the insertion/extraction of Zn$^{2+}$ at the zinc hexacyanoferrate cathode, and deposition/dissolution of zinc at the zinc anode.

It is worth to point out that a different reaction mechanism, which is based on the conversion reaction between $\alpha$-MnO$_2$ and MnOOH for a Zn/$\alpha$-MnO$_2$ system with preaddition of Mn$^{2+}$ in the electrolyte, has been reported.\(^{30}\) They revealed the formation of MnOOH at the fully discharged state, which is due to the reaction between MnO$_2$ and a proton from water. To achieve a neutral charge in the system, the OH$^-$ reacts with the aqueous electrolyte to form ZnSO$_4$[Zn(OH)$_2$]$_x$.

They have proposed the reaction mechanisms as below:

\[
\text{Cathode : } \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-
\]

\[
\alpha - \text{MnO}_2 + \text{H}^+ + e^- \leftrightarrow \text{MnOOH}
\]

\[
\frac{1}{2}\text{Zn}^{2+} + \text{OH}^- + \frac{1}{6}\text{ZnSO}_4 + \frac{x}{6}\text{H}_2\text{O} \leftrightarrow \frac{1}{6}\text{ZnSO}_4\text{[Zn(OH)$_2$]}_x \cdot x\text{H}_2\text{O}
\]

\[
\text{Anode : } \frac{1}{2}\text{Zn} \leftrightarrow \frac{1}{2}\text{Zn}^{2+} + e^-
\]
It is important to note that the recent works have further revealed that mechanism in the Zn/MnO2 system with preaddition of Mn2+ in the electrolyte is dynamic and the phase transformation at MnO2 cathode is irreversible during cycling. More importantly, they found out that Mn2+ in the electrolyte takes part in the reaction. In detail, Zn,MnO2, MnOOH, Mn3O4, and by-product ZnSO4·3Zn(OH)2·5H2O are formed in the first discharge process, followed by the formation of α-MnO2 and ZnMn3O4·3H2O in the first charge process. During cycling, ZnMnO4 and ZnMn2O4 are further formed on the surface of MnO2 and act as the hosts for Zn2+ insertion.

Moreover, another electrochemical mechanism of H+ and Zn2+ insertion/extraction has also been reported for the feasible cathode host materials with an open tunnel or layered framework. Owing to the observed significant difference in thermodynamics and kinetics between the two reaction regions by the capacitance voltage (CV) sweeps in various rates, galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) analysis, Sun et al. proposed a consequent H+ and Zn2+ insertion/extraction mechanism for Zn/α-MnO2 system. The consecutive presence of the MnOOH and ZnMn2O4 diffraction peaks in ex situ X-ray diffraction (XRD) analysis strongly confirms that the Zn/α-MnO2 system undergoes H+ insertion followed by Zn2+ insertion. Simultaneous insertion of H+ and Zn2+ mechanism has also been reported in ZIBs to achieve enhanced synergistic effect of their ion insertion thermodynamics and kinetics. For example, Wan et al. reported NaV3O8·1.5H2O nanosheets with a large interlayer spacing (0.708 nm) as an ideal cathode of ZIBs that enables the simultaneous insertion/extraction of H+ and Zn2+ into/from the V6O13 layer. They further revealed that the reaction mechanism was different from the consequent insertion/extraction mechanism of H+ and Zn2+ into/from MnO2, where the insertion/extraction of Zn2+ and H+ involved a two-step process. In detail, the H+ and Zn2+ simultaneously inserted into NaV3O8 to form H+NaZn3V3O9·1.5H2O in the first discharge process. This process was not a completely reversible reaction. After charging to 1.25 V, the H+ and partial Zn2+ were simultaneously extracted to form NaZn1.5V3O9·1.5H2O, which was a reversible process.

In additional to the aforementioned mechanisms, surface redox reactions have been proposed in a few cathode materials. For example, Wan et al. demonstrated surface redox reactions including the vanadium redox process and oxygen redox chemistry as the main energy storage mechanisms for Zn/layered VOPO4x system. Besides, Fang et al. have recently revealed that the energy storage mechanisms of vanadium nitride were based on not only the typical cationic (Zn2+/H+) insertion/extraction, but also the cationic redox reaction (V5+ ↔ V4+) and the release/uptake of anions on the vanadium nitride surface with reversible anionic redox reaction (N0 ↔ N−2). Zhi and co-workers have further revealed an unusual electrochemical behavior in MXene oxidation derivatives in an aqueous Zn/V2CTx MXene system. They found that the delamination of the V3CTx MXene and the gradual phase transition of the V3CTx MXene to V3O8 were the main contributions of the unusual capacity enhancement. It is worth mentioning that the phase transition behavior of electrodes generally results in performance degradation, showing not favorable for any energy storage system. Nonetheless, Zhi and co-workers have demonstrated that the outstanding cycle stability and excellent specific capacity can be achieved in an aqueous Zn/V2CTx MXene system.

Overall, different reaction mechanisms in ZIB cathodes have been proposed. These differences may be correlated to their various microstructure properties such as crystal structure arrangements, crystal defects, interlayer properties, and morphologies, which are highly related to the ion insertion thermodynamics, kinetics of H+/Zn2+, and surface redox reaction. Therefore, microstructure engineering of a cathode material plays an important role in determining and regulating the energy storage reaction mechanism in aqueous ZIBs.

3. Microstructure Engineering for High Performance Zinc Cathodes

Properties of functional materials are highly dependent on their microstructures. Therefore, to design a cathode material for aqueous ZIBs, it is important to understand the relationship between microstructures and their electrochemical performance. Microstructure engineering is an effective approach to functionalize a material by the configuration of its internal components, which can modulate the chemical, physical, and electrical properties of engineered materials, delivering potential candidates as cathode materials for ZIBs. Herein, we focus on the four aspects of microstructure engineering, including composition and crystal structure selection, crystal defect engineering, interlayer engineering, and morphology design to promote the electrochemical performance of cathode materials for ZIBs.

3.1. Composition and Crystal Structure Selection

The electrochemical properties of cathodes are usually governed by the intrinsic nature of the selected materials. The intrinsic nature properties such as composition and crystal structure arrangement exhibit significant effects on the chemical, electronic, electrochemical, and physical properties of a material. This will further result in significant variations in their electrochemical performance for the same type of cathode materials. Therefore, understanding the fundamental chemistry of cathode material composition and crystal structure is critical to provide a general guide for the construction of high-performance ZIB cathodes.

3.1.1. Manganese-Based Materials

To date, the development of suitable insertion/extraction host materials for aqueous ZIBs is still in its infancy. Intensive efforts are devoted to searching for crystal structures that can readily accommodate Zn2+ and exhibit a highly reversible insertion/extraction structure during the cycling process. Owing to the low cost, moderate operating voltage, and a high theoretical capacity of ≈308 mAh g−1, Mn-based materials are widely investigated as cathode materials for aqueous ZIBs. Up to date, MnO2 is the most commonly investigated cathode material for ZIBs due to its diversity of crystal structures and multivalent states of manganese. Manganese dioxide possesses...
a basic crystal structure with an octahedral unit comprised of six oxygen atoms and one manganese atom. Each MnO₆ octahedral unit can be interconnected by sharing corners/edge into tunneled, layered, or 3D-type structures. Generally, different polymorphs of manganese dioxide are formed through various corner/edge sharing of fundamental MnO₆ octahedra. They are classified into 1) tunnel-based, 2) layered-based, and 3) spinel-based structures of MnO₂. The widely investigated tunnel-based MnO₂ structures for ZIBs consist of: i) hollandite-type MnO₂ (α-MnO₂) which has a large 2 × 2 tunnel structure with four corner-sharing MnO₆ octahedra (Figure 2a); ii) pyrolusite-type MnO₂ (β-MnO₂) which comprises of a 1 × 1 tunnel framework structure by sharing corner (Figure 2b); iii) todorokite-type MnO₂ which comprises of large 3 × 3 tunnels with the same structure as α-MnO₂ (Figure 2c); and iv) Nsultite-type (γ-MnO₂) which is the intergrowth structures of 1 × 1 and 1 × 2 tunnels (Figure 2d). Other polymorphs such as v) layered-type MnO₂ (δ-MnO₂) which is constructed by 2D infinite MnO₆ octahedra sheets with a large interlayer spacing (Figure 2e) and vi) spinel-type (λ-MnO₂) which is comprised of 3D spinel structure with Mn⁴⁺ in the tetrahedral sites and Mn⁶⁺ in the octahedral sites (Figure 2f), have also been reported to exhibit the ability to allow the insertion/extraction of Zn²⁺.

By analyzing the electrochemical performance based on the crystal structure of MnO₂ polymorphs, tunnel-based α-MnO₂ (2 × 2 tunnels, ≈4.6 Å), γ-MnO₂ (1 × 1, 2.3 × 2.3 and 1 × 2, 2.3 × 4.6 Å), and layered-based δ-MnO₂, are proven to be potential cathode materials for aqueous ZIBs due to their capability of Zn²⁺ insertion/extraction.[7,39,52,53] While β-MnO₂, which consists of a narrow 1 × 1 tunnel structure, shows unfavorable property for the diffusion of Zn²⁺.[7,36] However, recent studies by Chen and co-workers revealed that reversible insertion/extraction of Zn²⁺ by a phase transition of β-MnO₂ to form a layered phase Zn-buserite during initial charge can be achieved via the preaddition of zinc salt with bulky anion (CF₃SO₃⁻).[31] It is worth to note that the cathode exhibits a high reversible capacity of 225 mAh g⁻¹ and excellent cycle ability (94% capacity retention over 2000 cycles). Despite todorokite MnO₂, consisting of large 3 × 3 tunnels, its tunnels are readily occupied by various cations other than Zn²⁺ and water molecules, which will affect the sites for Zn²⁺ accommodation.[54] Hence, todorokite MnO₂ prepared by hydrothermal treatment of Mg-buserite only obtained a specific capacity of 98 mAh g⁻¹ during the first cycle. It is interesting to note that todorokite MnO₂ exhibits long-term cycle ability and good rate performance owing to the large tunnel and the electrostatic shielding effect by the structural water. Unfortunately, the electrochemical mechanism of Zn²⁺ in todorokite MnO₂ is unclear and still requires a more detailed investigation. Spinel-type MnO₂ (δ-MnO₂) with 3D structure may not be suitable cathode materials for ZIBs due to their limited 3D tunnels.[7,14] Later, Yuan et al. demonstrated that preinserted cation λ-MnO₂ exhibited a specific capacity of 442.6 mAh g⁻¹ at 13.8 mA g⁻¹, indicating that the Zn²⁺ insertion into λ-MnO₂ was likely to take place.[55] Akhtenskite-structure (ε-MnO₂) has also been studied to be a potential cathode material for ZIBs. Akhtenskite-structure (ε-MnO₂) is a metastable phase, which exhibits hexagonal symmetry where Mn⁴⁺ ions are located randomly in one-half of the face-shared octahedral sites. For example, Sun et al. reported the interconnected nanoflakes ε-MnO₂ on carbon fiber paper as binder-free cathode materials for ZIBs.[49] Owing to the microstructure with intensive electrode/electrolyte interface and effective ion diffusion path of the ε-MnO₂, superior cycling performance of almost 100% retention over 10 000 cycles at 6.5C can be achieved.[13] Overall, the previous studies suggest that the large enough tunnel space and layered structure is favorable for allowing the high-rate insertion/extraction of Zn²⁺. Therefore, the electrochemical properties of MnO₂ influence significantly on its crystallographic form, which follows the reducing order of α = δ > γ > λ > β. Owing to the various crystallographic forms, MnO₂ polymorphs exhibit different insertion thermodynamics.
and kinetics of H\textsuperscript{+}/Zn\textsuperscript{2+}. This will further contribute to the different reaction mechanisms in various MnO\textsubscript{2} polymorphs, leading to different electrochemical properties such as operating voltage, specific capacity, rate capability, and cycling performance of MnO\textsubscript{2} polymorph for ZIBs.\cite{7,14,39,52-55} Also, it is worth mentioning that the electrolyte composition is another key parameter to determine the electrochemical properties of a Mn-based cathode. Different anion species electrolyte may significantly influence ion association properties in solution, possible water-induced side reactions, the stability, and dissolution effect in a Mn-based cathode.\cite{10,14} More research shall be employed to determine the correlation factors between the crystal structures of Mn-based cathode and electrolyte compositions for optimizing the electrochemical performance for Mn-based ZIB systems.

### 3.1.2. Vanadium-Based Materials

Besides manganese-based materials, vanadium-based materials especially for vanadium oxides exhibit a large tunnel framework and various oxidation states, showing high potential in Zn\textsuperscript{2+} storage applications. Various structures of vanadium-based materials, including layered- and tunnel-structure, have been reported as potential cathode materials for ZIBs (see Figure 3a,b). Most of the early stage investigations of vanadium-based materials for ZIBs are focused on layered vanadium oxides. The common layered-structure V\textsubscript{2}O\textsubscript{5} consists of the layer V\textsubscript{4}O\textsubscript{5} that formed from the sharing edges and corner of VO\textsubscript{5} square pyramids. It exhibits an interlayer spacing of 0.577 nm, which is much larger than the radius of Zn\textsuperscript{2+} (0.074 nm) and considered as potential cathode materials for ZIBs. Besides, layered V\textsubscript{2}O\textsubscript{5} has been predicted to deliver a high theoretical capacity of 589 mAh g\textsuperscript{-1}, which is ascribed from the two-electron redox center (V\textsuperscript{5+} → V\textsuperscript{3+}) property.\cite{43} However, in practice, the layered structure exhibits low capacity and structural instability upon the repeated insertion/extraction of Zn\textsuperscript{2+} ions.\cite{58,59} Intensive efforts have been devoted to exploring vanadium oxides with more stable structures to eliminate the capacity fading issues. Besides layered structure V\textsubscript{2}O\textsubscript{5}, tunnel-type VO\textsubscript{2} exhibits a reversible Zn\textsuperscript{2+} insertion/extraction performance and superior rate capability in
ZIBs.\textsuperscript{[60]} This robust structure is comprised of distorted VO\textsubscript{6} octahedra that share corners and edges with large surface areas, allowing fast diffusion kinetics of Zn\textsuperscript{2+} and structure stability during cycling. Another tunnel-based material, V\textsubscript{2}O\textsubscript{5}, not only provides a hybrid valence state of V\textsuperscript{4+}/V\textsuperscript{5+} but also consists of alternate single and double vanadium oxide layers, providing more accommodation sites for Zn\textsuperscript{2+} storage.\textsuperscript{[41]} It is worth noting that a high capacity of 206 mA h g\textsuperscript{-1} can be maintained at 10 A g\textsuperscript{-1} after 3000 cycles. Recently, stoichiometric rocksalt vanadium oxynitride with close-packed face-centered cubic lattice has been revealed to serve as potential cathode materials for ZIBs.\textsuperscript{[62]} The stoichiometric rocksalt vanadium oxynitride was claimed to exhibit a conversion reaction during the first cycle, where high-valent stoichiometric rocksalt vanadium oxynitride was converted to low-valent oxynitride (O\textsuperscript{2−}). This has further resulted in the formation of disordered rocksalt with abundant vacancies/defects, which not only provides intense active sites for zinc ions but also enables rapid diffusion of zinc ions. As a result, the nitrogen-rich oxynitride cathode shows a high reversible capacity (603 mA h g\textsuperscript{-1}, 0.2C) and high rate capability (124 mA h g\textsuperscript{-1} at 600C). In addition, Wan et al. have further reported VOPO\textsubscript{4}, which exhibits a typical layered structure comprising of corner sharing VO\textsubscript{6} octahedra connected to PO\textsubscript{4} tetrahedra, as potential cathode materials for high-performance ZIBs.\textsuperscript{[15]} They revealed that the introduction of P−O covalence into the layer of V\textsubscript{2}O\textsubscript{5} polyhedra can stimulate the occurrence of oxygen redox reaction in the Zn/VOPO\textsubscript{4} system, enhancing the capacity and average operating voltage of the vanadium-based ZIBs. Benefiting from the structural variety advantages, manganese- and vanadium-based cathode materials achieve high capacity and high energy density for ZIBs. However, their low intrinsic electronics conductivity, poor capacity retention at low current densities, low structure stability during insertion/extraction, and inevitable material dissolution effects still limited their electrochemical performance for ZIBs.\textsuperscript{[11]}

3.1.3. Organic-Based Materials

Recently, organic materials that exhibit weak intermolecular van der Waals forces between molecules and a modest Coulomb repulsion to the diffusing cations, have attracted intensive interests for monovalent and divalent cation energy storage applications.\textsuperscript{[36]} Besides, reversible insertion/extraction of divalent cations may take place by molecular reorientation due to their malleable and soft lattice. For example, Kundu et al. reported tetrachloro-1,4-benzoquinone with a high structural flexibility that exhibits a high capacity of ≥200 mA h g\textsuperscript{-1} with a very small voltage polarization for 1Zn\textsuperscript{2+}/2e\textsuperscript{-} reaction (Figure 3d).\textsuperscript{[36]} Based on their density-functional theory (DFT) calculations, a twisted rotation in the molecular column 1 of p-chloranil is revealed to be useful for accommodating the volume expansion during cycling and stabilizing the electrochemical processes. Zhao et al. also demonstrated the excellent Zn\textsuperscript{2+} storage performance with quinone cathode materials.\textsuperscript{[63]} They reported calix[4]quinone that exhibited a stable open bowl structure with eight carbons, delivering a high capacity of 335 mA h g\textsuperscript{-1} and a stable cycling performance with a capacity retention of 87% at 500 mA g\textsuperscript{-1} after 1000 cycles. Haupler et Al. have further reported a redox-active polymer based on a 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system in combination with a conjugated backbone as cathode material for ZIBs.\textsuperscript{[64]} This polymer cathode shows a superior rate capability of up to 120C (30 s) and an ultralong lifetime, of over 10 000 charge/discharge cycles (accompanied by a minor capacity loss of 14%). Although these organic materials show great potential as cathode materials for ZIBs, low solubility in the electrolyte and low electronic conductivity have greatly limited their practical applications. The introduction of a suitable organic-redox active group with high water stability for a wide range of pH values has been demonstrated to be an alternative approach to promote the zinc storage ability of organic-based materials. Nonetheless, the research is still in its infancy, which needs further efforts to develop a more effective structural design in organic materials with high electronic conductivity for achieving high specific capacity with long-term stability.

3.1.4. Prussian Blue Analog Materials

PBA materials that exhibit a face-centered cubic structure with 3D open framework and large interstitial sites are considered as potential host materials for reversible insertion/extraction of various cations.\textsuperscript{[65]} Zhang et al. reported zinc hexacyanoferrates with open framework structure as potential insertion hosts for Zn cations (Figure 3d). An energy density of 100 Wh kg\textsuperscript{-1} is achieved even when the discharge capacity is only 65.4 mA h g\textsuperscript{-1} at 1C due to the high operating voltage.\textsuperscript{[44]} However, the PBA-type cathodes usually suffer from unsatisfactory low capacity, low cycle stability, and inferior rate capability. Recently, Yang et al. have demonstrated that high voltage scanning can effectively activate the reduction of low-spin Fe(III) coordinated with the C atom of the cyano group in iron hexacyanoferrate (FeHCF) cathodes.\textsuperscript{[66]} With a voltage scan at 2.3 V, the Zn–FeHCF hybrid-ion battery exhibits a gradual increase in capacity. It is worth noting that the unsatisfactory electrochemical performance and low working voltage in FeHCF cathode are mainly caused by the coordination of high spin Fe (Fe atom coordinated with N atom of cyanogroup) whereas the limited utilization of low-spin Fe (Fe atom coordinated with C atom of cyanogroup). The increase of capacity is mainly due to the increased contribution from the high discharge voltage plateau at ≈1.5 V, which corresponds to the reduction of low-spin Fe(III) coordinated with the C atom of cyanogroup. As a result, the activated FeHCF cathode displays significantly enhanced cycling stability with an 82% capacity retention after 5000 cycles and superior rate performance of maintaining 53.2% capacity at a current density of 8 A g\textsuperscript{-1}. This work has demonstrated that the controllable chemical and electronics tuning in PBA-type cathodes by the increasing amounts of redox active structures may eventually promote their overall electrochemical performance such as cycling stability, rate capability, and operating potential window for ZIBs.

3.1.5. Polyanionic-Based Materials

Polyanionic compounds with a stable framework, high redox voltage, and vacancies existing in the structure that can store metal ions are also promising candidates for ZIBs.\textsuperscript{[46,47,67]} For
example, Li et al. synthesized a Na$_3$V$_2$(PO$_4$)$_3$ with sodium (Na) super ionic conductor (NASICON) structure as cathode material for ZIBs. Their electrochemical measurements indicate that an ion variation mechanism during the insertion of Zn$^{2+}$ and the Na$_3$V$_2$(PO$_4$)$_3$ delivers a reversible capacity of 97 mAh g$^{-1}$ at 0.5C and capacity retention of 74% after 100 cycles.[46] Besides, Zhao et al. further used NASICON-type M$_3$V$_2$(PO$_4$)$_3$ materials[7,14,39,52–55] as operating potential platforms and reaction mechanisms (see Table 1). It is worth noting that the unique features of their crystal structure also play important role in determining their zinc storage abilities. For example, various electrochemical reaction mechanisms have been reported for various MnO$_2$ polymorphs.[10,11,14] They revealed that the Zn$^{2+}$ insertion/extraction into Mo$_6$S$_8$ occurred stepwise and the charge/discharge process for the Mo$_6$S$_8$ over ZnMo$_6$S$_8$ to Zn$_2$Mo$_6$S$_8$ were reversible. Nonetheless, the insertion voltage was too low (0.35 V), resulting in low energy density and an unsuitable cathode candidate for ZIBs.[57] A 3D network crystal structure creating cavities surrounded by sulfur atoms is formed by the axially bonding between six of the T$_8$ to a molybdenum atom of a neighboring cluster. This type of compound exhibits the excellent capability to accommodate various cations with superior ionic and electronic diffusion kinetics. Chae et al. synthesized Mo$_6$S$_8$ through chemical extraction of copper ions from Cu$_2$Mo$_6$S$_8$.[68] They revealed that the Zn$^{2+}$ insertion/extraction into Mo$_6$S$_8$ occurred stepwise and the charge/discharge process for the Mo$_6$S$_8$ over ZnMo$_6$S$_8$ to Zn$_2$Mo$_6$S$_8$ were reversible. Nonetheless, the insertion voltage was too low (0.35 V), resulting in low energy density and an unsuitable cathode candidate for ZIBs.[57] A 3D network crystal structure creating cavities surrounded by sulfur atoms is formed by the axially bonding between six of the T$_8$ to a molybdenum atom of a neighboring cluster. This type of compound exhibits the excellent capability to accommodate various cations with superior ionic and electronic diffusion kinetics. Chae et al. synthesized Mo$_6$S$_8$ through chemical extraction of copper ions from Cu$_2$Mo$_6$S$_8$.[68] They revealed that the Zn$^{2+}$ insertion/extraction into Mo$_6$S$_8$ occurred stepwise and the charge/discharge process for the Mo$_6$S$_8$ over ZnMo$_6$S$_8$ to Zn$_2$Mo$_6$S$_8$ were reversible. Nonetheless, the insertion voltage was too low (0.35 V), resulting in low energy density and an unsuitable cathode candidate for ZIBs.[57] A 3D network crystal structure creating cavities surrounded by sulfur atoms is formed by the axially bonding between six of the T$_8$ to a molybdenum atom of a neighboring cluster. This type of compound exhibits the excellent capability to accommodate various cations with superior ionic and electronic diffusion kinetics. Chae et al. synthesized Mo$_6$S$_8$ through chemical extraction of copper ions from Cu$_2$Mo$_6$S$_8$.[68] They revealed that the Zn$^{2+}$ insertion/extraction into Mo$_6$S$_8$ occurred stepwise and the charge/discharge process for the Mo$_6$S$_8$ over ZnMo$_6$S$_8$ to Zn$_2$Mo$_6$S$_8$ were reversible. Nonetheless, the insertion voltage was too low (0.35 V), resulting in low energy density and an unsuitable cathode candidate for ZIBs.[57]

### Table 1. Comparison of the various typical cathode materials that are widely investigated for ZIBs.

| Typical cathode materials | Structure benefits | Operation voltage platforms [V] | Reaction mechanisms | Limitations |
|--------------------------|--------------------|-------------------------------|---------------------|------------|
| Mn-based material[7,9,10,14,39,52–55] | Polymorphs with various tunnel, layered structure, multivalence state | 1.3–1.4 | Reversible Zn$^{2+}$ insertion/extraction, coinsertion of Zn$^{2+}$ and H$^+$ mechanism, conversion reaction mechanism | Poor electrical conductivity, Mn$^{2+}$ dissolution, structural instability during cycling, insertion mechanisms, performance optimization of cathode materials |
| V-based material[8–11] | Various structures such as layered- and tunnelled structure and various oxidation states | 0.9–1.1 | Reversible Zn$^{2+}$ insertion/extraction, oxygen redox reaction | Low intrinsic electronic conductivity, poor capacity retention at low current densities, low structure stability during insertion/extraction, and inevitable material dissolution effects |
| Organic-based material[56,63,64] | Weak intermolecular van der Waals forces between molecules and a modest Coulomb repulsion, malleable and soft lattice | 1.0–1.1 | Reversible Zn$^{2+}$ insertion/extraction | Low solubility in electrolyte and low electronic conductivity |
| Prussian Blue Analog materials[44,65] | 3D open framework and large interstitial sites | 1.3–1.7 | Reversible Zn$^{2+}$ insertion/extraction | Unsatisfactory low capacity, low cycle stability, and inferior rate capability |
| Polyanionic-based materials[46,47,67] | Stable framework with NASICON structure, vacancies existing in the structure that can store metal ion | 1.6–1.7 | Reversible Zn$^{2+}$ insertion/extraction | Electrochemical performance is highly affected by the electrolyte composition |
| Chevrel phase materials[15,58] | 3D network crystal structure creating cavities surrounded by sulfur atoms | 0.5–0.6 | Reversible Zn$^{2+}$ insertion/extraction | Insertion voltage is too low, low capacity |

### 3.1.6. Chevrel Phase Materials

Chevrel phase compound with a general formula M$_6$Mo$_6$T$_8$, which consists of an octahedral Mo$_6$ surrounded by a cubic unit (T$_8$) of chalcogenide atoms (Figure 3f), has demonstrated promising potential as cathode materials for ZIBs.[57] A 3D network crystal structure creating cavities surrounded by sulfur atoms is formed by the axially bonding between six of the T$_8$ to a molybdenum atom of a neighboring cluster. This type of compound exhibits the excellent capability to accommodate various cations with superior ionic and electronic diffusion kinetics. Chae et al. synthesized Mo$_6$S$_8$ through chemical extraction of copper ions from Cu$_2$Mo$_6$S$_8$.[68] They revealed that the Zn$^{2+}$ insertion/extraction into Mo$_6$S$_8$ occurred stepwise and the charge/discharge process for the Mo$_6$S$_8$ over ZnMo$_6$S$_8$ to Zn$_2$Mo$_6$S$_8$ were reversible. Nonetheless, the insertion voltage was too low (0.35 V), resulting in low energy density and an unsuitable cathode candidate for ZIBs.[57]

In summary, various cathode materials with unique structure features such as tunnel-based, layered-based, and 3D framework-based structures have been investigated as cathode materials for ZIBs.[7,14,39,52–55] Generally, there is a strong relationship between the types of cathode materials and Zn$^{2+}$ storage abilities, that modulates the overall energy storage reaction mechanism such as operating potential platforms and reaction mechanisms (see Table 1). It is worth noting that the unique features of their crystal structure also play important role in determining their zinc storability. For example, various electrochemical reaction mechanisms have been reported for various MnO$_2$ polymorphs.[10,11,14] More efforts shall be focused on the more precise investigation...
of polyhedral or crystal structures for the Zn\textsuperscript{2+} storage reaction process by more advanced characterization to explore other potential cathode materials with zinc-intercalation favorable structures and morphologies for ZIBs.

### 3.2. Crystal Defect Engineering

Crystal defect engineering, which provides optimization of electrochemical active surface area for effective electrochemical reaction, is an effective approach to tackle the current limitations of cathode materials for ZIBs.\[17–19,69,70\]

Generally, manganese oxides exhibit a low utility rate of surface active sites, significantly impeding their electrochemical performance for ZIBs. Introducing defects such as oxygen vacancy and cation deficiency in manganese oxide cathode materials can lower Gibbs free energy of Zn\textsuperscript{2+} adsorption, facilitating the insertion/extraction of Zn\textsuperscript{2+}. For example, Xiong et al. designed an oxygen-deficient MnO\textsubscript{2} as cathode material for ZIBs.\[18\] They revealed that the existence of oxygen vacancies in the MnO\textsubscript{2} enabled an enhanced electrochemical performance owing to the high accessible electrochemical active surface area and the generation of available electrons by the formation of Zn–O bonding (see Figure 4a,b). As a result, the oxygen-deficient manganese oxide exhibits a high capacity of 345 mAh g\textsuperscript{-1}, superior rate capability, and long-term cycling stability at a low current density of 0.2 A g\textsuperscript{-1} (see Figure 4c). The recent theoretical study by Han et al. also demonstrated that the introduction of oxygen defect in the β-MnO\textsubscript{2} with a relatively narrow tunneled pathway could effectively facilitate the insertion of H\textsuperscript{+} into β-MnO\textsubscript{2}.\[69\] They further confirmed their theoretical conjecture by assembling aqueous Zn/β-MnO\textsubscript{2} battery. A high capacity of 302 mAh g\textsuperscript{-1} and superior cycling performance with a capacity retention of 94% after 300 cycles are achieved with the oxygen-deficient β-MnO\textsubscript{2} cathode. Liao et al. further revealed that oxygen-deficient vanadium oxide cathode exhibited unprecedented stability over 200 cycles with a superior capacity of 400 mAh g\textsuperscript{-1}, reaching 95% utilization of its theoretical capacity.\[71\] They suggested that the introduction of oxygen vacancies in vanadium oxide by synthetic strategy favored divalent Zn\textsuperscript{2+} reaction kinetics and enhanced Zn\textsuperscript{2+} reaction pathway for high reversible Zn\textsuperscript{2+} insertion/extraction. Besides, Li et al. have further investigated the effects of oxygen vacancies on Zn\textsuperscript{2+} intercalation in VO\textsubscript{2} for aqueous ZIBs.\[72\] They have revealed that oxygen-deficient manganese oxide cathode can result in a larger tunnel structure along the b-axis, which enhances the reactive kinetics and promotes Zn\textsuperscript{2+} storage capability in VO\textsubscript{2} cathode. As a consequence, a high specific capacity of 375 mAh g\textsuperscript{-1} at a current density of 100 A g\textsuperscript{-1} and excellent long-term cycling stability with retained specific capacity of 175 mAh g\textsuperscript{-1} at 5 A g\textsuperscript{-1} over 2000 cycles were achieved.

Other spinel structures such as ZnMn\textsubscript{2}O\textsubscript{4} and MnMn\textsubscript{2}O\textsubscript{4}(Mn\textsubscript{2}O\textsubscript{3}) may not be suitable cathode materials for ZIBs due to their limited 3D tunnel. Also, owing to the high electrostatic interaction between Zn\textsuperscript{2+} and the lattice of spinel structures such as ZnMn\textsubscript{2}O\textsubscript{4}, the Zn\textsuperscript{2+} insertion/extraction becomes more difficult.\[73\] The cation-deficient spinel ZnMn\textsubscript{2}O\textsubscript{4} was then prepared to lower the electrostatic barrier and promote the Zn\textsuperscript{2+} diffusion in the host.\[73\] A new mechanism with the insertion and extraction of Zn\textsuperscript{2+} into the Zn–O tetrahedron sites of zinc manganese oxide spinel is illustrated in Figure 5a; therefore, the basic spinel lattice can be maintained during the cycling process. They further suggested that the presence of abundant Mn vacancies in zinc manganese oxide is beneficial for the Zn\textsuperscript{2+} diffusion. It is worth noting that capacity retention of 94% over 500 cycles at 500 mA g\textsuperscript{-1} can be achieved with the cation-deficient spinel ZnMn\textsubscript{2}O\textsubscript{4} (see Figure 5b). Overall, this work has revealed that the cation defects in ZnMn\textsubscript{2}O\textsubscript{4} are beneficial to modulate the electronic properties and improve the cycling performance of ZIBs.

---

**Figure 4.** a) Scheme of oxygen-deficient α-MnO\textsubscript{2} for Zn\textsuperscript{2+} storage and theoretical calculated surface adsorption energies for Zn\textsuperscript{2+} of defect-free and oxygen-deficient α-MnO\textsubscript{2}. b) High resolution annular bright-field scanning transmission electron microscopy (ABF-STEM) images of defect-free and oxygen-deficient α-MnO\textsubscript{2}. Irregular lattices resulting from shrinkage of the interlayers spacing and the fragmented layer are observed in oxygen-deficient α-MnO\textsubscript{2}, which attributed to high density of oxygen vacancies in oxygen-deficient α-MnO\textsubscript{2}. c) Rate performance, the Ragone plots, and cycling performance of defectless and oxygen-deficient α-MnO\textsubscript{2}. Reproduced with permission.\[18\] Copyright 2019, Wiley-VCH.

---

\[2021\textsuperscript{©}TheAuthors. Published by Wiley-VCH GmbH\]

---

\[2020\textsuperscript{©}TheAuthors. Published by Wiley-VCH GmbH\]
conductivity, Zn\(^{2+}\) transport kinetics, and the energy barrier of Zn\(^{2+}\) mobility.

Besides, Zhu et al. developed an in situ electrochemical approach for the activation of MnO by the introduction of Mn cation defects.[19] They proposed the generated Mn defect via a charging process, which can transform the electrochemically inactive MnO into a highly active cathode for aqueous ZIBs. It is important to note that the proposed cathode exhibited a reversible Zn\(^{2+}\) insertion/extraction mechanism without structural collapse during cycling. Apart from the oxide-based materials, defect engineering in layered metal chalcogenides with an improved electrochemical performance for ZIBs has also been reported. Generally, ZH-MoS\(_2\) exhibits poor electrochemical activities toward Zn\(^{2+}\).[28] Recently, Xu et al. reported sulfur-deficient MoS\(_x\) nanosheets as cathode for ZIBs, which delivered a high reversible capacity as compared to the defect-free MoS\(_2\).[17] The defect-rich MoS\(_2\) consists of numerous edge sites and vacancies, which provide accommodation sites for Zn\(^{2+}\) (see Figure 5c,d), converting poor Zn\(^{2+}\) interaction host materials into functional active cathode materials for ZIBs and thus resulting in a high reversible capacity.

The electrochemical process generally involves three primary processes, namely, mass diffusion, electron transfer, and cathode/electrolyte reaction. The overall performance of a cathode is usually significantly influenced by the charge transport properties and redox-active site capabilities. Defect engineering has been a promising approach for tuning the electrical structure and surface morphology, resulting in novel physicochemical properties or strong synergistic effects that potentially improved electrochemical performance. Yet fundamentally, most of the reported works simply propose that the existence of defects has a powerful effect on electrochemical performance. Often other aspects such as controllable defect types and concentrations which may alter the electrochemical performance of cathode material were not taken into consideration. Particular attention should be employed to evaluate the defect-drive electrochemical performance via precise synthesis.

### 3.3. Interlayer Engineering

Owing to the (de)intercalation-type storage mechanism of ZIBs, the hydrated Zn\(^{2+}\) generally prefers to store in the layered structure. Interlayer engineering is another method to optimize microstructures, which plays an important role in endowing the electrode materials with high Zn\(^{2+}\) storage performance. Interlayer engineering can significantly enhance the diffusion kinetics of ions with large sizes and multivalence via reducing their diffusion barriers.[27] Besides, interlayer engineering also endows the cathode materials with a large specific surface area, which improves their electrochemical performance.[22,75]

Various efforts are developed to insert foreign species into the host layered lattice.[21,22,27,76] For example, metal-ion intercalation, including Li\(^+\), Na\(^+\), K\(^+\), Mn\(^{2+}\), and Zn\(^{2+}\), is explored to improve the performance of V\(_2\)O\(_5\) cathode materials.[77–81] It is worth to note that a recent report by Liu et al. revealed that the chemical insertion of Mn(II) cations in hydrated vanadates can act as structural pillars, which expand the interplanar spacing from 11.9 to 12.9 Å, linking the adjacent layers and partially reducing the pentavalent vanadium cations to tetravalent (see Figure 6a).[76] As a result, manganese-expanded hydrated vanadate achieved a high specific capacity of 415 mAh g\(^{-1}\) at 50 mA g\(^{-1}\) and an excellent cycling performance with a capacity retention of 92% over 2000 cycles at 4 A g\(^{-1}\) (see Figure 6b). They further demonstrated improved Zn\(^{2+}\) storage performance in expanded hydrated vanadates by introducing other intercalated transition metal cations such as Ni and Co (see Figure 6c). Nonetheless, the specific capacity of metal vanadate cathode materials is still
limited by the large molecular weight and volume of metal ions. In addition, the metal-ion intercalated host materials still suffer from structural damage owing to the insertion of metal ions between layers.

Other intercalating agents such as conductive polymers have also been investigated to modulate the interlayer spacing for zinc cathode materials. For example, Huang et al. reported mesoporous structure polyaniline inserted into MnO$_2$ nanolayers by an interface reaction, which eliminated phase transformation and delivered a stable cycling performance for ZIBs. Besides, Bin et al. synthesized the redox intercalative polymerization of 3,4-ethylenedioxythiophene into ammonium vanadate oxide (PEDOT–NVO) via a facile synthesis method, as illustrated in Figure 7a–c. The obtained PEDOT-intercalated NVO exhibits an expanded interplanar spacing crystal lattice (Figure 7d), which leads to an enhancement in the diffusion of cation species intercalating into the crystal lattice of the NVO. As a result, the hybrid of organic–inorganic-intercalated NVO layer cathode exhibits a high capacity with good cycling stability and excellent rate capability (Figure 7e–g). As mentioned earlier, MoS$_2$ is an intrinsically inactive Zn$^{2+}$ insertion/extraction host material to store Zn$^{2+}$. Liang et al. reported an effective approach by tuning the interlayer spacing and hydrophilicity of MoS$_2$, via oxygen incorporation and thus converted intrinsically inactive Zn$^{2+}$ insertion/extraction hosts into efficient Zn$^{2+}$ storage materials. Consequently, the capacity of the activated MoS$_2$ was enhanced by 10 times as compared to the inactive MoS$_2$, delivering a high capacity of 232 mAh g$^{-1}$ at 100 mA g$^{-1}$. Zhi and co-workers further demonstrated the excellent Zn$^{2+}$ storage performance with interlayer-spacing-expanded MoS$_2$ nanosheets on carbon fiber. The expanded interlayer spacing of $\epsilon$-MoS$_2$ nanosheets enabled effective ion diffusion kinetics and low energy barrier for Zn$^{2+}$ insertion/extraction, resulting in a good specific capacity of 202.6 mAh g$^{-1}$ at 100 mA g$^{-1}$, a high energy density of 148.2 Wh kg$^{-1}$ and high cyclic stability.

In short, interlayer engineering of layered materials plays a critical role in tuning properties and improving the performance of cathode materials for ZIBs. Nonetheless, challenges still

---

**Figure 6.** a) XRD patterns of Mn-expanded hydrated vanadium pentoxide (MnVO) and hydrated vanadium pentoxide (VOH). b) Comparison of rate capability and cycle stability of MnVO and VOH. c) Cycling stability measured at 4 A g$^{-1}$ of Ni-expanded, Co-expanded, and pristine hydrated vanadium pentoxides. Reproduced with permission. [76] Copyright 2019, The Royal Society of Chemistry.
exist in synthesizing microstructures with controllable amounts of intercalated foreign species, interlayer distance, and composition via large-scale and cost-effective synthesis process. Well-developed guidelines on the selection of suitable intercalated species for obtaining optimal interlayer spacing and electrochemical performance are thus required.

3.4. Morphological Design

3.4.1. Low-Dimensional Structures

Generally, low-dimensional materials demonstrate excellent mechanical flexibility, high specific surface area, numerous active sites, and high chemical stability than their bulk counterparts. Their superior structural features have attracted intensive attention to the design of low-dimensional microstructures for high-performance electrode materials. Growth of 0D nanocrystals has been widely developed to promote reaction kinetics and accommodate the volume expansion of the electrode materials during the insertion/extraction process. For example, Wei et al. synthesized various manganese dioxides with different tunnel structures and morphologies via a common liquid coprecipitation method based on the redox reaction of Mn$^{4+}$ and Mn$^{2+}$ for ZIBs.

Spherical nanoparticles of 20 nm in diameter, nanorods of 40–100 nm in length and 20 nm in diameter, or interlocked nanosheet of 10–20 nm thickness can be obtained based on the preparation procedure. Owing to the low-dimensional features of high surface area and abundant active sites for the Zn$^{2+}$ storage, the manganese dioxide composed of spherical nanoparticles and cylindrical nanorods exhibited a high specific surface area of 208 m$^2$ g$^{-1}$ (Figure 8a,b).

1D microstructures, including nanowires, nanorods, and nanobelts have attracted intensive attention for energy storage applications due to their distinct properties, such as large surface-to-volume ratio and inhibition to agglomeration. For example, Islam et al. demonstrated that β-MnO$_2$ nanorods with exposed (101) planes can be a potential cathode material for ZIBs (Figure 8c). β-MnO$_2$ nanorods with exposed (101) planes were synthesized by a rapid microwave-assisted hydrothermal reaction in 10 min. They revealed that β-MnO$_2$ nanorods exhibited a higher discharge capacity of 270 mAh g$^{-1}$ at 100 mA g$^{-1}$ and excellent rate capability as compared to bulk β-MnO$_2$, demonstrating that the unique rod-shaped materials enhance the insertion/extraction of Zn$^{2+}$ into/from the nanorod structures (Figure 8d). Besides, CuV$_2$O$_6$ nanobelts have been synthesized by a facile hydrothermal method (Figure 8e). Owing to the rational designed morphology of CuV$_2$O$_6$, enhanced Zn$^{2+}$ diffusion rate and better electrochemical performance with a high reversible capacity of 427 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$, and superior stability with a minor capacity loss of 0.7% after 3000 cycles at 5 A g$^{-1}$ can be achieved (Figure 8f). They further revealed that the Zn$^{2+}$ storage performance of the 1D microstructure can be further enhanced by combining with carbonaceous materials. In their work, they demonstrated a significantly improved specific capacity by at least 30% increment.

Besides 1D microstructures, 2D microstructures with an atomically thin layer structure, including layered metal oxides, metal chalcogenides, and MXene have been investigated for Zn$^{2+}$ storage. Owing to the layer structure with large interlayer spacing and high conductivity, transition metal dichalcogenide nanosheets such as MoS$_2$ and VS$_2$, demonstrate great potential for the insertion/extraction of multivalent ions such as Zn$^{2+}$. For example, Pan and co-workers synthesized VS$_2$ nanosheets via a facile hydrothermal process. When employed as the cathode material for ZIBs, VS$_2$ nanosheets delivered high capacity and exhibited long-term cyclic stability owing to the large interlayer spacing of 5.76 Å.
Figure 8. a,b) SEM image of $\alpha$-MnO$_2$ nanoparticles and comparison of the first discharge capacity and Brunauer–Emmett–Teller (BET) measurements for $\alpha$-MnO$_2$ with other MnO$_2$ structures for ZIBs, where A is $\alpha$-MnO$_2$ aggregated spherical nanoparticles and cylindrical nanorods, B is $\delta$-MnO$_2$ nanorods, C is interlocked short nanosheets $\gamma$-MnO$_2$, and D is aggregated nanorods $\beta$-MnO$_2$. Reproduced with permission.[36] Copyright 2012, Elsevier. c,d) SEM image and rate performance of $\beta$-MnO$_2$ nanorod cathode for ZIBs. Reproduced with permission.[53] Copyright 2017, The Royal Society of Chemistry. e,f) SEM image and discharge–charge profiles in the first four cycles at a current density of 0.1 A g$^{-1}$ of CuV$_2$O$_6$ nanobelt cathode for ZIBs. Reproduced with permission.[84] Copyright 2019, American Chemical Society. g,h) SEM image, rate performance, and Coulombic efficiency of A-V$_2$O$_5$/G cathode for ZIBs. Reproduced with permission.[103] Copyright 2020, Wiley-VCH.
that enabled the insertion/extraction of Zn$^{2+}$ (0.74 Å) and high conductivity of VS$_2$ nanosheets.

Recently, Wang et al. developed a novel 2D heterostructure of ultrathin amorphous vanadium pentoxide uniformly grown on graphene (A-V$_2$O$_5$/G) by 2D template based on ion-adsorption approach as cathode material for ZIBs (Figure 8g).[103] The 2D sandwich-like composite consists of ultrathin nanosheet (≈ 5 nm) with short ion diffusion, numerous active sites, and high electrical conductivity, which significantly promote the prominent capacitive-controlled kinetics process as well as facilitate the Zn$^{2+}$ intercalation reaction. As a result, the 2D A-V$_2$O$_5$/G heterostructures delivered a high specific capacity of 489 mAh g$^{-1}$ and an Outstanding rate capacity of 123 mAh g$^{-1}$ even at 70 A g$^{-1}$ (Figure 8h). Zhao et al. designed a robust structure of nanosheet MnO$_2$H$_{0.16}$(H$_2$O)$_{0.27}$ (MON) with a thickness of ≈2.5 nm as a promising cathode material for ZIBs.[95] High electrochemical performance of the Zn/MON cell with a high energy density of 228.5 Wh kg$^{-1}$ and superior cycling stability (capacity retention of 96% at 0.5C after 300 cycles) was achieved, owing to the ultrathin layer structure combined with H$^+$/Zn$^{2+}$ synergistic insertion/extraction mechanism.

3.4.2. Hierarchical Structures

With the combined advantages of the low-dimensional microstructures and large 3D framework, hierarchical structures show great potential for Zn$^{2+}$ storage. More specifically, low-dimensional units can facilitate the diffusion of Zn$^{2+}$/electrons and provide large electrode/electrolyte active contact surface area, while large 3D frameworks can provide stability of the structure with effective buffering on the volume change during charge/discharge process.

Recently, various hierarchical structures have been synthesized for ZIB applications.[22,103–110] For example, the direct synthesis of binder-free hierarchical 1T VS$_2$ flower-like structure on stainless steel mesh by hydrothermal method has been reported by Jiao et al. for ZIBs.[104] The synthesis of freestanding materials on conductive substrates which can be directly used as cathode materials for energy storage applications enables higher gravimetric/volumetric energy density as compared to the conventional slurry-coated electrodes which consist of inactive materials such as the binder and conductive additives (see Figure 9a,b). The open-structure 1T phase VS$_2$ flowers (Figure 9c,d) demonstrated a high reversible capacity of 198 mAh g$^{-1}$ and stable cycling performance with 80% capacity retention over 2000 cycles at 2 A g$^{-1}$ (Figure 9e,f).

In addition, the hierarchical structure which comprises of active materials and highly conductive 3D carbonaceous networks (e.g., graphene and carbon nanotubes (CNTs)), have been synthesized to improve the Zn$^{2+}$ storage performance. For example, Xu et al. prepared a freestanding and highly porous composite consisting of bilayer Na$_n$V$_{3}O$_{8}$·nH$_2$O nanobelts, carbon nanotubes, and reduced graphene oxide (RGO) with 3D interconnected structure.[106] With a unique hierarchical nanoarchitecture of the combined structure between 1D and 3D scaffold, the freestanding composites delivered a capacity of 459.1 mAh g$^{-1}$ at 0.5 A g$^{-1}$, superior rate capability, and excellent cycling stability of 83.1% retention after 1800 cycles at 10 A g$^{-1}$. A novel hydrophilic carbon substrate by acid-treated natural halloysite and carbon nanotube for loading V$_2$S$_3$ have been reported by Liu et al.[107] The coupling electrode materials with carbon substrate exhibited a high specific capacity of 148 mAh g$^{-1}$ at 0.5 A g$^{-1}$ and a high energy density of 155.7 Wh kg$^{-1}$ owing to the combined advantage of the high conductivity and the formation of the hydrophilic surface/interface of the composite electrode.

Fabrication of hierarchical structures that consist of a hybrid structure of layered materials with different carbon materials, has been reported to be an effective approach to promote the electrochemical performance of 2D microstructures.[26,92,94] For example, Huang and co-workers reported a MnO$_2$ nanosheet/RGO composite structure.[95] The RGO channels with mesopores not only increased the conductivity but also accommodated the volume change of MnO$_2$ during the charge/discharge process, resulting in a significantly enhanced capacity (332.2 mAh g$^{-1}$ at 0.3 A g$^{-1}$), improved rate capability, and cyclability. Zhi and co-workers reported expanded interlayer spacing MoS$_2$ nanosheets on a carbon cloth by a one-step glucose-assisted hydrothermal approach.[111] The as-synthesized composites demonstrated a high specific capacity of 206 mAh g$^{-1}$ at 100 mA g$^{-1}$, an energy density of 148.2 Wh kg$^{-1}$, and superior cycling performance with a capacity retention of 98.6% after 600 cycles. Besides, Wu et al. synthesized MnO$_2$-nanosheet-assembled hollow polyhedron on carbon cloth (CC) via a rapid hydrothermal method using zeolitic imidazole framework (ZIF)-67 as self-sacrificing template.[126] The hollow MnO$_2$, nanosheet polyhedron provided a large surface area which facilitated the penetration of electrolyte and accommodated volume change during charge and discharge processes, whereas the carbon cloth substrate promoted the electron transportation. Benefiting from the combined structural advantages, the MnO$_2$/CC delivered a high reversible capacity of 263.9 mAh g$^{-1}$ at 1.0 A g$^{-1}$ after 300 cycles, which was much better than that of a commercial MnO$_2$ electrode.

3.4.3. Hollow Structures

Owing to the well-defined shell and interior voids, effective diffusion path for ions and electrons, and large active surface area, hollow structured nanomaterials have shown the potential to be excellent electrode materials for ZIBs. In brief, the interior hollow architecture accommodates the volume expansion during the charge/discharge process, enabling excellent cycling stability. Meanwhile, most of the hollow structure can retain their original structure even after long cycling. Besides, the large surface area enables the hollow structures with intensive electrochemical active sites and the large effective contact area between electrolyte and electrode for efficient ion and electron diffusion, resulting in improved reversible capacity. Many previous works have reported that the energy storage ability of hollow structure materials can be further optimized via the design of the external shape, shell architecture, internal configuration, size, and chemical composition.[26,111–116]

Numerous hollow structures have been employed as cathode materials for sodium-ion batteries (SIBs) and LIBs and showed excellent electrochemical properties.[119–122] Nonetheless, hollow structuring in cathode materials for ZIBs is less reported. Recently, hollow spherical structures have been
investigated as electrode materials for ZIBs.\textsuperscript{[25,115,118,123]} For example, Chen et al. synthesized hollow $\text{V}_2\text{O}_5$ nanospheres with a shell thickness of 50 nm and a diameter of 450 nm through a template-free solvothermal method followed by calcination treatment.\textsuperscript{[25]} The nanosized hollow structure buffered the structural volume change, provided efficient ion/electron diffusion paths, and enhanced the surface capacitive behavior, showing an ultrahigh reversible capacity of 327 mAh g$^{-1}$ at 0.1 A g$^{-1}$, excellent rate capability, and cycling stability with 147 mAh g$^{-1}$ after 6000 cycles at 10 A g$^{-1}$. Even at a high current density of 15 A g$^{-1}$, a high capacity of 122 mAh g$^{-1}$ can still be maintained after 10 000 cycles.

Besides, Li et al. reported an anhydrous $\text{V}_2\text{O}_5$ yolk–shell cathode synthesized by a facile template-free solvothermal process (Figure 10a,b).\textsuperscript{[117]} Owing to the yolk–shell architectures, the obtained composites delivered a high reversible capacity of 410 mAh g$^{-1}$ at 100 mA g$^{-1}$ and a stable cycling performance with a capacity retention of 80% over 1000 cycles at 5 A g$^{-1}$.  

Figure 9. Schematic illustration of the preparation processes for a) the conventional slurry-coated electrode, and b) the binder-free hierarchical VS$_2$ grown on a stainless-steel mesh substrate (VS$_2$@SS) electrode. c,d) SEM images of VS$_2$@SS under different magnifications and the inset in (d) is the cross-section image of VS$_2$@SS. e,f) Cycling performance of VS$_2$@SS electrode and VS$_2$ slurry-coated electrode at 0.5 and 2 A g$^{-1}$. Reproduced with permission.\textsuperscript{[104]} Copyright 2019, The Royal Society of Chemistry.
(Figure 10c). Hu et al. reported porous V2O5 microspheres via the spray-drying approach as cathode materials for ZIBs (Figure 10d,e).[118] They suggested that the porous microspheres offered a structural advantage on accommodating volume expansion during cycling and provided effective ion diffusion pathway. As a result, the porous V2O5 microspheres demonstrated an excellent discharge capacity of 401 mAh g\(^{-1}\) at 100 mA g\(^{-1}\), superior rate capability (234 mAh g\(^{-1}\) at 5000 mA g\(^{-1}\)), and cycling performance with a capacity retention of 73% over 1000 cycles (Figure 10f).

Overall, morphology engineering enables the construction of cathode microstructure materials with morphology-dependent benefits such as high surface to mass/volume ratio, improved conductivity, intensive chemical active sites, and stable framework that can accommodate the volume expansion during the cycling process. It can be concluded that morphology engineering improves the structural stability, enhances the overall reaction kinetic, and enables high specific capacity without altering the overall redox reaction of cathode material in ZIBs (see Table 2).

4. Electrolytes for Aqueous ZIBs

It is worth mentioning that Zn\(^{2+}\) is usually present in hydrated Zn\(^{2+}\) form with water molecules surrounded in the water medium. The strong interaction between the Zn\(^{2+}\) and water molecules induces a high desolvation and deposition energy barrier for a solvated Zn\(^{2+}\).[125] The side product of a hydroxyl ion by water decomposition usually leads to the formation of Zn(OH)\(_2\), which further transforms into insoluble and electrochemically inactive ZnO. The nature of the zinc salt electrolyte has been reported to exhibit significant effects on the stability and electrochemical properties of ZIBs. Therefore, the exploration of suitable electrolytes is critical to control the Zn\(^{2+}\) reaction kinetics at the electrode/electrolyte interface.

Since the first use of a mild acidic or neutral electrolyte containing Zn\(^{2+}\) for ZIB application, such as ZnSO\(_4\) or Zn(NO\(_3\))\(_2\), a series of other zinc salts including Zn(CH\(_3\)COO)\(_2\), ZnF\(_2\), Zn(ClO\(_4\))\(_2\), ZnCl\(_2\), Zn(TFSI)\(_2\), and Zn(CF\(_3\)SO\(_3\))\(_2\) have been then explored for achieving high-performance aqueous ZIBs.[14,15,126–128] Although a mild acidic or neutral liquid electrolytes exhibit several advantages, some critical issues such as water-induced side reactions, uncontrollable solid–liquid interface reactions, cost, and corrosion-induced instability effects have greatly limited their practical applications for ZIBs. Table 3 summarizes the typical aqueous electrolytes for ZIBs in terms of their advantages and disadvantages based on previously reported works.[14,15,126–128] Overall, the types of zinc salt in the neutral electrolyte are likely to affect the overall zinc storage properties for ZIBs such as operating electrochemical potential window, reversible electrochemical reaction, and the reaction kinetics for Zn deposition and dissolution.

Besides the types of zinc salt, salt concentration and the choice of solvent are also revealed to have significant effects on the interfacial (de)solvation kinetics at the electrode/electrolyte interface.[125,129,130] Zhang et al. revealed that a better
The electrochemical performance is observed for the same electrolyte with a higher concentration, including enhanced cycling stability, wider operating potential window, improved specific capacity, and higher Coulombic efficiency of active ions. The obtained results can be attributed to the formation of an effective electrode–electrolyte interface with suppressed dendrite growth and negligible water-induced activity by an ultrahigh concentration zinc salt solution has been introduced into ZIBs by Wang et al. They further revealed that at LiTFSI concentration of more than 20 m, the TFSI\(^-\) can alter the Zn solvation behavior by eliminating the water molecules around Zn\(^{2+}\), which not only promote the electrochemical stability and kinetics but also inhibit the water-induced side reactions. However, the high voltage polarization induced by the concentrated electrolyte and the expensive Li/Zn salts with fluorinated anions has limited their practical applications. In addition, Han et al. further revealed that zinc electrolyte with organic solvents such as acetonitrile–Zn(TFSI)\(_2\), acetonitrile–Zn(CF\(_3\)SO\(_3\))\(_2\), and propylene carbonate–Zn(TFSI)\(_2\) electrolytes can provide better anodic stability (up to \(\approx 3.8\) V vs Zn/Zn\(^{2+}\)) and enable highly reversible Zn deposition behavior on a Zn metal anode. They demonstrated that types

| Cathode material | Morphology | Reaction mechanism | Potential window [V] | Main anodic and cathodic peaks [V] | Discharge capacity |
|-----------------|------------|-------------------|----------------------|-----------------------------------|------------------|
| α-MnO\(_2\) \(^{[38]}\) | Nanoparticles (20 nm) | Zn\(^{2+}\) ion insertion/extraction | 1–2 | 1.75 and 1.25 | 234 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| δ-MnO\(_2\) \(^{[36]}\) | Nanoplatelets (10–20 nm) | Zn\(^{2+}\) ion insertion/extraction | 1–2 | 1.7 and 1.3 | 213 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| γ-MnO\(_2\) \(^{[36]}\) | Spherical agglomerate nanosheets | Zn\(^{2+}\) ion insertion/extraction | 1–2 | 1.7 and 1.35 | 269 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| β-MnO\(_2\) \(^{[36]}\) | Spherical agglomerate nanosheets | Zn\(^{2+}\) ion insertion/extraction | 1–2 | 1.7 and 1.3 | 201 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| CuV\(_2\)O\(_6\) \(^{[85]}\) | Nanorods | Zn\(^{2+}\) ion insertion/extraction | 1–1.8 | 1.65/1.6 and 1.38/1.1 | 270 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| VS\(_2@SS\) \(^{[99]}\) | Hierarchical flower-like on stainless steel | Reduction and oxidation of Cu\(^{2+}\), Zn\(^{2+}\) ion insertion/extraction | 0.3–1.6 | 1.13/1.01/0.85 and 1.06/0.88/0.76 | 361 mA g\(^{-1}\) (200 mA g\(^{-1}\)) |
| V\(_2\)O\(_5/graphene\) \(^{[101]}\) | Ultrathin layer 2D nanosheet (≤ 5 nm) | Zn\(^{2+}\) ion insertion/extraction | 0.4–1.0 | 0.72/0.75 and 0.58/0.63 | 159.1 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| Mn\(_2\)O\(_4\) \(_{16}\) (H\(_2\)O)\(_{27}\) (MON) \(^{[93]}\) | Nanosheet (≤2.5 nm) | H\(^+/\)Zn\(^{2+}\) ion insertion/extraction | 1–1.8 | 1.55/1.6 and 1.21/1.37 | 300 mA g\(^{-1}\) (0.1C) |
| VS\(_2@SS\) \(^{[99]}\) | Hierarchical flower-like on stainless steel | Zn\(^{2+}\) ion insertion/extraction | 0.4–1 | 0.78/0.69 and 0.69/0.58 | 187 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| VS\(_2\) \(^{[99]}\) | Commercial bulk | Multistep Zn\(^{2+}\) ion insertion/extraction | 0.2–1.6 | 1.4/1.1/0.7/0.6 and 1.35/0.95/0.8/0.6/0.35 | 459 mA g\(^{-1}\) (500 mA g\(^{-1}\)) |
| Na\(_2\)V\(_2\)O\(_5\) H\(_2\)O/RGO/CNT \(^{[101]}\) | Nanosheet | Zn\(^{2+}\) ion insertion/extraction | 0.5–1.5 | 1.15 and 0.9 | 174 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| Hydrophilic composite cathode (HCC)-V\(_2\)S\(_4\) \(^{[102]}\) | Nanospherical/composite carbon heterostructure | Zn\(^{2+}\) ion insertion/extraction | 1.0–1.9 | 1.55/1.6 and 1.26/1.39 | 332.2 mA g\(^{-1}\) (300 mA g\(^{-1}\)) |
| MnO\(_2/RGO\) \(^{[88]}\) | Nanosheet | H\(^+\) and Zn\(^{2+}\) ion insertion/extraction | 1–1.9 | 1.55/1.6 and 1.26/1.39 | 259.1 mA g\(^{-1}\) (mA g\(^{-1}\)) |
| MnO\(_2\) \(^{[36]}\) | Nanosheet | Zn\(^{2+}\) and Zn\(^{2+}\) ion insertion/extraction | 0.3–1.5 | 1.28 and 0.64 | 202.6 mA g\(^{-1}\) (mA g\(^{-1}\)) |
| Mn\(_2\)O\(_4\) \(_{16}\) (H\(_2\)O)\(_{27}\) (MON) \(^{[93]}\) | Nanosheet | Multistep Zn\(^{2+}\) ion insertion/extraction | 0.8–1.8 | 1.61/1.38 and 1.38/1.16 | 350 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| MnO\(_2/CNT\) \(^{[14]}\) | Commercial bulk | Multistep Zn\(^{2+}\) ion insertion/extraction | 0.2–1.5 | 1.08/0.81 and 0.85/0.56 | 314 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| V\(_2\)O\(_5\) \(^{[25]}\) | Commercial bulk | Zn\(^{2+}\) and Zn\(^{2+}\) ion insertion/extraction | 0.2–1.5 | 0.97/0.62 and 0.98/0.97 | 410 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
| V\(_2\)O\(_5\) \(^{[112]}\) | Yolk–shell | Zn\(^{2+}\) and Zn\(^{2+}\) ion insertion/extraction | 0.3–1.5 | 0.99/0.71 and 0.89/0.55 | 219 mA g\(^{-1}\) (100 mA g\(^{-1}\)) |
of solvent exhibited significant effect in determining the anodic stability of most zinc salt electrolytes except for Zn(TFSI)2. Other approach such as the introduction of additives has been widely employed to inhibit the Zn dendrite formation and the cathode dissolution effect.\[50,131\] It is widely reported that preaddition of metal ion salts such as Na2SO4, MnSO4, etc., in aqueous ZnSO4 electrolyte can promote the reversibility of the cathodic reaction and reduce the cathode dissolution effect.\[50,131\] Recently, Song et al. have further employed various imidazolium ionic liquids as the additives for the ammoniacal electrolytes.\[131\] They revealed that imidazolium ionic liquid additives with different anions can coordinate with metal ions to form the new reduced species to alter the electrode/electrolyte interfacial properties, thereby directly regulate the growth of dendritic zinc, and improve the formation of compact deposits. Nonetheless, the addition of these additives will greatly alter the cathode–electrolyte interfacial reaction and the electrochemical reactions, leading to a series of complex electrochemical reactions and may induce unwanted side reactions that worsen their performance.

5. Summary

In summary, aqueous ZIBs have been considered as promising alternatives for large-scale energy storage systems. Despite the aforementioned achievements, many challenges still exist in aqueous ZIB applications. This review presents the issues in searching appropriate cathode materials for ZIBs, including the lack of suitable Zn2+ insertion/extraction cathode materials and controversial reaction mechanisms. Also, we summarize the recent progress in the microstructure engineering of cathode materials for ZIBs and classify them into crystalline structure optimization, crystal defect engineering, interlayer engineering, and morphology engineering. The recent exciting research advances on the investigation of various cathode materials for aqueous ZIBs have demonstrated their great potential in developing large-scale energy storage systems. Nonetheless, the research field is still in its infancy, and there are still many fundamental issues that need to be tackled toward advanced cathode materials for ZIBs. Therefore, future efforts should be employed for the following aspects to pursuing advanced cathode materials for ZIBs, as discussed below.

First, the cathode electrolyte interface remains a key factor that limited the practical development of ZIBs. In ZIBs, the interface between the electrode and electrolyte is important in determining the electrochemical stability window and governing the overall reaction mechanisms. Most of the current research has been focusing on the exploration of suitable electrolyte with wide electrochemical stability window and little water-induced side reactions to mitigate interface reaction. Owing to the complexities of cathode electrolyte interface composition and structure that are readily influenced by the type of electrolyte, concentration of electrolyte, additives, and electrochemical measurement condition, the interface issues such as interfacial contact and chemical compatibility of the electrolyte with both electrodes remains a great obstacle for the development of ZIBs. A deep understanding of cathode electrolyte interface formation and evolution based on the cathode properties is critical for the interface design of high voltage ZIBs.

Second, as defect engineering has been demonstrated as a promising approach for modulating the electrochemical activity of cathode materials for ZIBs, more in-depth characterization techniques such as in situ microscopic techniques (e.g., in situ transmission electron microscopy (TEM) and scanning tunneling microscope (STM)) are required for understanding the reaction pathway and the interactions between defects and Zn2+ during cycling. Nonetheless, existing research works usually simply characterize the existence of defects and then propose an outstanding effect on electrochemical performance. It is well-known that some defects are not always stable under practical conditions, resulting in unsatisfactory durability. The development of advanced in situ characterization enables real-time monitoring of the defect condition during the charge/discharge process, which helps researchers to establish the fundamental relationship of defect performance. Moreover, synthesis methodology with
controllable defect species and concentration is essential to realize defect functionalization and obtain a fundamental understanding of the defect-driven mechanism.

Third, considering the promising potential of layered materials as cathode materials for ZIBs, guidelines on the selection of suitable intercalated foreign species for obtaining appropriate interlayer expansion and promoting device performance are yet to be established. Previous studies have demonstrated that metal-ion intercalation, such as Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), and Zn\(^{2+}\), can act as pillars to improve the electrochemical performance of layered vanadium oxide cathode materials.\(^{[77–81]}\) However, the layered vanadium oxide cathode materials still suffer from structural degradation due to the large molecular weight and the volume of metal ions upon repeated insertion and extraction of zinc ions. Therefore, more efforts shall focus on overcoming the induced-structural degradation effects of metal-ion intercalation effect by introducing the co-intercalation of alkaline ions together with inactive small molecules and optimizing the electrolyte composition. Also, the intercalation and degradation mechanism of metal-ion intercalation in the host deserves much attention. Recently, the insertion of other neutral molecules or clusters such as polymeric materials has been investigated to modulate the interlayer spacing, which can avoid phase transition and provide stability to the extended interlayer structure for ZIBs. Nonetheless, the insertion of neutral molecules is still relatively less reported and should be further explored.

Fourth, rational microstructure engineering has provided structural benefits such as high surface to mass/volume ratio, improved conductivity, intensive chemical active sites, and stable framework and overcomes the intrinsic issues of bulk materials, such as electronic conductivity and structural stability, rendering ZIBs with high capacity, and stable cycling. However, most of these achievements were obtained with relatively low areal loading of cathode material (<1 mg cm\(^{-2}\)). To pave the way to practically viable ZIBs, the development of advanced self-standing cathodes with an industrial-level areal capacity (≥35 mAh cm\(^{-2}\)), superior gravimetric capacity, excellent rate, and cycling stability simultaneously is essential.\(^{[124]}\) With the increase of cathode loading, electrode–electrolyte interfacial issues that are possibly incu- bative under low loading may rise. More comprehensive works shall be employed to explore strategies toward advanced high-loading ZIBs.

Finally, the existence of zinc dendrite in the neutral electrolyte is remaining a great challenge to the practical application of aqueous ZIBs. Many approaches have been devoted to eliminating dendrites such as liquid electrolyte composition optimization, solid-state electrolyte, and electrode design.\(^{[132–134]}\) Specifically, the use of ultrahigh concentrated electrolyte with organic anions and organic cosolvent as additives has been reported to effectively suppress the dendrite deposition of zinc metal.\(^{[125]}\) However, the side effects of decayed H\(^+\) storage capacity still need more enhancement. Solid-state electrolytes such as poly(ethylene oxide) (PEO)–ZnX\(_2\) complexes (X = Cl, Br, I, ClO\(_4\), and CF\(_3\)SO\(_4\)), poly(vinylidine fluoride)/PEO–Zn(CF\(_3\)SO\(_4\))\(_2\) etc., have been introduced to physically shield dendrite growth but the low electronic conductivity in solid-state electrolyte induce huge solid–solid interface impedance, which reduces the rate capability of ZIBs. Electrode interface designs such as the electrode surface coating\(^{[135,137]}\) and application of 3D Zn hosts with conducting graphitic network\(^{[138,139]}\) as well as low-current-densities-controlled electrohealing methodology\(^{[122]}\) with slow galvanostatic charge/discharge appear to be economical approaches to eliminate the formation of zinc dendrite without degrading battery performance.\(^{[122]}\) Nonetheless, the practical parameters such as current density, stripped and/or deposited capacity, and the interelectrode distance, which can significantly manipulate the Zn cycling performance, were usually not taken into consideration. Therefore, much attention shall be focused to consider and evaluate the experimental conditions based on the practical conditions for achieving commercial large-scale storage applications.

Acknowledgements

The authors acknowledge funding support from the Ministry of Education, Singapore, under its MOE Tier2 Grant No. MOE2019-T2-1-181.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cathode materials, microstructural engineering, zinc-ion aqueous batteries

Received: July 19, 2020
Published online: November 19, 2020

[1] J. M. Tarascon, M. Armand, Nature 2001, 414, 359.
[2] N. Nitta, F. Wu, J. T. Lee, G. Yushin, Mater. Today 2015, 18, 252.
[3] M. A. Hannan, M. S. H. Lipu, A. Hussain, A. Mohamed, Renewable Sustainable Energy Rev. 2017, 78, 834.
[4] Y. Fang, L. Xiao, Z. Chen, X. Ai, Y. Cao, H. Yang, Electrochim. Energy Rev. 2018, 1, 294.
[5] K. Liu, Y. Liu, D. Lin, A. Pei, Y. Cui, Sci. Adv. 2018, 4, eaas9820.
[6] Z. P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. Chen, Nat. Energy 2018, 3, 279.
[7] C. Xu, B. Li, H. Du, F. Kang, Angew. Chem., Int. Ed. 2012, 51, 933.
[8] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, Nature 2015, 520, 324.
[9] D. Selvakumaran, A. Pan, S. Liang, G. Cao, J. Mater. Chem. A 2019, 7, 18209.
[10] G. Fang, J. Zhou, A. Pan, S. Liang, ACS Energy Lett. 2018, 3, 2480.
[11] F. Wan, Z. Niu, Angew. Chem., Int. Ed. 2019, 58, 16358.
[12] C. Li, X. Xie, S. Liang, J. Zhou, Energy Environ. Mater. 2020, 3, 146.
[13] J. Meng, J. Guo, C. Xia, W. Wang, H. N. Alshareef, Mater. Sci. Eng., R 2019, 135, 58.
[14] M. Song, H. Tan, D. Chao, H. J. Fan, Adv. Funct. Mater. 2018, 28, 1802564.
[15] Y. Zhao, Y. Zhu, X. Zhang, Infomat 2020, 2, 237.
[16] B. Tang, L. Shan, S. Liang, J. Zhou, Energy Environ. Sci. 2019, 12, 3288.
[17] W. Xu, C. Sun, K. Zhao, X. Cheng, S. Rawal, Y. Xu, Y. Wang, Energy Storage Mater. 2019, 16, 527.
[18] T. Xiong, Z. G. Yu, H. Wu, Y. Du, Q. Xie, J. Chen, Y.-W. Zhang, S. J. Pennycook, W. S. V. Lee, J. Xue, Adv. Energy Mater. 2019, 9, 1803815.
[19] C. Zhu, G. Fang, S. Liang, Z. Chen, Z. Wang, J. Ma, H. Wang, B. Tang, X. Zheng, J. Zhou, Energy Storage Mater. 2020, 24, 394.
Zhaojun Han is with the Faculty of Engineering, The University of New South Wales (UNSW), and the Commonwealth Scientific and Industrial Research Organisation. His research focuses on developing low-dimensional functional materials, including carbon nanotubes, graphene, and metal oxide nanostructures, to tackle the challenges in materials, energy, and environmental science.

Hui Ying Yang is currently an associate professor at the Pillar of Engineering Product Development, Singapore University of Technology and Design, Singapore. She studies low-dimensional nanomaterials for electrochemical energy-storage and water-treatment devices, which are centered on exploring the influence of functional engineering and chemical doping on the synthesis of materials and device performances. Her team is applying fundamental knowledge and new manufacturing methods to develop exceptional nanoscale materials and structures for efficient lithium storage and scalable-water purification.