Developing high-performance aqueous Zn-based batteries with mild electrolyte

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Developing high-performance aqueous Zn-based batteries with mild electrolyte

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This thesis is submitted to fulfil the requirement for the award of the degree

Doctor of Philosophy

Institute for Superconducting and Electronic Materials
Australian Institute of Innovative Materials
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Certification

I, Junnan Hao, declare that the original work presented in this thesis was carried out in the laboratories of the Institute for Superconducting and Electronics Materials, University of Wollongong, Australia, and has not been submitted for a degree to any other academic institution for higher education.

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Junnan Hao

19th Jun 2020
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How time flies, it has been almost four years since I first arrived at Wollongong, Australia for pursuing my Ph.D. degree. In my opinion, this life journey is a valuable experience. On one hand, leaning abroad is challenging. Since everything for me was new at that time, I had to start a new life without my family numbers and friends. On the other hand, leaning abroad is interesting. Its significantly broadened my horizons, as I meet lots of new friends who come from different countries, which makes me learn about the different culture and living habits. This four-year learning experience has definitely enriched my life, improved my characters, and even changed my destiny. Here, I would like to take this great opportunity to express my sincere gratitude to my supervisors, families, friends, and colleagues.

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Abstract

Aqueous Zn-ion batteries (ZIBs) with the mild electrolyte, as a highly promising alternative to lithium-ion batteries (LIBs) for the grid application, have gained a considerable attention in recent ten years. Nevertheless, state-of-the-art ZIB technique is far from satisfactory. To date, numerous strategies have been proposed to develop the advanced ZIBs, including the exploring of high-performance cathode candidates and their working mechanism, developing new functional electrolytes, and designing advanced Zn metal electrodes, which is reviewed in this thesis. My doctoral work main focuses on enhancing the performance of aqueous Zn-based batteries by optimizing the Zn electrode, including introducing electrolyte additive, ex-situ and in-situ building the artificial solid/electrolyte interphase (SEI) layers on Zn metal electrode. In addition, the insights of the promoted electrochemical performance of Zn electrode are thoroughly studied.

In the first case, the effects of electrolyte additive, sodium dodecyl benzene sulfonate, on the electrochemical performance of hybrid LiFePO₄(LFP)/Zn battery was studied. The results show the additive modifies the intrinsic deposit pattern of Zn²⁺ ion, rendering dendrite-free Zn plating/stripping highly reversible in aqueous media. Meanwhile, the wettability of LFP electrode was visibly meliorated by introducing this additive, accelerating the Li-ion diffusion at the LFP electrode/electrolyte interface. Benefiting from these effects, the LFP/Zn batteries deliver high rate capability and cycling stability in both coin-cell and pouch-cell. More importantly, this additive could also be extended to aqueous MnO₂/Zn battery, assisting in its encouraging cycling stability.

In the second case, Zn metal plating/stripping mechanism is thoroughly investigated in 1 M ZnSO₄ electrolyte, demonstrating that the poor performance of Zn metal in mild electrolyte should be ascribed to the formation of a porous by-product (Zn₄SO₄(OH)₆·xH₂O) layer, H₂
Abstract

evolution, and serious dendrite growth. To suppress the side reactions and dendrite growth, a highly viscoelastic polyvinyl butyral (PVB) film, functioning as an artificial SEI layer, is homogeneously deposited on the Zn surface via a simple spin-coating strategy. This dense artificial SEI film not only effectively blocks water from the Zn surface but also guides the uniform stripping/plating of Zn ions underneath the film due to its good adhesion, hydrophilicity, ionic conductivity, and mechanical strength. Consequently, this side-reaction-free and dendrite-free Zn electrode exhibits high cycling stability and enhanced Coulombic efficiency (CE), which also contributes to enhancement of the full-cell performance when it is coupled with MnO₂ and LiFePO₄ cathodes.

In the third case, a robust and homogeneous ZnS interphase is in-situ built on Zn surface by a vapour-solid strategy to enhance Zn reversibility. The thickness of ZnS film is controlled via treatment temperature, thus the performance of the protected Zn electrode is optimized. The dense ZnS artificial layer obtained at 350 °C not only suppresses Zn corrosion by forming a physical barrier on the Zn surface, but also inhibits dendrite growth via guiding the homogenous Zn plating/stripping. Accordingly, a side reaction-free and dendrite-free Zn electrode is developed, whose effectiveness is also convincing in a MnO₂/ZnS@Zn full-cell with 87.6% capacity retention after 2500 cycles.

In summary, the poor CE and limited reversibility of Zn electrode due to the Zn electrode corrosion, H₂ evolution, and Zn dendrite growth in mild electrolyte seriously restrains the further development of aqueous Zn-based batteries. To develop the high-performance Zn anode by addressing Zn issues is of great importance to enhance the performance of Zn-based batteries. I believe this doctoral work can offer a good understanding of Zn metal surface chemistry and pave the way to developing the practical Zn metal batteries with mild electrolyte.
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lifespan from \( \sim 100 \) h to \( \sim 250 \) h, the performance of the polished Zn cell is still far from satisfactory due to the notorious Zn dendrite growth and uninterrupted side reactions.

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### Abbreviations

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<td>LIB</td>
<td>Lithium-ion battery</td>
</tr>
<tr>
<td>NIB</td>
<td>Sodium-ion battery</td>
</tr>
<tr>
<td>KIB</td>
<td>Potassium-ion battery</td>
</tr>
<tr>
<td>ZIB</td>
<td>Zinc-ion battery</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
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<td>Two-dimensional</td>
</tr>
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<td>Atomic force microscope</td>
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<td>Polyvinylidene fluoride</td>
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<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Wetting free energy</td>
</tr>
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<td>Energy dispersive X-ray spectroscopy</td>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<td>GITT</td>
<td>Galvanostatic intermittent titration technique</td>
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<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>----------------------------------</td>
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<td>Metal element</td>
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<td>Centimeter</td>
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<td>Millimeter</td>
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<td>Nanometer</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
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<td>Raman Spectroscopy</td>
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<td>Lithium ions</td>
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<tr>
<td>Zn²⁺</td>
<td>Zinc ions</td>
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<td>Milliamperre</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
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<td>SEI</td>
<td>Solid electrolyte interphase</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna Ab-Initio Simulation Package</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized gradient approximation</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
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<tr>
<td>SDBS</td>
<td>Sodium dodecyl benzene sulfonate</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<td>--------------</td>
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<tr>
<td>PVB</td>
<td>Polyvinyl butyral</td>
</tr>
<tr>
<td>LFP</td>
<td>LiFePO₄</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>SBS/C</td>
<td>Few-layered antimony sulphide/carbon sheets</td>
</tr>
<tr>
<td>σ</td>
<td>Conductivity</td>
</tr>
<tr>
<td>$t_{zn^{2+}}$</td>
<td>Transference number</td>
</tr>
<tr>
<td>C</td>
<td>Current rate</td>
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## Organizations

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<th>Full name</th>
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<tr>
<td>ARC</td>
<td>Australian Research Council</td>
</tr>
<tr>
<td>ISEM</td>
<td>Institute for Superconducting and Electronic Materials</td>
</tr>
<tr>
<td>AIIM</td>
<td>Australian Institute of Innovative Materials</td>
</tr>
<tr>
<td>EMC</td>
<td>Electron Microscopy Centre</td>
</tr>
<tr>
<td>UOW</td>
<td>University of Wollongong</td>
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Chapter 1

Introduction

1.1 Research background

The research on clean energy has been boosted over past decades, but the intermittent nature of these renewable resources requires an effective medium to store and transfer energy. Among the various energy storage technologies, rechargeable batteries have been regarded as among the most feasible and reliable devices, and they already play a prominent role in our modern lives.\(^1\)\(^2\) For example, lithium-ion batteries (LIBs) have been dominated portable electronics due to their high energy density, long cycle life, and high energy efficiency. They are also now being used in electric vehicles (EVs) and in large-scale energy storage for the electrical grid. The limited nature of lithium resources and the increasing prices of LIBs have aroused great concern, however, which has led to the development of sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs), because sodium and potassium are abundant and relatively low cost.\(^3\)\(^-\)\(^5\) Even so, the application of LIBs, SIBs, and PIBs still presents safety and environmental challenges, especially for large-scale energy storage due to the use of toxic, flammable, and volatile organic electrolytes.

Compared to nonaqueous batteries, aqueous batteries have the advantages of low cost, high safety, high ionic conductivity, easy processing, and reduced manufacturing cost, so that they are ideally suited for large-scale energy storage applications.\(^6\) Because of the narrow electrochemical window of water (Figure 1.1a),\(^7\) the exploration, design, synthesis, and application of electrode materials that are compatible with aqueous electrolytes are critical to achieve satisfactory performance in aspects such as long cycle life and high power/energy density for practical applications, although achieving this is a great challenge.
Figure 1.1 a) Pourbaix diagram of Water. Reproduced with permission from Wikipedia.[7] b) Aqueous rechargeable batteries working in different pH ranges. Reproduced with permission.[8] Copyright 2018, Society of Photo-optical Instrumentation Engineers (SPIE). c) Pourbaix diagram of the Zn/H$_2$O system, 10$^{-4}$ M Zn$^{2+}$ considering ZnO as solid substance. Reproduced with permission.[10] Copyright 1991, Elsevier.

To date, various aqueous rechargeable batteries working in different pH ranges have been reported, as presented in Figure 1.1b.[8] The applications of strongly acidic and alkaline batteries have suffered, however, due to their poor cycle life, low energy density, and the serious ecological threat posed by them. For example, the lead (Pb)-based acidic batteries suffer from low energy density (~30 Wh kg$^{-1}$), poor cycle life (200 cycles for deep cycling), the corrosivity of the strong acid used as electrolyte and the toxicity of Pb. In the case of the nickel (Ni)-based alkaline batteries, in addition to the corrosivity of the strongly alkaline electrolyte, Ni-Cd suffers from the low energy density and the toxic nature of Cd, while nickel metal hydride (Ni-MH) suffers from the low energy density, limited high-rate capability and high self-discharge. In contrast, aqueous metal-ion batteries (M = Li, Na, K, Mg, Zn, Ca, Al) using less corrosive, near-neutral electrolytes show enhanced energy density and cycle life compared with their acidic and alkaline siblings, since the charge is reversibly stored in a host material where the structure does not change.
significantly. In principle, most of the intercalation type materials used in organic electrolyte can be used in aqueous electrolyte, but they are subject to the narrow stable electrochemical window of water (~1.23 V). Also, compared to cathode materials, finding suitable anode materials is more challenging. As shown in Table 1.1, metal anodes could provide low voltages and large specific capacities, so as to maximize battery energy densities. Apart from Zn, however, other metals cannot be directly used as anode in aqueous electrolytes, since their electrochemical redox voltages are outside of the stable potential window of water. Therefore, the Holy Grail remains the discovery of suitable anode materials for application in current aqueous rechargeable battery systems.

Table 1.1 Comparison of monovalent and multivalent metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic mass</th>
<th>Standard potential (V) vs. SHE</th>
<th>Gravimetric capacity (mA h g⁻¹)</th>
<th>Volumetric capacity (mA h cm⁻³)</th>
<th>Ionic radius (Å)</th>
<th>Abundance in the Earth’s crust (ppm)</th>
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<td>Li</td>
<td>6.94</td>
<td>−3.040</td>
<td>3860</td>
<td>2061</td>
<td>0.76</td>
<td>20</td>
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<tr>
<td>Na</td>
<td>23.00</td>
<td>−2.713</td>
<td>1166</td>
<td>1129</td>
<td>1.02</td>
<td>23550</td>
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<tr>
<td>K</td>
<td>39.10</td>
<td>−2.924</td>
<td>685</td>
<td>610</td>
<td>1.38</td>
<td>20850</td>
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<tr>
<td>Mg</td>
<td>24.31</td>
<td>−2.356</td>
<td>2206</td>
<td>3834</td>
<td>0.72</td>
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<tr>
<td>Ca</td>
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<td>1337</td>
<td>2072</td>
<td>1.00</td>
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<td>Zn</td>
<td>65.41</td>
<td>−0.763</td>
<td>820</td>
<td>5855</td>
<td>0.75</td>
<td>70</td>
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<tr>
<td>Al</td>
<td>26.98</td>
<td>−1.676</td>
<td>2980</td>
<td>8046</td>
<td>0.53</td>
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</table>

Metallic Zn is unique in aqueous electrolyte due to its low redox potential (−0.76 V vs. standard hydrogen electrode (SHE)) and high over-potential for hydrogen evolution (Figure 1.1c) [10-14]. Furthermore, the theoretical capacity of metallic Zn is 820 mA h g⁻¹, which is higher than for the intercalation type anode materials that can be used in aqueous electrolyte. Therefore, based on its low redox potential, high capacity, abundance, and nontoxicity, Zn is a very promising anode material for aqueous batteries [14-16]. As anode, Zn is not only used in aqueous zinc ion batteries
(AZIBs), but also in aqueous Zn hybrid batteries [17]. The difference between them is that the zinc ion batteries work based on the movement of Zn$^{2+}$ ions between the cathode and Zn anode, whereas two different ions are involved in the Zn hybrid batteries: Zn stripping/plating on the anode side, and extraction/insertion of Li/Na/K or another multivalent metal ion on the cathode side, as shown in Figure 1.2. Both aqueous ZIBs and hybrid Zn batteries with mild aqueous electrolyte have been attracting tremendous attention in recent ten years [18-20]. Although the aqueous Zn battery technique is promising as an alternative of LIBs in the large-scale energy storage, the challenges are still there, such as less high-performance cathode candidates, poor reversible Zn metal anode, and the unclear mechanism of side reaction between Zn electrode and mild electrolyte.

![Figure 1.2](image)

**Figure 1.2** Schematic illustrations of the principles of (a) aqueous ZIBs and (b) aqueous Zn hybrid batteries.

### 1.2 Objectives of the research

As discussed above, Zn-based batteries with mild electrolytes have been attracted aggressive research efforts in the past ten years, however, most of them have been spent on exploration of cathode candidates as well as their Zn$^{2+}$ storage mechanisms. Unfortunately, Zn metal anode so far has attracted much less attention than it deserved. Zn anode persistently suffers from the poor CE and limited reversibility in mild electrolyte due to the dendrite growth and side reactions (including Zn electrode corrosion and H$_2$ evolution). The poor performance of
Zn electrode gravely restrains the development of aqueous Zn-based batteries. Therefore, the purpose of such research is developing the advanced Zn metal electrode via suppressing the Zn dendrite and side reactions. In this doctoral thesis, the surface chemistry of Zn metal electrode in electrolyte of 1 M ZnSO$_4$ solution has been studied, indicating that the Zn dendrite growth is the main potential hazard for the battery failure by leading the short circuit. Meanwhile, the fresh Zn metal is highly unstable in 1 M ZnSO$_4$ electrolyte and generates a loose Zn$_4$SO$_4$(OH)$_{6-x}$H$_2$O layer that cannot block the electrolyte to protect Zn electrode, and simultaneously produces hydrogen gas which easily causes the battery swelling. To address the Zn electrode issues, different strategies have been proposed including introducing electrolyte additions and building artificial SEI layers, which effectively enhance the Zn metal electrode performance.

1.3 Thesis structure

The structure of this thesis work is briefly outlined as follows

Chapter 1 introduces the background for aqueous batteries and the background for the Zn-based batteries with mild electrolyte.

Chapter 2 presents a literature review on cathode materials, Zn$^{2+}$ storage mechanism, electrolyte, as well as the Zn anodes of aqueous Zn-based batteries.

Chapter 3 illustrates the general experimental procedures including functional Zn electrodes preparation, physical characterization methods, and the electrochemical measurements.

Chapter 4 introduces the electrolyte additive effects on the Zn metal electrode and cathode material in aqueous hybrid Zn-based batteries

Chapter 5 displays an artificial polymer layer on Zn electrode surface towards the dendrite-free and side reaction-free Zn anode for advanced aqueous Zn-based batteries.

Chapter 6 investigates stability and Zn plating/stripping effects of the passivation
layer on Zn metal electrode in mild electrolyte. Meanwhile, artificial ZnS layer was built on Zn metal surface via an in-situ strategy to inhibit the dendrite growth and side reactions.

Chapter 7 summarizes the work in this thesis and provides some prospects for development of high-performance Zn-based batteries with mild electrolyte.

1.4 References


Chapter 2

Literature review

2.1 Progress on cathode materials

In past ten years, various cathode materials have been developed to storage Zn$^{2+}$ ion in aqueous Zn batteries, which can be divided into five different types: transition-metal oxides, transition metal sulfides, polyanion compounds, Prussian blue analogues, and organic cathodes. These five types materials have been reviewed in detail as follows.

2.1.1 Transition-metal oxides

2.1.1.1 Tunnel oxides

Motivated by the low cost, environmental compatibility, and large theoretical capacity of MnO$_2$, electrochemical intercalation of Zn-ions in a number of known MnO$_2$ polymorphs has received much attention. The fundamental building units, MnO$_6$ octahedra, can be linked by sharing edges and/or corners, forming varieties of MnO$_2$ polymorphs with different crystallographic structures (Figure 2.1a).[1] Typical tunnel structures, as in $\alpha$-MnO$_2$ (2 × 2), $\beta$-MnO$_2$ (1 × 1), $\gamma$-MnO$_2$ (1 × 1 and 1 × 2), todorokite-type MnO$_2$ (3 × 3), and spinel-type MnO$_2$ (3D tunnels), can accommodate different cations or coordination ions. During Zn insertion into the 2 × 2 tunnels, the $\alpha$-MnO$_2$ nanorods display considerable structural stability by accommodating a unit cell volume expansion of only 3.12%, enabling a high initial discharge capacity (233 mA h g$^{-1}$ at 83 mA g$^{-1}$) with nearly 100% Coulombic efficiency (CE) during long-term cycling.[2] Although $\beta$-MnO$_2$ has the narrowest tunnels compared with other MnO$_2$ polymorphs, it possesses the most thermodynamically stable structure.[3] As a result of their stability and compact tunnel structure, $\beta$-MnO$_2$ nanorods ensure reversible insertion/extraction of Zn ions, in contrast to their inactive bulk counterpart. The storage mechanism of $\beta$-MnO$_2$ as electrode material for AZIBs remains controversial. Kim et al.[3] claimed that $\beta$-MnO$_2$ transforms into a spinel structure during repeated Zn-ion
(de)intercalation, challenging the previous view that \( \beta \)-MnO\(_2\) electrodes undergo a phase transition to a layered structure (Zn-buserite) in the first discharge process, which allows for reversible insertion of Zn\(^{2+}\) in the following cycles. Mesoporous \( \gamma \)-MnO\(_2\) has also been investigated in-depth as a host material for aqueous ZIBs\([4]\). The mesoporous \( \gamma \)-MnO\(_2\) cathode exhibits a plateau around 1.25 V and a high capacity of 285 mA h g\(^{-1}\) at 0.05 mA cm\(^{-2}\). The reaction process of Zn-insertion into \( \gamma \)-MnO\(_2\) is illustrated in Figure 2.1b. With the continuous intercalation of Zn\(^{2+}\), the parent \( \gamma \)-MnO\(_2\) undergoes a transformation into ZnMn\(_2\)O\(_4\) (a spinel-type phase), tunnel-type \( \gamma \)-Zn\(_x\)MnO\(_2\), and layered-type L-Zn\(_y\)MnO\(_2\). The three phases coexist on the completion of Zn-insertion, a majority of which can revert back to the orthorhombic \( \gamma \)-MnO\(_2\) phase on the completion of Zn-extraction. The large 3 \( \times \) 3 tunnels of todorokite-type MnO\(_2\) allow for fast and reversible Zn\(^{2+}\) intercalation. The structural water in the wide tunnel can effectively reduce the electrostatic interaction between Zn\(^{2+}\) and the host. Tunnedell Mn\(_2\)O\(_3\) and Mn\(_3\)O\(_4\) have also shown good electrochemical performance as host materials for AZIBs.\([5-6]\) In addition, Yang and co-workers enriched the tunnel-oxide cathode family by exploring VO\(_2\)(B) nanofibers\([7]\). It is confirmed that VO\(_2\)(B) with its large tunnel size (0.82 and 0.5 nm\(^2\) along the \( b \)- and \( c \)-axes, respectively) ensures ultrafast kinetics of Zn\(^{2+}\) that is moving into the unique tunnels with little structural change. \textit{In-situ} XRD analysis revealed an intercalation pseudocapacitance mechanism in the VO\(_2\)(B) electrode, accounting for the highest rate capability seen in AZIBs so far (171 mA h g\(^{-1}\) at 300 C, Figure 2.1c).
2.1.1.2 Layered oxides

Layered type MnO₂ cathode with large interlayer spacing of 0.7 nm has been synthesized and used in AZIBs. Kim et al. observed an irreversible phase transformation from layered MnO₂ to spinel ZnMn₂O₄ after prolonged cycling, and typical characteristics of only Zn²⁺ (de)intercalation.⁷ More comprehensive studies are required to unravel the mystery of the reaction mechanism of layered MnO₂. Since the vanadium oxidation states and V-O coordination polyhedra are various, diverse layered vanadium oxides with open frameworks have been constructed for the storage of Zn²⁺ in AZIBs. Typically, the V₂O₅ is built up from...
square pyramid layers and the large space between the layers is suitable for the insertion of Zn ions.[8] Recent studies have shown that the metal ions (such as Zn$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Li$^+$, Na$^+$, K$^+$) and water molecules in the interlayer of V$_2$O$_5$ can not only work as pillars to increase the structural stability, but also significantly affect the charge/discharge processes.[9-13] In the double-layered calcium vanadium oxide bronze (Ca$_{0.25}$V$_2$O$_5$·nH$_2$O) cathode, the intercalated Ca$^{2+}$ ions strongly bond to V$_2$O$_5$ layers and H$_2$O, effectively binding the layers together and expanding the interlayer gap of V$_2$O$_5$, as shown in Figure 2.1d.[14] The representative SEM and transmission electron microscope (TEM) images in Figure 2.1e reveal the nanobelt morphology with a smooth surface and the single crystallinity of Ca$_{0.25}$V$_2$O$_5$·nH$_2$O. After immersion in aqueous electrolyte, the open crystal structure of Ca$_{0.25}$V$_2$O$_5$·nH$_2$O allows for water intercalation with increased interlayer spacing from 10.6 to 14.1 Å, ensuring highly reversible electrochemical (de)intercalation of Zn$^{2+}$. Thus, the layered calcium vanadium oxide nanobelts exhibit a high capacity of 340 mA h g$^{-1}$ at 0.2 C and a capacity retention of 96% after 3000 cycles. In addition, Layered M$_y$V$_3$O$_8$ (M = Li, Na, K) and H$_2$V$_3$O$_8$ (V$_3$O$_7$·H$_2$O), comprising VO$_6$ octahedra and VO$_5$ square pyramids, have also been studied as cathode materials in AZIBs.[15-16] For example, the phase evolution of LiV$_3$O$_8$ related to the storage of Zn$^{2+}$ is illustrated in Figure 2.1f. [15] During the consecutive Zn insertions, two single-phase domains proceed via a stoichiometric ZnLiV$_3$O$_8$ phase to Zn$_y$LiV$_3$O$_8$ ($y > 1$) phase. The Zn$_y$LiV$_3$O$_8$ is gradually transformed back to LiV$_3$O$_8$ via a single-phase reaction during the charge process, and the overall framework undergoes negligible modification during cycling.

2.1.2 Transition-metal sulfides

Transition-metal sulfides with varied crystal structures have shown great potential to host multivalent ions (Mg$^{2+}$, Al$^{3+}$, Zn$^{2+}$, etc.).[17] In particular, layered transition-metal sulfides possess large interlayer spacing and enable the storage of Zn$^{2+}$. Using this concept, layered
VS₂ nanosheets were synthesized and suggested as a promising cathode material for AZIBs by Mai’s group.¹⁸ Benefiting from its large interlayer spacing (5.76 Å) and ideal electronic conductivity, the graphene-like VS₂ delivered a high capacity of 190.3 mA h g⁻¹ at 0.05 A g⁻¹ and exhibited long-term cycling stability. *Ex-situ* XRD, as shown in Figure 2.2a and the TEM images in Figure 2.2b, indicated that the layer spacing of VS₂ can self-adapt to the insertion of Zn²⁺ with an expansion of only 1.73%, which is vital to the realization of long-life AZIBs. A highly reversible insertion/extraction process has been revealed, in which 0.09 Zn²⁺ is first intercalated, followed by the insertion of another 0.14 Zn²⁺ into the interlayer of VS₂ nanosheets. As an analogue of VS₂, VS₄ with a unique chain like structure, has been reported as an energy storage material.¹⁹ In the crystal structure of VS₄ (Figure 2.2c), each V-S chain comprises central V atoms and two S₂²⁻ moieties combined by alternating covalent bonds, in which V atoms adopt an eight coordinated configuration. The distance between two adjacent V-S chains is 6.2 Å, and the crystal structure is relatively loose, both of which are beneficial for the insertion process of Zn²⁺. VS₄@rGO composite has been presented as a high-performance cathode for AZIBs. The peculiar crystallographic structure of VS₄ and the high conductivity of rGO ensure high capacity and superior rate performance. A synergetic storage mechanism composed of conversion and intercalation reactions is proposed, which requires further study and a more detailed understanding.
Molybdenum-based sulfides, including Mo$_6$S$_8$ and MoS$_2$, have also been found to be successful host materials for Zn-ions. Chevrel phase Mo$_6$S$_8$ has a crystal structure with a unique 3D network and a rigid framework (Figure 2.2d), leading to favourable zinc storage behaviour.

A discharge capacity of 134 mA h g$^{-1}$ was achieved in the first cycle. As depicted in the cyclic voltammetry (CV) curves (Figure 2.2e), the process for the electrochemical Zn$^{2+}$ intercalation could be divided into two steps: the transformation of ZnMo$_6$S$_8$ from Mo$_6$S$_8$ at a potential of around 0.45–0.50 V and the formation of Zn$_2$Mo$_6$S$_8$ from ZnMo$_6$S$_8$ at a potential of around 0.35 V. The low redox potentials make this kind of cathode material more suitable as an alternative anode material for Zn-based energy storage.
2.1.3 Polyanion compounds

A desired cathode host for fast and reversible Zn$^{2+}$ (de-)intercalation is expected to have a robust crystal architecture. Polyanion compounds possess such stable frameworks and can offer minimum steric hindrance with manipulated insertion potentials. Sodium superionic conductor (NASICON)-type M$_3$V$_2$(PO$_4$)$_4$ (M = Li, Na) have been applied in AZIBs, as reported in several works. Huang et al.[22] first developed Na$_3$V$_2$(PO$_4$)$_3$/C as a host material for AZIBs, which delivered excellent rate and cycling performances. The structural evolution of Na$_3$V$_2$(PO$_4$)$_3$ cathode during the charge/discharge process is depicted in Figure 2.3a. In the initial charge process, two Na$^+$ ions can be extracted from the 18e sites and one Na$^+$ ion remains at the 6b site. The initial charge product NaV$_2$(PO$_4$)$_3$ provides open sites and enables reversible insertion of Zn$^{2+}$ during the subsequent cycle. The utilization of F-doped Na$_3$V$_2$(PO$_4$)$_2$F$_3$ as intercalation electrode for Zn$^{2+}$ was reported to further enhance the work voltage.[23] Recently, a very promising cathode host, LiV$_2$(PO$_4$)$_3$, was prepared by in-situ electrochemical extraction of two Li$^+$ ions from Li$_3$V$_2$(PO$_4$)$_3$, leaving two unoccupied lithium sites for the insertion of Zn$^{2+}$.[24] The novel Zn/LiV$_2$(PO$_4$)$_3$ battery exhibited excellent cycling stability (up to 4000 cycles, Figure 2.3b), unprecedented high-power density (8000 W kg$^{-1}$ at 60 $^\circ$C), and energy density (200 Wh kg$^{-1}$ at 1 C). The X-ray absorption near edge spectroscopy (XANES) spectra (Figure 2.3c) in the fully discharged state demonstrated that Zn-ions with valence lower than bivalence were present in LiV$_2$(PO$_4$)$_3$ electrodes. First-principles calculations showed that the inserted Zn$^{2+}$ displays an effective charge of only 1.336, allowing for significantly decreased electrostatic interaction and high mobility. As shown in Figure 2.3d, the charge around Zn is obviously reduced, and the vanadium and partial oxygen sites undergo increasing charge, revealing that the $p$-$d$ hybridization between the V-$d$ and O-$p$ orbitals successfully delocalized the nominal bivalence of Zn$^{2+}$, which endows the polyanion cathode with reversible and ultrafast Zn$^{2+}$ (de-)intercalation.
Figure 2.3 a) Schematic representation of the phase transitions of Na$_3$V$_2$(PO$_4$)$_3$ cathode during cycling. Reproduced with permission.\textsuperscript{[23]} Copyright 2016, Elsevier. b) The cycling performance and the corresponding coulombic efficiency of the Zn/LiV$_2$(PO$_4$)$_3$ battery at the high rate of 10 C (inset the low rate of 2 C). c) The X-ray absorption near edge spectroscopy (XANES) spectra collected at the Zn K-edge of the Zn metal, Zn(OTf)$_2$ salt, and the LiV$_2$(PO$_4$)$_3$ electrode discharged to 0.2 V. d) Schematic illustration of the change in the charge distribution after Zn$^{2+}$-insertion into the LiV$_2$(PO$_4$)$_3$ framework (blue: charge decrease; yellow: charge increase). Reproduced with permission.\textsuperscript{[25]} Copyright 2018, Royal Society of Chemistry.

2.1.4 Prussian blue analogues

Prussian blue analogues (PBAs) have a general formula of A$_x$PR(CN)$_6$·yH$_2$O, the crystallographic structure of which is analogous to that of ABX$_3$ perovskites, with P$^{m+}$ and R$^{n+}$ ions forming an ordered arrangement on the B sites.\textsuperscript{[25]} The separation between P$^{m+}$ and
R\(^{n+}\) ions is enhanced by the triple-bonded CN ligands expanding the structure for ion intercalation. The occupancy of the tetrahedrally coordinated ‘A sites’ in the crystallographically porous structure (Figure 2.4a) varies from \(x = 0\) to \(x = 2\). PBAs are mixed ionic-electronic conductors with a 3D open framework containing large octahedral interstitial sites and open channels for ionic insertion.\(^{[26]}\) Because of their open structure, superior structural stabilities, and abundant redox-active sites, PBAs have attracted great attention as hosts for cation intercalation. The feasibility of electrochemical Zn\(^{2+}\) storage in copper hexacyanoferrate (CuHCF) in aqueous solution was first proposed by Wang et al.\(^{[27]}\) Cyclic voltammetry of the CuHCF nanocube cathode showed a pair of cathodic and anodic peaks, corresponding to the (de)intercalation of Zn\(^{2+}\). XPS analysis suggested that the Fe\(^{3+}\)/Fe\(^{2+}\) redox couple was responsible for the Zn storage behaviour during cycling. The Zn storage mechanism of CuHCF can be expressed as:

\[
xZn^{2+} + 2xe^- + CuHCF \leftrightarrow Zn_xCuHCF \quad (0 < x < 0.5)
\]  

(2-1)

Mantia et al. carried out further work on CuHCF as a cathode for AZIBs, improving the cycling stability by using a low concentration electrolyte (20 mM ZnSO\(_4\)), which was favourable for the stabilization of Zn metal.\(^{[28]}\) They also explored how the nature and concentration of the electrolyte, and the current rate affect the aging of CuHCF cathode in charge/discharge processes.\(^{[29]}\) In-depth investigation of the structural changes and Zn\(^{2+}\) storage process in the CuHCF was conducted by means of in operando synchrotron X-ray diffraction (Figure 2.4b-d).\(^{[29]}\) The contour maps of diffraction patterns and the voltage profile with the refined lattice parameter (Figure 2.4b) highlight the entire trend of the charge/discharge process. To conclude, the repeated (de)insertion of Zn\(^{2+}\) in the CuHCF host is accompanied by a non-linear contraction and expansion of the unit cell in the range 0.36 <
$x < 1.32$ for $\text{Zn}_{x/3}\text{Cu[Fe(CN)₆]}_{2/3} \cdot n\text{H₂O}$, and the inserted $\text{Zn}^{2+}$ can swap positions between the tunnels and the vacant $\text{Fe(CN)}₆$ sites.

![Diagram of CuHCF crystal structure](image)

**Figure 2.4** a) Typical Prussian blue crystal structure of CuHCF, in which octahedrally coordinated transition metals such as Cu and Fe are linked by CN ligands, forming a face-centred cubic structure. Reproduced with permission.[26] Copyright 2011, Springer Nature. b) Top-view elevation map (intensity axis is perpendicular to the plane of the figure) displaying peak shifts of a CuHCF/Zn cell during the in operando XRD experiment. c) Time evolution of the corresponding voltage profile (continuous line) of the first two cycles with the refined lattice parameter (circles) superimposed. d) A plot of the time-derivative of both the voltage ($dE/dt$) and the cell parameter ($da/dt$). Reproduced with permission.[30] Copyright 2017, Elsevier. e) The proposed redox mechanism of PANI/CFs. f) Schematic diagram of the charge/ discharge mechanism of PANI/CFs. Reproduced with permission.[35] Copyright 2018, John Wiley and Sons.
In addition, zinc hexacyanoferrate (ZnHCF) as intercalation host for Zn\(^{2+}\) has been reported by Liu’s group.\[^{30-31}\] The Zn\(^{2+}\) intercalation chemistry of ZnHCF is similar to that of CuHCF, relying on the following electrochemical reaction:

\[
\alpha\text{Zn}^{2+} + 2\alpha e^- + Zn_3[Fe(CN)_6]_2 \leftrightarrow Zn_{3+\alpha}[Fe(CN)_6]_2
\]

An average operating voltage as high as 1.7 V was delivered in the Zn/ZnSO\(_4\)/ZnHCF battery, with a specific energy of 60 Wh kg\(^{-1}\). Later, the same group developed three polyhedral ZnHCF particles (cuboctahedral, truncated octahedral, and octahedral shapes) and revealed that the PBAs with special facets exposed were an essential factor in their electrochemical behaviour.\[^{31}\] Nevertheless, because of the limited specific capacity (less than 70 mA h g\(^{-1}\)) of these materials, the energy density of PBAs is still uncompetitive. Making more vacancy sites and appropriate nanostructure design may be feasible strategies to improve the electrochemical performance of PBAs cathodes.

### 2.1.5 Organic cathodes

In addition to the inorganic cathode materials mentioned above, organic cathodes are also feasible for ZIBs.\[^{32-33}\] Polyaniline (PANI), a typical organic conducting polymer, possesses conjugated chemical bonds (C=N) and an extended conjugated composition. The C-N\(^+\) in the oxidized PANI can interact with anions from the electrolyte, and the electronegative nitrogen sites (C-N\(^-\)) in reduced PANI can also store cations. Inspired by this unique characteristic, Chen and co-workers designed aqueous Zn/PANI batteries using PANI/carbon felts (PANI/CFs) as cathodes and Zn(CF\(_3\)SO\(_3\))\(_2\) solution as electrolyte.\[^{34}\]

This aqueous Zn/PANI system utilizes a supercapacitor-like hybrid mechanism, which combines a typical Zn\(^{2+}\) intercalation/de-intercalation process and a dual-ion process. The electrochemical storage mechanism is shown in Figure 2.4e,f. During the discharge process, the PANI in the full oxidation state undergoes a stepwise conversion to the reduced PANI, accompanied by the
continuous release of CF₃SO₃⁻ and the subsequent insertion of Zn²⁺. In the following charge process, Zn²⁺ is first released from the host, and CF₃SO₃⁻ continuously interacts with PANI. The XPS results revealed that the capacity contributions arising from the insertion/extraction of Zn²⁺ and the dual-ion process are 39.7% and 60.3%, respectively. Benefiting from high stability of PANI and the fast charge transfer, the Zn/PANI battery exhibited a capacity of 95 mA h g⁻¹ at 5 A g⁻¹ and had a long-term cycle life up to 3000 cycles with a capacity retention of 92%. Very recently, a new aqueous Zn/PANI battery was developed by using low-cost ZnSO₄ electrolyte and a sulfo self-doped PANI cathode. A high H⁺ concentration is essential to promote the redox process in PANI cathodes, which is not compatible with the Zn anode. In weak acidic ZnSO₄ electrolyte, the -SO₃⁻ self dopant can act as a proton reservoir to ensure an internal highly acidic environment and maintain the electrochemical activity of PANI cathode materials. As a result, the self-doped cathode shows a high capacity of 110 mA h g⁻¹ at 10 A g⁻¹ after 2000 cycles. Chen’s group also enriched the family of organic electrode materials for AZIBs with a series of quinone compounds. Quinone compounds store ions through an ion-coordination mechanism. Among the various quinone compounds with carbonyls, calix quinone (C4Q) delivers a relative high capacity (335 mA h g⁻¹) and good cycling stability (1000 cycles at a current density of 500 mA g⁻¹). Although many organic electrodes show great potential for AZIBs, further studies are required to inhibit the phase evolution and dissolution of discharge products during cycling.
To conclude, cathode materials for various AZIBs consist of transition-metal oxides (Mn-based oxides and V-based oxides, mainly), transition-metal sulfides, polyanion compounds, Prussian blue analogues, and organic cathodes. A summary of the configurations and electrochemical performances of AZIBs using mild aqueous electrolytes is presented in Figure 2.5. A variety of MnO$_2$ polymorphs with tunnelled or layered structures have been applied as the most promising candidates for AZIBs, which show relatively high specific capacities and working potentials. Compared with Mn-based oxides and organic cathodes, V-based oxides exhibit much more stable cyclability, better rate capability, and lower operation voltage. It also was found that Prussian blue analogues have high working voltage, but with inferior capacities and cycling performance.

### 2.2 Zn-ion storage mechanisms in AZIBs

Most ion storage materials in aqueous alkali metal ion batteries can be applied as host materials in aqueous zinc-ion batteries (AZIBs), although the energy storage chemistries for AZIBs are more complicated than in the former systems. So far, the reaction mechanisms of...
Zn-ion storage are still in dispute and underdeveloped. Three different redox mechanisms in AZIB systems have been proposed: reversible Zn\(^{2+}\) insertion/extraction; chemical conversion reactions; and reversible Zn\(^{2+}\) and H\(^+\) co-insertion/co-extraction.

### 2.2.1 Reversible Zn\(^{2+}\) insertion/extraction

Basically, reversible (de)intercalation of Zn\(^{2+}\) from host materials during redox reactions is the first mainstream view. Oh and co-workers first clarified the insertion mechanism of Zn\(^{2+}\) into α-MnO\(_2\) and the corresponding structural transformations.\[^{38}\] As shown in Figure 2.6a, Upon electrochemical intercalation of zinc ions into the α-MnO\(_2\) with its 2 × 2 tunnels, the Mn\(^{4+}\) is partially reduced to highly unstable Mn\(^{3+}\), which disproportionates into Mn\(^{4+}\) and Mn\(^{2+}\), resulting in the dissolution of some Mn and the formation of layered Zn-birnessite. During the charge process, Mn\(^{2+}\) ions in the electrolyte are reversibly incorporated back into Zn-birnessite to recover the original tunnelled structure. Afterwards, the same research group corrected the proposition that the direct product of Zn\(^{2+}\) insertion into α-MnO\(_2\) was layered Zn-birnessite instead of layered Zn-buserite.\[^{39}\] They claimed that the birnessite phase was generated due to the loss of the inserted Zn\(^{2+}\) and H\(_2\)O from the interlayers of buserite. The tunnel structured β-MnO\(_2\) also experiences a phase conversion to layered buserite, followed by reversible Zn\(^{2+}\) (de)intercalation from the latter phase (Figure 2.6b).\[^{34}\] In addition to a series of Mn-based cathodes (α-, β-, γ-, δ-, todorokite-, spinel-type, etc.) based on Zn-ion intercalation chemistry, V-based cathode materials are the other big family of insertion hosts. For example, VO\(_2\)(B) with an open framework has been revealed as a candidate material for zinc storage.\[^{40}\] Through first-principles calculations and experiments, the researchers demonstrated that ~0.57 mol of Zn\(^{2+}\) could be (de)intercalated reversibly from the host structure VO\(_2\)(B). Upon discharge, the oxidation state of vanadium was reduced to trivalence, and it was oxidized to tetravalence with contraction of the crystal structure upon charge. The reaction mechanism is shown in Figure 2.6c. Because of its high theoretical
capacity for Zn-storage, vanadium pentoxide (V₂O₅) is regarded as a promising cathode host for AZIBs among the various V-based oxides. Particularly, Cheng et al. reported a rechargeable aqueous Zn–V₂O₅ system, where the layered V₂O₅ electrode displayed high reversibility in hydrated Zn²⁺ insertion/extraction (Figure 2.6d). The co-intercalation of H₂O molecules can efficiently buffer the electrostatic reactions between Zn²⁺ and the host anions, contributing to the improved rate performance. In addition, Zn²⁺ ions can also be inserted/extracted reversibly into/from other open frameworks, including Prussian blue analogues and organic materials, which will be discussed in detail in the next section.

![Figure 2.6 Schematic illustration of Zn²⁺ insertion/extraction mechanism in a) α-MnO₂. Reproduced with permission. Copyright 2014, Springer Nature. b) β-MnO₂ c) VO₂(B), Reproduced with permission. Copyright 2018, American Chemical Society. and d) layered V₂O₅. Reproduced with permission. Copyright 2018, American Chemical Society.](image-url)
2.2.2 Chemical conversion reaction

Besides the $\text{Zn}^{2+}$ insertion/extraction mechanism, another mechanism for a chemical conversion reaction between $\alpha$-MnO$_2$ and H$^+$ has also been proposed.\textsuperscript{[42]} To reveal the conversion reaction processes, the structural and morphological evolution of $\alpha$-MnO$_2$ was comprehensively investigated. In the fully discharged state, MnOOH nanorods are formed from the reaction between MnO$_2$ with H$^+$ from H$_2$O. The consequent OH$^-$ ions further react with ZnSO$_4$ in the aqueous electrolyte to form a flake-like zinc hydroxide sulfate (ZHS), creating a neutral environment. Interestingly, after charging, the products above revert to the original $\alpha$-MnO$_2$, which indicates reversible electrochemical behaviour between MnO$_2$ and MnOOH/ZHS. The reaction mechanism can be formulated as follows:

**Cathode:** $H_2O \leftrightarrow H^+ + OH^-$

\[
\text{MnO}_2 + H^+ + e^- \leftrightarrow \text{MnOOH} \quad (2-4)
\]

\[
\frac{1}{2}Zn^{2+} + OH^- + \frac{1}{6}ZnSO_4 + \frac{x}{6}H_2O \leftrightarrow \frac{1}{6}ZnSO_4[Zn(OH)_2]_3 \cdot xH_2O \quad (2-5)
\]

**Anode:** $\frac{1}{2}Zn \leftrightarrow \frac{1}{2}Zn^{2+} + e^-$

\[
(2-6)
\]

The conversion reaction mechanism is further confirmed by the fact that in organic Zn-based electrolytes, the $\alpha$-MnO$_2$ nanofiber cathode exhibits very limited capacity owing to the absence of H$^+$ ions, while after adding water into organic Zn-based electrolytes, $\alpha$-MnO$_2$ displays a similar electrochemical behaviour to that in an aqueous system. Actually, the conversion reaction of the secondary Zn/$\alpha$-MnO$_2$ battery is the same as that of the primary alkaline Zn/MnO$_2$ system. The only difference between them lies in the reversibility of the product formed at the zinc anode under different pH conditions. In addition, a reversible conversion reaction mechanism between CoO and Co$_3$O$_4$ was revealed in a Zn/Co$_3$O$_4$ battery with a mild aqueous electrolyte.\textsuperscript{[43]} The CoO layer formed during the discharge process reveals the conversion process of H$^+$ ion insertion into Co$_3$O$_4$. Similar to the already
discussed Zn/α-MnO₂ system, the subsequent OH- interacts with the electrolyte to generate ZnSO₄[Zn(OH)₂]₃·xH₂O. The reversible conversion reaction of the Zn/Co₃O₄ system can be summarized as follows:

Cathode: \[ H₂O \leftrightarrow H^+ + OH^- \] \hspace{1cm} (2-7)  
\[ Co₃O₄ + 2H^+ + e^- \leftrightarrow 3CoO + H₂O \] \hspace{1cm} (2-8)  
\[ Zn^{2+} + 2OH^- + ZnSO₄ + xH₂O \leftrightarrow ZnSO₄[Zn(OH)₂]₃ \cdot xH₂O \] \hspace{1cm} (2-9)  
Anode: \[ Zn \leftrightarrow Zn^{2+} + 2e^- \] \hspace{1cm} (2-10)

2.2.3 Reversible Zn²⁺ and H⁺ co-insertion/co-extraction.

Because of the much smaller size of H⁺, it is understandable that H⁺ may be inserted into host materials with an open framework. Wang’s group first proposed a sequential H⁺ and Zn²⁺ insertion/extraction process into/out of an akhtenskite nano-MnO₂ cathode.²⁴ Due to the remarkable difference in reaction kinetics between H⁺ and Zn²⁺, the charge and discharge profiles show two distinct reaction regions. As shown in Figure 2.7a, with an increase in rate, the decreases of capacity and voltage in region I are much smaller than those in the region II, suggesting much faster reaction kinetics in region I. The discharge galvanostatic intermittent titration technique (GITT) profiles (Figure 2.7b) further clarify that the overvoltage in the second discharge plateau (0.6 V) is much bigger than that in the first discharge plateau (0.08 V). Given the large size of bivalent Zn²⁺ and the strong electrostatic interactions, H⁺ insertion is responsible for region I, and the insertion of Zn²⁺ contributes to region II. Different electrochemical behaviour of the MnO₂ electrode in the Zn²⁺-absent electrolyte further confirms this theory, where only one high plateau is demonstrated. In the ex-situ X-ray diffraction (XRD) measurements (Figure 2.7c), a typical MnOOH phase and ZnMn₄O₄ phase were observed upon discharging, which strongly supports the Zn²⁺ and H⁺ co-insertion theory.
Figure 2.7 a) Charge and discharge curves of a Zn/MnO$_2$ cell at different rates in the first cycle. b) Discharge galvanostatic intermittent titration technique (GITT) profiles of the Zn/MnO$_2$ cell (50 mA g$^{-1}$ for 120 s followed by a 4 h rest). c) Ex situ XRD patterns of the MnO$_2$-based cathode at depth of discharge of 1.3 and 1.0 V, respectively. Reproduced with permission.[44] Copyright 2017, American Chemical Society. d) Second charge/discharge curves of sodium vanadate nanobelts at 0.1 A g$^{-1}$. e) Ex situ XRD patterns and f) solid state $^1$H nuclear magnetic resonance (NMR) at selected states of the zinc/sodium vanadate system. Reproduced with permission.[49] Copyright 2018, Springer Nature.

The phenomenon of Zn$^{2+}$ and H$^+$ co-insertion in AZIBs is also found in other Mn-based and V-based cathode materials.[45] Recently, Chen et al. reported a Zn/sodium vanadate system that delivered a simultaneous H$^+$ and Zn$^{2+}$ (de)intercalation process.[46] Reversible formation/decomposition of Zn$_4$SO$_4$(OH)$_6$·4H$_2$O (ZHS) was proved by the ex-situ XRD analysis (Figure 2.7d,e), which resulted from the insertion of H$^+$ ions and the consequent change of pH condition in aqueous electrolyte. The ex-situ solid state $^1$H NMR spectrum is displayed in Figure 2.7f. An extra peak at 2.7 ppm increases gradually and finally recovers to the initial state during cycling, indicating the continuous and reversible processes of H$^+$ insertion/extraction in the sodium vanadate system. The successive insertion/extraction of Zn$^{2+}$ was also verified by the ex-situ X-ray photoelectron spectroscopy (XPS) spectra.
In a word, there are three different reaction mechanisms involving the cathode materials for AZIBs. The diversity of crystallographic polymorphs may bring about different ion insertion thermodynamics and kinetics. In some cases, it is hard to clarify the authentic redox processes for host materials. As discussed above, two contradictory reaction mechanisms for the Zn/α-MnO$_2$ system have been reported, the intercalation reaction and the conversion reaction, respectively. Thus, further investigation and more characterization methods are expected to disclose the reaction chemistry of some cathodes, especially highly controversial Mn-based materials.

2.3 Electrolyte formulation

The choice of the electrolyte is clearly important for both the Zn anode and the cathode materials by influencing the formation of protective layers and side reactions. Most of the electrolytes for aqueous zinc ion batteries contain one or more soluble zinc salts, such as ZnCl$_2$, ZnNO$_3$, Zn(CH$_3$COO)$_2$, ZnSO$_4$, zinc trifluoromethanesulfonate (Zn(CF$_3$SO$_3$)$_2$), and zinc bis(trifluoromethanesulfonyl)imide (Zn(TFSI)$_2$). Chen and co-workers found that ZnCl$_2$ and ZnNO$_3$ electrolytes have a poor CE due to the instability of Cl$^-$ and NO$_3^-$.[46] In contrast, both the ZnSO$_4$ and Zn(CF$_3$SO$_3$)$_2$ electrolytes exhibit a wide electrochemical window and good reversibility of Zn stripping/plating (Figure 2.8a,b). Compared to ZnSO$_4$, Zn(CF$_3$SO$_3$)$_2$ shows better reversibility and faster kinetics on Zn deposition/dissolution. The CE of Zn(CF$_3$SO$_3$)$_2$ electrolyte gradually increased and reached 100% after the third cycle, while the CE in ZnSO$_4$ electrolyte was lower at each cycle and decreased with cycling. Zn(CF$_3$SO$_3$)$_2$ is also superior to ZnSO$_4$ to alleviate the dissolution and promote the kinetics of cathode materials. The superior electrochemical properties of Zn(CF$_3$SO$_3$)$_2$ could be attributed to the bulky CF$_3$SO$_3^-$ anions, which decrease the number of water molecules surrounding Zn$^{2+}$ cations and reduce the solvation effect, facilitating Zn$^{2+}$ transportation and
charge transfer. Zn(CF$_3$SO$_3$)$_2$ is much more expensive than ZnSO$_4$, however, which would be a drawback in large-scale applications. Currently, both the ZnSO$_4$ and Zn(CF$_3$SO$_3$)$_2$ electrolytes are widely used in aqueous zinc batteries, although 1 M ZnSO$_4$ or Zn(CF$_3$SO$_3$)$_2$ electrolyte still suffers from low CE of Zn stripping/plating. Increasing the concentration of zinc salt has been found to be an effective way to increase the CE. Chen et al. found that highly-concentrated Zn(CF$_3$SO$_3$)$_2$ electrolyte displays a better Zn stripping/plating CE than that of its low concentration counterparts.\[^{46}\]

Also, the CE of the ZnMn$_2$O$_4$ cathode increases significantly when the salt concentration increases from 1 to 3 M (Figure 2.8c). As a result, the Zn/ZnMn$_2$O$_4$ battery has impressive cycling performance with a capacity retention of 94% over 500 cycles at 500 mA g$^{-1}$. Clearly, the salt concentration plays an important role in achieving long-term stability, which could change the solvation and transport behaviour of cations/anions and reduce the water-induced side reactions. Jeong et al. also reported similar results, that 3 mol dm$^{-3}$ Zn(NO$_3$)$_2$ enhanced the charge/discharge capacities and cycling performance of zinc hexacyanoferrate (Zn$_3$[Fe(CN)$_6$)$_2$, ZnHCF) better than 1 mol dm$^{-3}$ Zn(NO$_3$)$_2$.\[^{47}\]

More recently, the discovery of water-in-salt electrolytes offers a new way to resolve the irreversibility issue of Zn anode in aqueous electrolytes. Accordingly, Wang et al. developed a highly concentrated aqueous electrolyte consisting of 1 m Zn(TFSI)$_2$ and 20 m LiTFSI,\[^{48}\] where TFSI is bis(trifluoromethanesulfonyl)imide, which enables dendrite-free plating/stripping of Zn with nearly 100% CE, and brings unprecedented reversibility to aqueous Zn batteries with either LiMn$_2$O$_4$ or O$_2$ cathodes (Figure 2.8d,f). This is attributed to the unique Zn$^{2+}$ solvation-sheath, in which Zn$^{2+}$ is surrounded by TFSI$^{-}$ instead of water when the LiTFSI concentrations $\geq$ 20 m, which effectively prevents H$_2$ evolution and the formation of (Zn-$(\text{H}_2\text{O})_6$)$_{2+}$. Because of the high cost of LiTFSI, an alternative electrolyte consisting of 0.5 m
zinc trifluoromethanesulfonate (Zn(OTf)$_2$) and 18 m NaClO$_4$ at a much lower cost was also developed, which also provides an excellent CE of ~98% as well.$^{[48]}$

**Figure 2.8** Cyclic voltammograms of Zn electrode in aqueous electrolyte of (a) 1 M ZnSO$_4$ and (b) 1 M Zn(CF$_3$SO$_3$)$_2$. c) Coulombic efficiency (CE) of ZnMn$_2$O$_4$ (ZMO)/C electrode as a function of cycle number at aqueous Zn(CF$_3$SO$_3$)$_2$ electrolyte with different concentrations (1−4 M). Reproduced with permission.$^{[46]}$ Copyright 2016, American Chemical Society. d) Cyclic voltammogram of Zn plating/stripping in a three-electrode cell using a Pt disc (2 mm in diameter) as the working and Zn as the reference and counter electrodes at a scan rate of 1 mV s$^{-1}$. Inset: chronocoulometry curves. e) The Zn plating/stripping time (left) and CE (right) on a Pt working electrode at 1 mA cm$^{-2}$. f) SEM image and X-ray diffraction (XRD) pattern (inset) of a Zn anode after 500 stripping/plating cycles in highly concentrated Zn-ion electrolyte. Reproduced with permission.$^{[48]}$ Copyright 2018, Springer Nature. g) Cycling performance (1 A g$^{-1}$) of Zn/ NaV$_2$O$_5$·1.5H$_2$O (NVO) batteries in ZnSO$_4$ and ZnSO$_4$/Na$_2$SO$_4$ electrolytes. Reproduced with permission.$^{[49]}$ Copyright 2018, Springer Nature. h) Comparison of the cycling performance of Zn-MnO$_2$ cells with electrolytes of 45wt.% KOH (at 0.32 C), 3M ZnSO$_4$, 3M Zn(CF$_3$SO$_3$)$_2$, and 3M Zn(CF$_3$SO$_3$)$_2$ with 0.1M Mn(CF$_3$SO$_3$)$_2$ additive at 0.65 C. nC equals the rate to
charge/discharge the theoretical capacity (308 mA h g\(^{-1}\)) of MnO\(_2\) in 1/n hours. Reproduced with permission.\(^{[50]}\) Copyright 2017, Springer Nature. i) Platting/stripping efficiency of Zn in 2 M ZnSO\(_4\) electrolyte with and without MnSO\(_4\). Reproduced with permission.\(^{[51]}\) Copyright 2018, Springer Nature.

Another commonly used effective method to suppress dendrite growth and improve the Zn stripping/plating CE is the introduction of additives into the electrolyte. It has been reported that the addition of Na\(_2\)SO\(_4\) to ZnSO\(_4\) electrolyte could alleviate the growth of Zn dendrites, because Na\(^+\) with a lower reduction potential could form a positively charged electrostatic shield around the initial plating of Zn. Also, the addition of Na\(_2\)SO\(_4\) into the ZnSO\(_4\) electrolyte could inhibit the dissolution of NaV\(_3\)O\(_8\)·1.5H\(_2\)O (NVO). As a result, the electrochemical performance of NVO is greatly enhanced with the addition of Na\(_2\)SO\(_4\) (Figure 2.8g).\(^{[49]}\) Moreover, it has been demonstrated that Mn\(^{2+}\) in the electrolyte not only avoids dissolution of MnO\(_2\), but also can effectively improve the CE of the zinc electrode, and thus enhance the cyclability of MnO\(_2\) (Figure 2.8h,i).\(^{[50-51]}\) In addition, organic additives such as polymers, organic molecules, or surfactants can be directly introduced into the electrolyte to constrain the formation of dendrites. This method is similar to that in the above discussion on the introduction of organic additives into the plating electrolyte to synthesize the electroplated Zn anodes, as it can lead to different crystallographic surfaces and morphologies. Different organic additives, such as thiourea (TU),\(^{[52]}\) hexadecyl trimethyl ammonium bromide (CTAB),\(^{[52]}\) polyethylene glycol nanowire (NPEG),\(^{[53]}\) sodium dodecyl sulfate (SDS),\(^{[54]}\) and polyethylene glycol (PEG, M.W. = 200),\(^{[55]}\) have been introduced directly into the electrolyte to improve the efficiency of electrodeposition and tune the morphology and reactivity of the zinc deposition. For example, Banik and Akolkar found that PEG200 is an effective electrolyte additive to suppress dendrites during zinc electrodeposition from halide-based electrolytes, and the dendrite suppression efficacy
increases as the PEG concentration increases.\textsuperscript{[55]} As shown in Figure 2.9a, \textit{in-situ} optical microscopy revealed rapid development of dendritic morphology at the wire electrode in the absence of PEG, but the addition of 100 ppm of PEG to the electrolyte marginally suppressed dendrite formation. Furthermore, marked suppression of dendrite growth could be obtained at PEG concentrations of 1000 and 10000 ppm. At these PEG concentrations, deposits were more compact and did not exhibit the classical dendritic morphology. Chen et al. also investigated the impact of PEG polymer additives in an aqueous electrolyte on Zn dendrites.\textsuperscript{[56]} They found that PEG200 in the electrolyte decreases the corrosion and chronoamperometric current density of the zinc electrode by up to four-fold. Scanning electron microscopy (SEM) studies have shown that dendrites in the PEG-containing electrolyte are inhibited, leading to much smaller/smooth surface features than those of the control. As shown in Figure 2.9b, flake-type dendritic growth is evident on the surface of zinc on the control sample, while the PEG sample shows uniform nucleation of boulder-type dendrites along the surface. Meanwhile, the dendrites in the control sample are larger and less densely packed than in the PEG sample. As a result, 1 vol.% PEG200 in the electrolyte was sufficient to obtain a discharge capacity of 122.1 mA h g\textsuperscript{-1} in an aqueous rechargeable lithium/zinc battery, an improvement of approximately 32\% over the control. A mechanism is proposed to explain the contribution of PEG polymer to the nucleation and growth of dendrites on the surface of the zinc anode, compared with the control sample (Figure 2.9c). Without PEG200, the zinc ions on the electrode surface are very likely to aggregate to minimize surface energy by decreasing the overall area exposed to the electrolyte due to the lack of a barrier to their diffusion. These aggregated ions will then be reduced at these sites, eventually resulting in large dendrites. After adding PEG200, the PEG molecules are able to absorb on the electrode surface slightly quicker than the zinc ions from solution, and this will restrict the free diffusion of zinc ions from the solution onto the surface and prevent the
aggregation of Zn ions. Restricted motion leads to a higher numerical density of small dendrites and hence prevents the runaway growth of large dendrites. As such, the organic molecules on the surface of the substrate suppress the kinetics of zinc electrodeposition and decrease the grain growth rate, thus enabling a homogeneous distribution of the current density, which can guarantee uniformity of the deposited layer. Moreover, by adding a surfactant such as sodium dodecyl sulfate (SDS) to the aqueous electrolyte, the electrochemical stability window of the electrolyte was expanded to about 2.5 V (Figure 2.9d).\textsuperscript{[54]} The results of the experiments and calculations based on density functional theory indicate that SDS can not only inhibit the decomposition of water and suppress the dissolution of Mn and the corrosion of zinc, but also increases the cycle life and rate capability (Figure 2.9e).

\textbf{Figure 2.9} a) Optical microscope images of Zn dendrites protruding from the tip of polyvinyl chloride (PVC) coated wire electrode at which Zn was electrodeposited potentiostatically for 8 minutes. The
electrolyte contains 0.1 M ZnCl$_2$ with various concentrations of PEG: 0 ppm [(a) and (e)], 100 ppm [(b) and (f)], 1000 ppm [(c) and (g)], and 10000 ppm [(d) and (h)]. Two operating voltages are compared: $-1.25$ V vs. Ag/AgCl [(a)–(d)] and $-1.30$ V vs. Ag/AgCl [(e)–(h)]. Reproduced with permission.\textsuperscript{[55]} Copyright 2013, The Electrochemical Society. b) SEM images of zinc electrodes after exposure to 1 h Chronoamperometry (CA) measurements at $-135$ mV overpotential vs. Open-circuit voltage (OCV) for 3600 s in a) control electrolyte and b) 1 vol.% PEG200 electrolyte. c) Model of interaction mechanism. Schematics of the step-by-step zinc reduction and deposition process in control and PEG200 electrolytes under negative potential bias on the zinc electrode. Reproduced with permission.\textsuperscript{[53]} Copyright 2018, John Wiley and Sons. d) The electrochemical stability window of the pristine electrolyte and after the addition of sodium dodecyl sulfate (SDS) at the critical micelle concentration (referred to as CMC), as measured by linear sweep voltammetry on titanium grid electrodes versus Ag/AgCl at 10 mV s$^{-1}$, where the potentials have been referred to a standard hydrogen electrode (SHE) reference. e) Cycling stability tests of Na$_2$MnFe(CN)$_6$/Zn full cell in pristine electrolyte and SDS-added electrolyte in the voltage range of 1.0-1.8 V at 0.5 C (1 C = 160 mA g$^{-1}$, 0.5 C = 80 mA g$^{-1}$), respectively. Reproduced with permission.\textsuperscript{[56]} Copyright 2017, Royal Society of Chemistry.

In summary, the electrolyte salt and concentration play a significant role in alleviating dendrite formation, improving the CE of Zn electrode, and stabilizing the cathode materials. An organic or inorganic additive can also be introduced to constrain the formation of dendrites, but the influence on the cathode materials and whole battery needs further investigated. Moreover, the most used electrolytes, 1 M ZnSO$_4$ (pH~4.0) and 3 M Zn(CF$_3$SO$_3$)$_2$ (pH~3.6), are acid electrolytes and can cause corrosion of Zn and dissolution of the transition metal and current collectors. The reversibility behaviour of zinc electrode in the mild acid electrolyte systems is not well understood, however, and it requires extensive work in this field.

### 2.4 Zn anode

Most researchers use commercial zinc foil directly as Zn anode. The commercial Zn foil is made by extrusion or roll pressing, however, may have cracks or defects. Even if Zn foil has a smooth and flat surface, after stripping/plating, it will have defects on the surface. Thus, the
Zn\(^{2+}\) distribution on the surface of Zn metal is uneven, and slow Zn\(^{2+}\)-ion diffusion at the interface facilitates dendrite growth. An effective strategy is to coat a surface layer on the Zn foil. Various functional materials, such as reduced graphene oxide (rGO), active carbon, carbon black, TiO\(_2\), and porous nano-CaCO\(_3\) have been reported as protective layers to restrain the dendrite growth, gas evolution, and by-product formation. For example, the rGO layer on top of the Zn can suppress the dendrite growth and significantly decrease the over-potential between plating and stripping.\[^{57}\] The introduction of a porous active carbon layer also facilitates a homogeneous current distribution and the accommodation of Zn deposition, and hence results in stable Zn stripping/plating efficiency, improved kinetics, and long cycle stability (Figure 2.10a).\[^{58}\] In addition to carbon-based materials, Mai et al. demonstrated that an ultrathin coating of TiO\(_2\) could serve as a stable passivation layer to avoid direct contact between the zinc metal and the electrolyte,\[^{59}\] and suppress the zinc corrosion and hydrogen evolution, resulting in enhanced electrochemical performance in both Zn–Zn symmetric cells and Zn–MnO\(_2\) batteries (Figure 2.10b). More recently, Kang et al. significantly improved the electro-stripping/electroplating stability of Zn via a porous nano-CaCO\(_3\)-coating and highlighted the importance of porous coatings.\[^{60}\] As shown in Figure 2.10c, the nanoporous CaCO\(_3\) coated Zn exhibits much lower polarization than the bare Zn one, even at the very beginning. Morphology examination showed that numerous microsized protrusions (from several to several tens of microns) appeared on the smooth and flat surface of the bare Zn foil after 100 stripping/plating cycles. In contrast, the surface morphology of the nanoporous CaCO\(_3\)-coated Zn foil remained smooth and porous without any detectable protrusions after 100 stripping/plating cycles. Therefore, compared to the very uneven Zn stripping/plating in bare Zn, the nanoporous CaCO\(_3\)-coated Zn shows smooth and stable Zn stripping/plating. With high porosity, the nano-CaCO\(_3\)-coating can be readily permeated by the aqueous electrolyte, which allows a relatively uniform electrolyte flux and Zn plating rate over the
entire Zn foil surface, and hence results in a uniform, bottom-up Zn plating process (Figure 2.10d). More interestingly, they also demonstrated the similar functionality in Zn foil coated with porous acetylene black or nano-SiO$_2$ layers.

**Figure 2.10** a) Schematic illustration of carbon-coated Zn (Zn@C) film. Reproduced with permission. Copyright 2018, American Chemical Society. b) Cross-sectional STEM image of TiO$_2$ coated Zn (100TiO$_2$@Zn). Reproduced with permission. Copyright 2018, John Wiley and Sons. c) Typical galvanostatic charge-discharge (GCD) profiles of Zn|ZnSO$_4$+MnSO$_4$|Zn symmetric cells with bare (black) and nano-CaCO$_3$-coated (red) Zn electrodes at a current density of 0.25 mA cm$^{-2}$. d) Schematic illustrations of morphology evolution for bare and nano-CaCO$_3$-coated Zn foils during Zn stripping/plating cycling. Reproduced with permission. Copyright 2018, John Wiley and Sons. e) Energy dispersive spectrometer (EDS) images and corresponding Zn and C elemental maps of Zn + acetylene blacks (AB) + 12 wt.% activated carbon (AC) anode before (a) and after (b)

In addition to the commercial Zn foil, the Zn anode can also be prepared by slurry coating a mixture of zinc powders, conductive carbon, and binder on a current collector. By using suitable additives in this method, the dendrite formation can be also alleviated. For example, Kang et al. prepared a composite anode by mixing zinc particles and activated carbon (AC) for aqueous zinc ion batteries,[61] and found that the AC induces preferential deposition in the pores of AC rather than on the surface of Zn particles (Figure 2.10e,f). As a result, the electrochemical reaction kinetics and reversibility of zinc anode were greatly improved. Mantia et al. found that the addition of layered double hydroxides could avoid the hydrogen evolution and increase the plating/stripping efficiency of zinc anode from 85% to 98%.\cite{62-63}

Another effective strategy is to synthesize novel zinc anodes via electroplating. In this method, the crystallographic properties and morphology of the Zn surface can be tuned by using different additives during the electroplating process. Chen et al. systematically studied the effects of organic additives such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyethylene-glycol (PEG-8000), and thiourea (TU), and of inorganic additives such as indium sulfate, tin oxide, and boric acid.\cite{52-53} They found that each additive can produce a distinct crystallographic orientation and surface texture, and that all these electroplated zinc samples exhibit 6–30 times lower corrosion currents than zinc foil when in contact with the aqueous electrolyte (Figure 2.11a). When these electroplated anodes were used in the Zn/LiMn$_2$O$_4$ hybrid batteries, 79%, 76%, and 80% of the capacity was retained after 1000 cycles with Zn-SDS, Zn-PEG, and Zn-TU, respectively, which are much higher than for the battery assembled with the commercial zinc foil (67%) (Figure 2.11b).
contrast, the Zn/LiMn$_2$O$_4$ hybrid batteries with Zn-inorganic additives displayed 15% higher capacity retention than the battery containing commercial Zn after 1000 cycles (Figure 2.11c).

Furthermore, hierarchical zinc anodes can be synthesized by depositing Zn on a conductive and hierarchical current collector, where the hierarchical morphology and high electroactive surface area could alleviate by-product and dendrite formation. For example, Guo et al. synthesized a three-dimensional (3D) zinc anode on carbon fibers (CFs) by using an electrochemical deposition method,\cite{64} which had larger electroactive areas and low charge transfer resistance. They also fabricated a self-supported Zn@GF negative electrode by directly depositing Zn on a highly conductive carbon fiber-graphite felt (GF) (Figure 2.11d).\cite{65} The GF provides a large electroactive area for Zn plating/stripping and inhibits the growth of dendritic zinc, as well as decreasing voltage hysteresis and increasing cycling stability. Moreover, Zn deposited on 3D graphene foam,\cite{66} carbon cloth,\cite{67} carbon nanotube paper,\cite{68} and carbon nanotube yarns\cite{69} have been also reported to enhance the high rate capability and long durability of zinc batteries by diminishing the formation of dendrites.
In brief, the dendrite formation in mild aqueous electrolyte may not be as severe as in alkaline electrolyte, but it is still a big issue for achieving long cycling performance. The
most effective methods to suppress dendrite growth seem to change the architectures of the 
Zn anode. Compared to planar Zn, the porous and hierarchical Zn possesses higher surface 
area for electrolyte contact and facilitates a uniform electric field. Also, the crystallographic 
surfaces and morphology of the Zn can significantly affect the dendrite formation. The 
methods for solving the problems of dendrite formation are limited, however, and more 
research is very much needed.

2.5 Hybrid Zn batteries using mild aqueous electrolytes

The operation of aqueous Li-ion batteries is fundamentally based on the similar “rocking 
chair” working mechanism with the traditional organic Li-ion batteries. It was first proposed 
in 1994 by Dahn and his co-workers,[70] where LiMn$_2$O$_4$, $\beta$-VO$_2$, and 5 M LiNO$_3$ aqueous 
solution were employed as cathode, anode, and electrolyte, respectively. Since then, various 
aqueous batteries based on alkali metal cations (Li$^+$, Na$^+$, and K$^+$) and naturally abundant 
multivalent cations (Mg$^{2+}$, Zn$^{2+}$ and Al$^{3+}$) have also been developed due to their great 
advantages in term of high operational safety, low overall cost, and environmental 
friendliness.[71] For the traditional Li/Na/K aqueous batteries, unfortunately, the serious 
capacity fading is still a bottleneck for their utilization on a large scale, despite significant 
progresses have been achieved based on the new materials design and electrolyte 
optimization.[71-72] Moreover, unlike the organic system, it is difficult to explore the potential 
of new electrode materials using half-cells in aqueous media, since Li/Na/K metals cannot be 
used directly as the anode. The complicated full-cell assembly processes involved in such as 
the strict capacity ratio also makes it difficult to fully develop an efficient aqueous battery 
system. Recently, Zn metal has served as a highly promising anode candidate for the 
assembly of rechargeable aqueous Zn ion batteries, which helps to achieve a simplified 
rechargeable battery configuration. Because it is significantly important to select a suitable 
and stable anode material to couple with and explore new potential electrode materials,
similar to the half-cells in organic system.\textsuperscript{[73]} Nevertheless, the reversible intercalation/de-intercalation of multivalent Zn\textsuperscript{2+} into/from the cathode host materials cannot be achieved easily due to the sluggish Zn\textsuperscript{2+} diffusion in host lattices, which introduces a huge challenge for the development of advanced cathode materials in aqueous Zn ion batteries. Currently, poor cycling stability and low operating voltage are major problems for cathode materials. To address the aforementioned problems of traditional aqueous Li/Na/K batteries and Zn ion batteries, aqueous Zn hybrid batteries were designed by employing commercial cathode materials in traditional LIBs/SIBs/PIBs with Zn anode. Compared with the traditional aqueous Li/Na/K batteries and Zn ion batteries, the aqueous Zn hybrid batteries feature a simplified rechargeable battery configuration, high operating voltage, long cycling life, and high energy and power density. For example the LiMn\textsubscript{2}O\textsubscript{4}-Zn hybrid battery exhibits a high operating voltages at \~1.9 and 1.7 V and excellent cycling performance over 1000 charge-discharge cycles.\textsuperscript{[74]} Furthermore, differing from the “rocking chair” working mechanism of the usual type of aqueous batteries, Li\textsuperscript{+} ions are insertion/extracted into/from the LiMn\textsubscript{2}O\textsubscript{4} cathode, while Zn\textsuperscript{2+} ions are simultaneously deposited/dissolved into/from the Zn metal anode in this LiMn\textsubscript{2}O\textsubscript{4}-Zn hybrid battery. This novel hybrid battery not only enhances the electrochemical behaviour of the aqueous batteries, but also broadens the research field of rechargeable aqueous batteries by shifting from a single-ion to a double-ion mechanism.\textsuperscript{[77-79]}
The cathode materials based on monovalent ions (Li\(^+\), Na\(^+\)) have been widely employed to couple with Zn to assemble hybrid batteries, which features high voltage plateaus and high energy density.\(^{[80]}\) The first aqueous hybrid battery consisted of an olivine-phosphate LiCo\(_{1/3}\)Mn\(_{1/3}\)Ni\(_{1/3}\)PO\(_4\) cathode and a Zn foil anode was proposed in 2012.\(^{[81]}\) A hybrid solution of LiOH and 1 M ZnSO\(_4\) with a pH equal to ~10.5 served as the electrolyte. The authors compared the electrochemical performance of LiCo\(_{1/3}\)Mn\(_{1/3}\)Ni\(_{1/3}\)PO\(_4\) materials that were prepared by solid-state synthesis and the sol-gel method, respectively. The results indicated that the sol-gel synthesised LiCo\(_{1/3}\)Mn\(_{1/3}\)Ni\(_{1/3}\)PO\(_4\) offered superior performance with an initial discharge capacity of ~45 mA h g\(^{-1}\) and a stabilized capacity of ~60 mA h g\(^{-1}\) over the initial 25 cycles. Nevertheless, the capacity is unsatisfactory, as it is still much lower than
the theoretical capacity. Furthermore, this work failed to provide the working mechanism for this aqueous hybrid battery.\textsuperscript{[82-84]}

More comprehensive working mechanism of a hybrid system was reported in the LiMn\textsubscript{2}O\textsubscript{4}/ZnCl\textsubscript{2} + LiCl/Zn battery.\textsuperscript{[75]} Firstly, the CV measurements of LiMn\textsubscript{2}O\textsubscript{4} and Zn electrode were conducted separately to evaluate the feasibility of assembling the hybrid battery. As shown in Figure 2.12a, the reversible redox peak observed at ~0 V was assigned to the reversible deposition/dissolution of Zn, which is higher than the hydrogen evolution potential. Two redox peaks at ~1.7-1.9 V can be attributed to two-phase lithium extraction/intercalation from/into the spinel LiMn\textsubscript{2}O\textsubscript{4} cathode, which are lower than the oxygen evolution potential. The results indicate that both the LiMn\textsubscript{2}O\textsubscript{4} and Zn metal provide favourable conditions for efficient battery operation within the stability window of the aqueous electrolyte. Then, the ex-situ XRD analysis of the Zn/LiMn\textsubscript{2}O\textsubscript{4} battery (Figure 2.12b,c) confirmed the Li\textsuperscript{+} extraction/insertion into/from the LiMn\textsubscript{2}O\textsubscript{4} cathode and the reversible deposition/dissolution of Zn on the current collector during charge-discharge process. Thus, this hybrid battery works based on the mechanism of Li\textsuperscript{+} ions intercalation/de-intercalation into/from the LiMn\textsubscript{2}O\textsubscript{4} cathode while Zn\textsuperscript{2+} ions are simultaneously deposited/dissolved into/from the Zn anode, differing from the “rocking chair” working mechanism of traditional LIBs (Figure 2.12d). The electrochemical reaction of LiMn\textsubscript{2}O\textsubscript{4} electrode and Zn metal anode can be concluded as follows:

\begin{align*}
\text{Cathode: } & \text{LiMn}_2\text{O}_4 \leftrightarrow \text{Li}_{1-x}\text{Mn}_2\text{O}_4 + x\text{Li}^+ + xe^- \\
\text{Anode: } & \text{Zn}^{2+} + 2e^- \leftrightarrow \text{Zn}
\end{align*}  \hspace{1cm} (2-11)  \hspace{1cm} (2-12)

Benefiting from the hybrid ions contribution, the aqueous battery displays high discharge plateaus at ~1.9 and 1.7 V (Figure 2.12e), and excellent cycling performance, with a capacity retention of ~90\% over 1000 charge-discharge cycles (Figure 2.12f). However, compared to
other commercial cathode material in LIBs, such as LiFePO$_4$\cite{76} Li$_3$V$_2$(PO$_4$)$_3$ (LVP),\cite{77} and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$;\cite{82} LiMn$_2$O$_4$ cathode still suffers from the low capacity and unstable structure stability, which limits its application on a large-scale.

As a promising cathode candidate in non-aqueous LIBs, the monoclinic LVP has attracted much attention because of its high theoretical specific capacity (~191 mA h g$^{-1}$), high operating voltage and thermodynamically stable structure.\cite{77,83} Theoretically, the discharge plateaus of LVP in the aqueous media should be obtained at ~1.25 V, 1.35 V, 1.75 V, and 2.2 V (vs. Zn$^{2+}$/Zn) by calculation (Figure 2.13a). Unfortunately, the plateau voltage at ~2.2 V assigned to the de-intercalation of the third Li ion from LVP is higher than oxygen evolution potential, which indicates that the third Li$^+$ is unlikely to extract from LVP in aqueous media. CV measurements (Figure 2.13b) of Zn/LVP battery in hybrid electrolyte of 1 M Li$_2$SO$_4$ + 2 M ZnSO$_4$ show three pairs of cathodic/anodic peaks in the voltage range of 0.7-2.1 V,
demonstrating that the partial Li ions are intercalated/de-intercalated during the charge-discharge process. Specifically, the two cathodic peaks at ~1.48 and 1.58 V corresponds to the extraction of the first Li ion, which was attributed to the phase transition from LVP to Li$_{2.5}$V$_2$(PO$_4$)$_3$ phase and from Li$_{2.5}$V$_2$(PO$_4$)$_3$ to Li$_2$V$_2$(PO$_4$)$_3$ phase, respectively.$^{[77, 84]}$ The third pair of cathodic/anodic peaks at ~1.72 V/2.01 V is related to the extraction/insertion of the second Li ion, corresponding to the phase transition between Li$_2$V$_2$(PO$_4$)$_3$ and LiV$_2$(PO$_4$)$_3$ phase.$^{[85]}$ However, the third Li ion is impossible to extract from in LVP lattice as the oxygen evolution caused by decomposition of H$_2$O occurred early, which was further confirmed by the charge/discharge curves at the current density of 0.2 C (Figure 2.13c). The three discharge plateaus on the charge/discharge profiles can be observed with a high capacity of ~130 mA h g$^{-1}$, demonstrating that LVP cathode features a two Li$^+$ ion insertion/extraction behaviour. Furthermore, the structure transitions of LVP cathode was analysed by ex-situ XRD to explore its electrochemical mechanism in the hybrid system (Figure 2.13d,e). Only minor change of XRD patterns without new Zn related phase can be observed, demonstrating that Li$^+$ instead of Zn$^{2+}$ extraction/insertion from/into the host lattice of LVP, although the ionic radius of Zn$^{2+}$ is similar to that of Li$^+$. Based on the electrochemical behaviours as well as the ex-situ XRD results, the reaction mechanism of this LVP-Zn hybrid battery could be described as following:

\[
\text{Li}_3\text{V}_2(\text{PO}_4)_3 + 0.25\text{Zn}^{2+} \leftrightarrow \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 + 0.5\text{Li}^+ + 0.25\text{Zn} \tag{2-13}
\]

\[
\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 + 0.25\text{Zn}^{2+} \leftrightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3 + 0.5\text{Li}^+ + 0.25\text{Zn} \tag{2-14}
\]

\[
2\text{Li}_2\text{V}_2(\text{PO}_4)_3 + 0.5\text{Zn}^{2+} \leftrightarrow 2\text{LiV}_2(\text{PO}_4)_3 + \text{Li}^+ + 0.5\text{Zn} \tag{2-15}
\]

In addition to the exploration of cathode materials, some efforts focused on the optimization of the hybrid electrolyte were also made, in which the some additives including thiourea (0.14 wt.%),$^{[86]}$ SiO$_2$ (5 wt.% and 10 wt.%),$^{[87]}$ and mixture of b-cyclodextrin (CD) and
fumed silica\[88\] were mentioned for enhancing the electrochemical performance. Furthermore, the effect of the pH value of the hybrid electrolyte on the electrochemical performance was also discussed in the Zn/LVP hybrid system by Chen et al.\[77\] The dilute LiOH or H\(_2\)SO\(_4\) was employed to modify the electrolyte with different pH (3.5-5) and evaluate the effect on the cycling performance. The results suggest that the optimized electrolyte with a pH at about 4 to 5 is more suitable for the hybrid Zn/LVP system. The low pH (~ 3.5) of electrolyte causes the sluggish dissolution of Zn anode, leading to the obvious capacity fading. In contact, with the pH increases to 5.5, the OH\(^-\) concentration will increase and precipitate with Zn\(^{2+}\), which effects the Zn\(^{2+}\) concentration and slower Zn\(^{2+}\) mobility. Overall, the adaptable pH electrolyte plays an important role in developing the high-performance hybrid system. Very recently, Wang et al. reported a highly concentrated aqueous electrolyte based on Zn and Li salts as an effective way to address irreversibility issues of Zn anode in terms of low CE and dendrite growth during plating/stripping.\[48\] As a result, the high concentration of hybrid electrolyte consist of 1 M Zn(TFSI)\(_2\) + 20 M LiTFSI renders the Zn/LiMn\(_2\)O\(_4\) battery have a long cycling life by enhancing the CE and suppressing the growth of Zn dendrite.

Recently, Na-Zn hybrid batteries have emerged as promising sustainable energy-storage devices for large-scale applications aiming to substitute Li-Zn system owing to the low cost, naturally abundant, and environmentally benign of the sodium resource. In 2013, Wu and his co-workers developed a first Na-Zn hybrid battery, where the metallic Zn and a rod-like Na\(_{0.95}\)MnO\(_2\) function as anode and cathode in the aqueous electrolyte of 0.5 M CH\(_3\)COONa and 0.5 M Zn(CH\(_3\)COO)\(_2\).\[76\] Although this battery shows a good cycling stability, with only 8% capacity loss after 1000 cycles, Na\(_{0.95}\)MnO\(_2\) still suffers from low capacity of ~60 mA h g\(^{-1}\) and low CE (~90% at 4 C). Subsequently, tunnel-type Na\(_{0.44}\)MnO\(_2\),\[90\] Na\(^+\) ion superionic conductor (NASICON) structure Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) (NVP) and carbon-coated NVP with the high theoretical capacity of ~117 mA h g\(^{-1}\) were investigated in the hybrid system.\[91\] Very
recently, Kim et al. designed a carbon-wrapped sponge-like NVP@C electrode material prepared by a simple pyro synthesis to pair with Zn foil to assemble hybrid system in the electrolyte of 1 M Zn(CH$_3$COO)$_2$ and 2 M CH$_3$COONa solution, as illustrated in Figure 2.14a.[89] The CV measurement shows the distinct cathodic/anodic peaks at ~1.45/1.58 V, corresponding to the de-intercalation/intercalation of Na$^+$ ions from/into the NVP phase, which was accompanied with the transition between V$^{3+}$ and V$^{4+}$ (Figure 2.14b). The 1$^{st}$, 2$^{nd}$, 5$^{th}$, and 9$^{th}$ cycles of the CV curves of the NVP@C-Zn hybrid battery suggested identical profiles, indicating its high reversibility. The typical charge/discharge profiles display a clear single discharge plateau at ~1.45 V with a high capacity of ~91 mA h g$^{-1}$ at 0.4 C (Figure 2.14c), indicating stable Na$^+$ ion intercalation into the NVP@C cathode. Figure 2.14d presents in-situ XRD patterns of the NVP@C electrode in the NVP@C-Zn hybrid battery during charging/discharging process. All peaks are indexed to the NVP phase before charging. Several new peaks located at ~14.7, 29.7, 32.9, and 37.18 emerge upon continuous charging, assigned to the NaV$_2$(PO$_4$)$_3$ phase, which demonstrates two Na$^+$ ions were completely de-intercalated from the NVP host structure along with the oxidation of V$^{3+}$ to V$^{4+}$. During subsequent discharging process, the intensity of the characteristic peaks of NaV$_2$(PO$_4$)$_3$ weaken gradually before completely disappearing. As the discharge was finished, the electrode was reverted to the NVP structure again. Based on the in-situ XRD studies, it can be easily concluded that the NVP@C electrode in this hybrid battery is of high stability and high reversibility. The overall electrochemical reactions of this hybrid NVP@C-Zn battery can be written as:

\[
\text{Cathode: } \text{Na}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{NaV}_2(\text{PO}_4)_3 + 2\text{Na}^+ + 2\text{e}^- \quad (2-16)
\]

\[
\text{Anode: } \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn} \quad (2-17)
\]
Apart from the traditional Na-containing cathode materials, Prussian blue and its analogues have been considered as the highly promising cathode candidates for the Na-Zn hybrid system due to their open framework crystal structures and unique properties, including chemical stability as well as high environmental compatibility[92-93]. Most of Prussian blue and its analogues feature a good rate capability and cycling performance, however, the capacity (~50–80 mA h g⁻¹) is limited compared with the traditional Na-containing cathode materials. Very recently, Prussian yellow was also firstly proposed as a cathode material in the K-Zn hybrid system by Baioun and co-workers[94], which not only broadens their application in the aqueous hybrid systems but also paves the way to develop the hybrid K-Zn system.

Figure 2.14  a) Schematic illustrations of the operation mechanism for a Zn/Na₃V₂(PO₄)₃ hybrid battery. b) CV profiles of the Zn/Na₃V₂(PO₄)₃ battery at 0.5 mV s⁻¹. c) Charge/discharge profiles of the Zn/Na₃V₂(PO₄)₃ battery at various current densities. d) In-situ XRD pattern of Na₃V₂(PO₄)₃@C electrodes during charging-discharging process. Reproduced with permission[89] Copyright 2018, John Wiley and Sons.
In a word, although the electrochemical performance of Li/Na/K-Zn hybrid systems is not as good as that of the MnO$_2$-based or V$_2$O$_5$-based ZIB system, it is still meaningful for the development of aqueous hybrid batteries. Furthermore, these studies also help to ease hurdles that will be encountered in realizing the aqueous hybrid batteries as environment-friendly energy storage devices on a large scale.

2.6 References


[70] Li, W., Dahn, J. R., Wainwright, D. S. *Science* 1994, 264, 1115.


[91] Li, G., Yang, Z., Jiang, Y., Zhang, W., Huang, Y. J. Power Sources 2016, 308, 52-57.


Chapter 3

Experimental section

3.1 Overview

The general procedure and the logical framework of this thesis work are summarized in Figure 3.1. The artificial layers on Zn metal surface were built via different techniques (ex-situ coating, in-situ vapour-solid strategy). The structural features of the coating layers before and after battery operation were characterized by numerous techniques, including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM), Brunauer-Emmett-Teller (BET) measurements, and scanning electron microscopy (SEM). The electrochemical performance was measured for the protected Zn electrode in aqueous ZIBs and hybrid Zn batteries in the coin cell and pouch cell by CV, change-discharge, and EIS, etc. In-situ characterizations such as Operando synchrotron XRD and in-situ optical microscope were also conducted to investigate the structural changes of LFP cathode and Zn dendrite growth during electrochemical cycling. All the theoretical calculations were performed by employing the first-principles projector augmented wave (PAW) method based on density functional theory (DFT) with the Perdew-Burke-Ernzehof (PBE) functional as implemented in the Vienna ab initio simulation package.
Figure 3.1 Outline of the research framework, which includes the characterization, the evaluation of the electrochemical performance, and the theoretical calculations.

3.2 Chemicals and materials

The chemicals and materials used in this work are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
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<td>C₂H₅OH</td>
<td>Reagent</td>
<td>Q-store, Australia</td>
</tr>
<tr>
<td>Acetylene black</td>
<td>C</td>
<td>Super P</td>
<td>Timcal, Belgium</td>
</tr>
<tr>
<td>Lithium iron phosphate</td>
<td>LiFePO₄</td>
<td>99.0%</td>
<td>Kejing Star Technology</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>N/A</td>
<td>N/A</td>
<td>Kejing Star Technology</td>
</tr>
<tr>
<td>Copper foil</td>
<td>Cu</td>
<td>N/A</td>
<td>Kejing Star Technology</td>
</tr>
<tr>
<td>Zinc foil</td>
<td>Zn</td>
<td>N/A</td>
<td>Kejing Star Technology</td>
</tr>
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<td>(C₂F₄)ₙ</td>
<td>60%/ water</td>
<td>Sigma-Aldrich</td>
</tr>
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<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Zinc trifluoromethanesulfonate</td>
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<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Manganese trifluoromethanesulfonate</td>
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<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>SDBS</td>
<td>CH₃(CH₂)₁₁C₆H₄SO₃Na</td>
<td>N/A</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
3.3 Materials preparation

In this doctoral work, three strategies have been proposed to address the Zn metal issues in mild electrolyte, in which one is adding the commercial surfactant as the electrolyte additive to study the effects on the Zn dendrite growth. In this case, no electrode material needs to be synthesized. In addition, the artificial layers of PVB polymer and ZnS were built on the Zn metal surface to inhibit the dendrite growth and side reactions by \textit{ex-situ} and \textit{in-situ} strategies, respectively. Specifically, the artificial PVB film coated on the surface of Zn foil was obtained via a spin-coating method. The bare Zn foil was polished using abrasive paper to remove the oxidation layer. The PVB powder was dissolved in ethanol to prepare a 10 mg ml\(^{-1}\) PVB solution. Subsequently, the PVB was homogeneously coated on the fresh Zn foil using a spin-coater at a spin-speed of 400 rpm for 5 min. For the ZnS layer preparation, Zn foil was cut into Zn ribbon (5 cm \(\times\) 2 cm), then the one side of Zn ribbon was polished. Two polished Zn ribbons were put in a specially designed tube with 100 g sulfur powder below it. Then, the tube was evacuated and sealed. After that, a high-temperature treatment was carried out with a given heating rate of 5 °C min\(^{-1}\) at target temperature of 300, 350, and 400 °C for 2 h in a Muffle Furnace (151H1TN). Finally, the ZnS coated Zn foils were obtained, which were denoted as ZnS@Zn-300, ZnS@Zn-350, and ZnS@Zn-400, respectively.
3.4 Characterization techniques

3.4.1 X-ray powder diffraction (XRD)

XRD is a facile and basic analytical technique mainly employed to investigate the crystal structures and phases of materials. There is characteristic relationship between the wavelength and spacing of the crystal, and Bragg’s law \(2dsin\theta = n\lambda\) is employed to describe the diffraction from planes with spacing \(d\), where \(\theta\) is the angle of incidence with the lattice planes, \(d\) is the distance between lattice planes, \(n\) is any integer, and \(\lambda\) is the X-ray wavelength of the beam. In this thesis, A GBC MMA X-ray generator with Cu K\(\alpha\) radiation \((\lambda = 1.5406 \text{ Å})\) was hired to detect different Zn electrodes at various states and the powders, such as ZnS and PVB. The Zn electrode or the powder materials are uniformly stacked on a disk holder, and the holder is placed on the axis of the diffractometer at an angle \(\theta\). The detector rotates around the diffractometer at the corresponding angle \(2\theta\). The current and working voltage were set at 40 kV and 25 mA, respectively.

3.4.2 Scanning electron microscopy (SEM)

SEM is one of the most commonly used electron microscopes to observe the microscopic information of the material. It can use a high energy electron beam to scan and collect images of the target materials. The electrons can interact with the atoms derive from the samples surface, producing signals that referring to the sample’s surface composition and topography. In this thesis, the morphology of various Zn electrodes and other materials was investigated with the field-emission scanning electron microscope (FE-SEM, JEOL JSM-7500FA). For the preparation Zn electrode samples, Zn electrode would be directly pasted onto an aluminium holder with black conductive carbon tape or placed in the special cross-section holder.

3.4.3 Atomic force microscopy (AFM)
The atomic force microscope (AFM) is one kind of scanning probe microscopes (SPM) and they are designed to measure local properties, such as height, friction, magnetism, with a probe. To acquire an image, the SPM raster-scans the probe over a small area of the sample, measuring the local property simultaneously. In this thesis, a commercial AFM (Asylum Research MFP-3D) was used to measure the morphology and thickness of the SBS nanosheets in trapping mode. An Al coated n-silicon probe with resonance frequency of 204-497 kHz and force constant of 10-130 N m\(^{-1}\) was used in the AFM measurements.

### 3.4.5 Raman Spectroscopy

Raman spectroscopy as a common spectroscopic technique can observe rotational, vibrational, and low-frequency modes. Laser light can shift up and down when it interacts with phonons molecular vibrations, or other kind excitations. The different energy indicates information on the vibrational modes, and these vibrational information can suggest the chemical bonds and symmetry of molecules. In this thesis, Raman spectroscopy (Jobin Yvon HR800) employing a 10 mW helium/neon laser at 632.8 nm and Raman spectra of the targets samples were captured via mapping.

### 3.4.6 Fourier-transform infrared spectroscopy (FTIR)

FTIR is a useful tool to investigate the infrared spectrum of adsorption or emission from solid, liquid, or gas. Specially, it can gather high-spectral-resolution signals over a wide spectral range. Therefore, it would offer significantly wider information than a dispersive spectrometer. In this thesis, FTIR maps of the interphase between PVB protected Zn electrode and electrolyte were collected using a PerkinElmer Spotlight 400 equipped with a mercury cadmium tellurium (MCT) detector, which consists of single point (point mode) and 16-array (image mode) detectors all in one. Maps of \(2 \times 8\) points (~200 \(\times\) 100 \(\mu\)m\(^2\) area) in reflectance mode were acquired at 4 cm\(^{-1}\) resolution with 16 scans per pixel from 4000 to 400 cm\(^{-1}\). The drop down average true range is determined by a Ge crystal 100 \(\mu\)m in
diameter. Principal component analysis is one of the most widely used methods for data reduction and exploratory analysis. In this work, PCA analyses of the selected FTIR regions corresponding to the 400–4000 cm\(^{-1}\) range were obtained to reveal the uniformity of the functional groups and SEI layer.

3.4.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is kind of a surface-sensitive quantitative spectroscopic technique. It primarily used to investigate the empirical formula, elemental composition, chemical states and electronic states of the elements in target material. When it is underworking, a beam of X-rays is used to interact with the material, and then numbers of electrons and the kinetic energy produced from the top surface of the material (0–10 nm) are monitored simultaneously, which could result in the XPS spectrums. In this thesis work, the XPS analysis of PVB and ZnS layers or Zn electrodes were carried out to characterize the chemical bonds in samples. These XPS analysis were conducted on a VG Scientific ESCALAB 2201XL system with aluminium Ka X-ray radiation.

3.4.8. Operando synchrotron XRD

XRD is a useful tool to study the phase structure as mentioned in 3.4.1. The reaction mechanism of the electrode during cycling is very important to help understand the volume changes, phase transitions, and structural stability. Ex-situ XRD could be used to study the discharge or charge products, although the possibly exposure to the air and the uncertain phase stability of the electrode may lead to unreliable results. In terms of these concerns, in-operando measurements are an effective tool which reflects the phase transitions in real time during cycling. In this thesis work, a customized CR2032 coin cell was assembled for conducting the operando synchrotron XRD experiments, and the details of cell assembly can be found elsewhere. The operando synchrotron XRD experiments of the hybrid Zn batteries were conducted on the Powder Diffraction beamline at the Australian Synchrotron. The
wavelength of synchrotron radiation was determined to be 0.68899 Å using LaB6 (Standard Reference Material SRM 660b).

### 3.4.9. Contact angle measurements

The contact angle is the angle, conventionally measured through the liquid, where a liquid–vapor interface meets a solid surface. It quantifies the wettability of a solid surface by a liquid via the Young equation. A given system of solid, liquid, and vapor at a given temperature and pressure has a unique equilibrium contact angle. In this thesis, the contact angles of different Zn electrodes with electrolyte were measured on Dataphysics OCA15 optical contact angle system with 1 µL of electrolyte for each test at the temperature of 25 °C.

### 3.5. Theoretical calculations

Since the last century, starting with the 1970s, density functional theory (DFT) was very popular for the solid-state physics. It is a commonly accepted method used to investigate electronic structures, especially in atoms, molecules, and condensed phases in substances, relying on computational quantum mechanical modelling methods. It has its name because it is calculated based on the functional of the electron density. In this thesis work, the calculations of LFP/Zn battery and ZnS protected Zn electrode were performed based on the DFT approach using the DMol3 package. The effects of the exchange correlation interaction were treated according to the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE). Ab initio calculations were based on density functional theory as applied successfully to a range of battery materials. The VASP code was used with the PBE exchange-correlation functional and an energy cut-off for plane-waves of 400 eV. Interactions between core and valence electrons are described by the projector augmented wave (PAW) method. The gamma-point is used for the Brillouin zone sampling. Molecular dynamics simulations were performed using the NVT ensemble with a Nose–Hoover thermostat. Each interface is simulated at 500 K with a time step of 1.5 fs for 15 ps. The
LiFePO₄ (010)/H₂O interface is modelled by a seven-layer LiFePO₄ slab along the b axis and a cross-section of a 1 × 2 ac plane, and 8 water molecules above the surface. The LiFePO₄ (010)/sodium dodecyl benzene sulfonate (SDBS) interface is modelled using the same LiFePO₄ slab configuration and one SDBS molecule above the surface.

3.6 Electrochemical measurements

3.6.1 Cyclic voltammetry (CV)

CV as common technique can investigate the redox reactions for the energy storage systems. The CV gives information on the stability of the reaction products, the intermediates participating in the redox reaction, the electron stoichiometry, the reversibility of a reaction and the electron transfer kinetics. CV show a hysteresis curves in the absolute potential between the cathodic peaks and anodic peaks due to the polarization caused by low diffusion rates and the activation barrier preventing the electron transfer among the electrodes. Typically, in the CV test, the cell potential can be scanned with a specified rate, and the relevant current is obtained. Herein, in this thesis, the CV data were collected on a Biologic VPM3 workstation in ISEM of UOW.

3.6.2 Galvanostatic charge/discharge

Galvanostatic charge-discharge are normally performed in a constant current density in order to study the specific capacity and cycling performance of the electrode in a certain voltage range. Moreover, it is also an effective technique to investigate the rate capability of the target electrodes via employing the different of current densities. The specific capacity during charge and discharge can be regarded as the total electrons in the corresponding charge/discharge process. The specific capacity can be calculated from the employed current and the waste time. In this thesis, galvanostatic charge-discharge tests were performed via an
automatic battery tester system (Neware®, China) and the galvanostatic charge/discharge performances of the LIB and KIB were collected in air with the room temperature.

3.6.3 Electrochemical impedance spectroscopy (EIS)

EIS as a significant measurement technique, can be applied to estimate the internal resistance of target electrodes and cells. The EIS technique could indicate the important information including the ohmic resistance, charge transfer resistance, and double layer capacitance. In an impedance spectrum, normally, it is consisting of a semicircle at high frequency and a linear tail at low frequency. Among them, the semicircle can be regarded as the charge transfer resistance, which could reflect the double layer capacitance and the kinetic processes. The linear tail ascribes to the diffusion of ions that from migrates from the electrolyte into the electrode. What is more, EIS can be used to measure the apparent energy activation and ion diffusion of the electrode. EIS data were recorded on a Biologic VPM3 electrochemical workstation in this thesis in UOW.
Chapter 4

Electrolyte additive effects on the aqueous hybrid Zn-based batteries

4.1 Introduction

LIBs are the state-of-the-art secondary battery techniques in the market of portable electronics, and widely regards as a potential technology for electric vehicles due to their long cycle life and high energy density.[1-2] Unfortunately, the growing concerns about the safety issues as well as high cost limit their further developments. Moreover, the abandoned LIBs with the flammable organic electrolytes and toxic elements rise another huge environmental concern.[3] Therefore, seeking the safe, inexpensive and environmental-friendly alternatives to LIBs is of utmost urgency especially for smart-grid applicants.[4] Aqueous rechargeable batteries are particularly attractive for large-scale energy storage in terms of innate safety advantages, economy and environmental benignity, in which ZIBs with zinc metal as anode have been investigated intensively due to its low potential (~0.76 V vs. SHE), high theoretical capacity (~820 mA h g⁻¹), and high over-potential for hydrogen evolution in aqueous media.[5-6]

Although ZIBs based on the mild aqueous electrolyte have gained some progress presently, their further development still faces the huge challenges due to the sluggish multivalent Zn-ion diffusion in host materials, which mainly caused by their strong electrostatic interaction with host lattice.[7] Recently, the hybrid Zn-based batteries were designed using the conventional cathode materials of LIBs or sodium ions batteries (e.g. LFP or Na₀.₄₄MnO₂) and Zn foil anode.[8-9] Theoretically, this novel hybrid battery can not only avoid the sluggish Zn-ion diffusion kinetics in the cathode materials, but also broaden the research field of aqueous batteries by shifting from a single-ion to a double-ion mechanism.[10] Despite
different hybrid Zn-based systems with advanced performance have been proposed in recent years, their hybrid working mechanism is still confusing. As the radius of $\text{Li}^+$ ion (0.76 Å) or $\text{Na}^+$ ion (1.02 Å) is larger than that of $\text{Zn}^{2+}$ ion (0.74 Å), indicating the higher energy barriers may encounter for the larger ion’s intercalation. Additionally, some polyanion based robust crystal architectures, such as $\text{LiV}_2(\text{PO}_4)_3$ and $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$, for the reversible intercalation/de-intercalation by $\text{Zn}^{2+}$ ions have also been confirmed. Thus, systematic exploring the working mechanism is needed.

Apart from the operational mechanism, the existing hybrid Zn-based techniques are still far from fulfilling the ambitions of excellent performances demanded by the ever-increasing energy consumption. Moreover, the electroplating on the Zn metal anode with uneven morphology leads to the inhomogeneous distribution of $\text{Zn}^{2+}$ ion near to its surface. The protrusions with high curvature have a considerably higher electric field at the tips, which tends to attract more $\text{Zn}^{2+}$ ions, leading to further growth of the protrusions and finally evolving into Zn dendrites. The growth of Zn dendrites during plating/stripping process not only causes the “loss” of reversible capacity by formation of “dead” Zn, but also seriously fades the CE and cycle life. But even worse, Zn dendrites normally grow up in the direction perpendicular to the surface of Zn metal, which is a potential safety hazard for internal shorting failure of the battery after they pierce the separator. On the other hand, the wetting property of electrode in aqueous media is limited, which severely impacts on ion diffusion at the interface of electrode and electrolyte. Furthermore, insufficient electrolyte wetting on the cathode surface causes uneven electrochemical reactions and accelerates the degradation of cathode material, resulting in a poor rate capability and shortened cycle life. Therefore, suppressing the Zn dendrite growth on Zn anode as well as improving the ion diffusion kinetics at the cathode/electrolyte interface are of top priority to enhance the electrochemical properties of hybrid Zn-based batteries.
Here, the working mechanism of hybrid LFP/Zn battery was studied by *operando* synchrotron XRD in detail, revealing only Li$^+$ ion involves in the reaction on the cathode during charge-discharge process. In addition, a cheap electrolyte additive, SDBS, was reported to improve the electrochemical behaviors of a hybrid LFP/Zn battery. Based on the operating mechanism, the effects of the additive on this hybrid battery was investigated in detail. Specifically, the additive not only inhibits the Zn dendrite growth by manipulating the Zn plating pattern but also accelerates Li-ion diffusion at the LFP cathode/electrolyte interface at the same time. With the assistance of additive, Zn$^{2+}$ ions are deposited smoothly on the surface of Zn metal instead of vertical growth of Zn dendrite in the flake-shape. Simultaneously, the Li-ion diffusion coefficient was increased from $1.78 \times 10^{-11}$ cm$^2$s$^{-1}$ to $8.22 \times 10^{-11}$ cm$^2$s$^{-1}$ by improving the wettability of LFP electrode, which contributes to the rate capability of the battery. As a consequence, the hybrid LFP/Zn battery with the surfactant additive delivers a reversible capacity of 158.2 mA h g$^{-1}$ with a high initial CE of 94.5% at 0.5 C and an excellent cycling stability over 500 cycles at 5 C. Additionally, the hybrid LFP/Zn pouch cell with electrolyte additive was assembled, which also shows an impressive electrochemical properties. To evaluate the broad feasibility of this additive, the electrochemical behaviours of the aqueous MnO$_2$/Zn batteries with/without additive were compared. The results confirmed that the battery with additive delivered a superior cycling stability to that without additive.

### 4.2 Experimental Section

#### 4.2.1 Material Characterization

The crystalline structure of LFP was investigated by XRD (GBC MMA diffractometer) with Cu Kα radiation. The morphologies of the LFP, Zn foil, and the electrodeposit Zn electrodes were investigated by field emission SEM. Contact angles were measured on a Dataphysics OCA15 apparatus with 1 µL of hybrid electrolyte solution for each test. A synchrotron cell
was used for *operando* XRD measurements, for the LFP/Zn battery, which is similar to the coin cells used in electrochemical testing. The cell was galvanostatically charged-discharged in 0.8-1.4 V (vs. Zn\(^{2+}\)/Zn) at a current rate of 0.2 C. The XRD patterns were collected every 3 min using a MYTHEN micro-strip detector during the charge-discharge process. The used wavelength was detected to be 0.6887 Å using a LaB\(_6\) NIST SRM 660b (Australian Synchrotron).

### 4.2.2 Electrochemical measurement

Electrochemical characterization of the LFP/Zn batteries was performed by using both 2032-type coin-cell and pouch-cell. The LFP electrode was made from a mixture of 75% active materials (LFP), 15% acetylene black, and 10% PTFE binder. The mixture was rolled out into a thin sheet, then was cut into 8.0 mm pellets and pressed on the stainless steel (10 mm). Subsequently, the electrode was dried at 80 °C for 12 hours in vacuum oven. The electrolyte is 1 M Li(SO\(_3\)CF\(_3\)) and 1 M Zn(SO\(_3\)CF\(_3\))\(_2\) solution in deionized water. The CV and constant current charging/discharging tests were completed using a Bio Logic VMP3 Multi-Channel Potential/Electrochemical Impedance Spectrometer and Land BT2000 battery test system (Wuhan, China), respectively. The electro-deposition of Zn was performed in a standard two-electrode glass cell consisting of the clean Cu foil working electrode, a Pt plate counter electrode at a current density of 5 mA cm\(^{-2}\) for 1 h. The MnO\(_2\) electrode was obtained by the constant piezoelectric electro-deposition in the coin-cell using carbon cloth as cathode, Zn as anode, the solution of 1 M Mn(SO\(_3\)CF\(_3\))\(_2\) and 1 M Zn(SO\(_3\)CF\(_3\))\(_2\) as electrolyte. The electrochemical performance of MnO\(_2\)/Zn battery was tested in coin-cell, in which 0.5 M Mn(SO\(_3\)CF\(_3\))\(_2\) and 1 M Zn(SO\(_3\)CF\(_3\))\(_2\) used as electrolyte.

### 4.2.3 Theoretical Calculations

In current work, the behaviour of molecular dynamic is stimulated by using the NVT ensemble with a Nose-Hoover thermostat at 300K, and all Ab initio calculations were
performed at VASP package (Revision 5.4.1). To reduce computational cost, $3 \times 3$ LFP (010)/H$_2$O and four water molecules above surface and $3 \times 3$ LFP (010)/SDBS slab model is used and one SDBS molecule and seven water molecules above the surface. The default cut-off energies of H, Li, C, O, Na, P and Fe atoms, PBE exchange-correlation functional are used, and the gamma point is $2 \times 1 \times 1$. Furthermore, the time step is 1 fs for 139 fs.

Ab initio calculations were based on density functional theory as applied successfully to a range of battery materials. Here, the VASP code was used with the PBE sol exchange-correlation functional and an energy cut-off for plane-waves of 400 eV. Interactions between core and valence electrons are described by the projector augmented wave (PAW) method. The gamma-point is used for the Brillouin zone sampling. Molecular dynamics simulations were performed using the NVT ensemble with a Nose–Hoover thermostat. Each interface is simulated at 500 K with a time step of 1.5 fs for 15 ps. The LFP(010)/H$_2$O interface is modelled by a seven-layer LFP slab along the $b$ axis and a cross-section of a $1 \times 2$ ac plane, and 8 water molecules above the surface. The LFP (010)/SDBS interface is modelled using the same LFP slab configuration and one SDBS molecule above the surface.

**4.3 Results and Discussion**
Figure 4.1 a) The scheme of the hybrid aqueous Zn-LFP battery. b) The in-operando synchrotron patterns of the hybrid Zn-LFP (left) and the corresponding charge-discharge curve (right). c) The contour plots of the operando synchrotron XRPD data: 15.5°–16.5°, in which the (131) peak of LFP is converted to the (311) peak of FePO$_4$ during the initial charge process.

The configuration and operational mechanism of this hybrid LFP/Zn battery were presented in Figure 4.1a, where LFP services as the cathode material, Zn foil functions as anode and current collector, and the hybrid 1 M Zn(SO$_3$CF$_3$)$_2$ and 1 M Li(SO$_3$CF$_3$) solution works as the electrolyte. In this hybrid cell, Li$^+$ ion will be extracted from LFP cathode and migrates into the electrolyte in the charging process. Meanwhile, the Zn$^{2+}$ ion from the hybrid electrolyte will deposit on the surface of Zn anode as the potential of Zn$^{2+}$/Zn (–0.76 V vs. SHE) is higher than that of Li$^+$/Li (–3.04 V vs. SHE).$^{[20]}$ In the discharging process, it was proposed that Li$^+$ ion from the hybrid electrolyte will inserted into the heterosite (FePO$_4$) by
generating LFP. Simultaneously, Zn metal will lose electrons by forming Zn$^{2+}$ ion and migrate back to the electrolyte. However, as the radius of Li$^+$ ion (0.76 Å) is slightly larger than that of Zn$^{2+}$ ion (0.74 Å), it is confusing whether the Zn$^{2+}$ ion could co-insert into FePO$_4$ cathode or not.$^{[21]}$ Although the similar Zn-based batteries, including LiMn$_2$O$_4$/Zn, Li$_3$V$_2$(PO$_4$)$_3$/Zn and LiV$_2$(PO$_4$)$_3$/Zn batteries, have been reported before,$^{[10, 12, 22]}$ few work focus on exploring the operational mechanism of hybrid ions involving reaction was carried out. Therefore, to deeply understand the operational mechanism, in operando synchrotron XRD of the hybrid LFP/Zn battery first was conducted to study the LFP phase evolution during charge-discharge process. From the charge-discharge curves (Figure 4.1b), only one discharge plateau located at ~1.1 V can be observed, indicating the single-phase transition. The uncycled LFP exhibits obvious some peaks at 7.7°, 9.2° and 11.4° that can be indexed to (020), (011), (021) and (121) planes, respectively.$^{[23]}$ During charging process, these peaks gradually disappeared along with new reflections at ~8.0°, 9.2°, 11.5° and 13.8° appear, which can be indexed to 200, 101, 201 and 211 reflections of FePO$_4$ phase, suggesting that LFP phase is fully transformed into the heterosite phase.$^{[24]}$ Upon discharging, all of LFP peaks completely re-emerge with the crystalline phase of FePO$_4$ disappears, suggesting the excellent phase reversibility. More distinct changes can be observed in the contour maps (Figure 4.1c), which indicates that only Li$^+$ ion instead of Zn$^{2+}$ ion inserted into FePO$_4$ during discharge process although the size of Li$^+$ ion is slightly larger than that of Zn$^{2+}$ ion. The main reason could be ascribed to the nature of Zn$^{2+}$ and Li$^+$ ions: Zn$^{2+}$ ion features a higher charge density (a double charge divided by a small radius of 0.74 Å) compared to Li$^+$ ion, leading to reduced diffusivity within common polar crystalline hosts due to strong Coulomb interactions and inhibited issues with respect to the electrolyte chemistry, such as the balancing of solvation/de-solvation energies for efficient planting/stripping.$^{[25]}$ Overall,
the working mechanism of LFP/Zn hybrid batteries can be expressed as the following equations.

Cathode: \( \text{LiFePO}_4 \leftrightarrow e^- + \text{Li}^+ + \text{FePO}_4 \) \hspace{1cm} (3-1)

Anode: \( \text{Zn}^{2+} + 2e^- \leftrightarrow \text{Zn} \) \hspace{1cm} (3-2)

Overall: \( 2\text{LiFePO}_4 + \text{Zn}^{2+} \leftrightarrow 2\text{Li}^+ + 2\text{FePO}_4 + \text{Zn} \) \hspace{1cm} (3-3)

![Figure 4.2](image)

**Figure 4.2** The first discharge curves of LFP/Zn batteries with additive at different concentrations (0.1, 1, 2 and 5 mg mL\(^{-1}\)).

To explore the influence of SDSB additive concentration on the electrochemical performance of hybrid Zn/LFP batteries, the charge-discharge measurements were conducted at a current rate of 0.5 C (1 C=170 mA h g\(^{-1}\)), as presented in Figure 4.2. The hybrid LFP/Zn battery with 1 mg mL\(^{-1}\) additive displays the highest capacity of ~158.2 mA h g\(^{-1}\) at 0.5 C with the highest initial CE of 94.5% among these with different concentration (0.1, 2, and 5 mg mL\(^{-1}\)). In addition, the performance of battery with 1 mg mL\(^{-1}\) additive is also superior to that without additive (the capacity is 147.4 mA h g\(^{-1}\) with an initial CE of 89.4%) (Figure 4.3a), which suggests that the electrolyte additive contributes to the improvement of
reversible capacity. More importantly, the voltage difference of charge and discharge plateau in the battery with additive (1 mg mL$^{-1}$) is less than that without additive, demonstrating that the high reversibility of electrochemical reactions with additive, which was also confirmed by the CV measurements (Figure 4.3b). The CV curves of the battery with/without additive collected at 0.1 mV s$^{-1}$. Based on the CV results, the Li$^+$ diffusion coefficient ($D_{Li^+}$) of LFP electrode with additive was calculated to be $8.22 \times 10^{-11}$ cm$^2$s$^{-1}$ (Figure 4.3c), much higher than that without additive ($1.78 \times 10^{-11}$ cm$^2$s$^{-1}$).[26] The high reversibility as well as the high Li-ion diffusion coefficient of LFP electrode will benefit to its rate capability and cycling stability. Figure 4.3d shows the rate capability of LFP/Zn batteries with/without additive. Only the capacity of 22.5 mA h g$^{-1}$ was remained in LFP/Zn battery without additive when the current rate increase to 20 C, with a capacity retention of ~15.3% compared to that obtained at 0.5 C. In comparison, a high capacity of 57.8 mA h g$^{-1}$ was still obtained at the same current rate when the electrolyte additive was added. Additionally, the influence of the additive on cycling stability of LFP/Zn batteries was studies at 1 C, as shown in Figure 4.3e. The capacity obtained from the battery without additive decayed obviously with only ~92.3 mA h g$^{-1}$ remaining after 100 cycles (75.1% capacity retention). In contrast, the battery with additive delivered a high capacity of 132.2 mA h g$^{-1}$ after 100 cycles at 1 C (the capacity retention of 88.6%).
Figure 4.3 The electrochemical properties of LFP/Zn coin-cells with/without additive (1 mg mL$^{-1}$).

- a) The charge-discharge profiles at 0.5 C.
- b) The CV curves at 0.1 mV s$^{-1}$.
- c) The Li-ion diffusion coefficient in both systems, calculated based on the CV data at various scan rates.
- d) The rate capability tested from 0.5 to 20 C.
- e) The long cycling stability with the responding Coulombic efficiency measured at 5 C.

In order to deeply understand working mechanism of electrolyte additive in hybrid LFP/Zn battery, the effect of additive on both Zn anode and LFP cathode were studied, respectively. It is well-known that Zn metal anode suffers from the irreversibility issues caused by the dendrite growth during plating/stripping process, rendering the cycle performance of aqueous Zn-based batteries highly unstable. The Zn dendrite growth during cycling would eventually result in the internal shorting failure after the separator was pierced. Even before the battery failure, some Zn dendrites turn into “dead” part during the electrochemical reaction, leading to the loss of the capacities and electrolyte consumption. Thus, it is of great importance to suppress the Zn dendrites growth for developing a high-performance Zn-based batteries.
To study the influence of the surfactant additive on the Zn dendrite growth, the electrochemical deposition of Zn was performed in a two-electrode system, in which the hybrid solution of 1 M Zn(SO$_3$CF$_3$)$_2$ and 1 M Li(SO$_3$CF$_3$) with/without 1 mg ml$^{-1}$ additive services as the electrolyte and Pt foil functions as the counter electrode. Figure 4.4a,c illustrate the morphologies of commercialized Zn foil, and electrodeposited Zn electrodes with/without additive, respectively. Apparently, the surface of the fresh Zn foil is smooth and flat with some stripes produced possibly by its manufacturing process. The accumulated Zn nano-sheets were clearly found without additive (Figure 4.4b), indicating that the Zn dendrites were generated on the surface and further grew in the flake shape.$^{15,29}$ Moreover, the similar morphology of the Zn dendrite was also observed on the Zn foil anode that stripped out from the LFP/Zn battery after 100 cycles (Figure 4.5a,b). Serious corrosion occurred on the surface of Zn foil during charge-discharge process, which, in turn, leads to a poor CE and unstable cycling performance of the battery.$^{30}$ Furthermore, the similar dendrite sheets perpendicular to the surface of Zn foil were observed, demonstrating that the Zn dendrites is a potential threat to battery safety by piercing the separator.
Chapter 4 Electrolyte additive effects on the aqueous hybrid Zn-based batteries

Figure 4.5 SEM images of Zn foil anodes stripped out from the LFP/Zn battery without additive after 100 cycles: a) and b). The contact angle measurements at the Zn foil electrode/electrolyte interface: c) without additive, d) with additive.

On the contrary, the electrodeposited Zn electrode with surfactant additive displays a rough surface without Zn dendrite sheets (Figure 4.4c), which mainly due to a strong blocking effect of electrolyte additive. Specifically, the surfactant additive molecules are absorbed on the electrode surface and forming a surface passivating film, which not only affects the kinetics of the electron transfer but also increases the competition between the nucleation and crystal growth. Additionally, the additive also facilitates the wettability of Zn foil, the initial contact angle of 89.8° was reduced distinctly to 31.2°. (Figure 4.5c,d). Thermodynamically, the good wettability changes the the total Gibbs free energy of transformation of a spherical cap-shaped deposit from a liquid electrolyte, which promotes the generation of electroplating nucleation on the electrically charged substrate, resulting in a uniformly plated surface. As a result, the pattern of Zn deposit was manipulated by the additive, suggesting strong suppression of Zn dendrite growth. Similarly,
the Zn foil electrode, which was stripped out from the LFP/Zn battery within the additive electrolyte after 100 cycles, also show a rough surface without Zn dendrite flakes (Figure 4.6). No obvious corrosion was found on the surface of Zn foil, indicating that the additive relieves the Zn corrosion and restrains the growth of Zn dendrites, which assists in the high CE and long cycling stability of battery.

**Figure 4.6** SEM images of Zn foil anodes stripped out from the LFP/Zn battery with additive after 100 cycles.

XRD patterns of different Zn electrodes were collected to deeply study the Zn deposit with/without surfactant additive, as presented in Figure 4.7a. The bottom XRD pattern belongs to the commercial Zn foil, the peaks located at ~36.3°, 39.0°, and 43.2° are indexed to the (002), (100), and (101) planes of Zn (PDF#00-004-0831).[34] The electrodeposited Zn without additive shows the similar XRD pattern with the highest intensity peak at 42° (middle), suggesting the Zn crystal growth mostly is in the orientation of (101). Although the dominant (101) peak is also found at the XRD pattern of electrodeposited Zn electrode with additive (top), the XRD pattern changes demonstrate that the growth of Zn crystal was modified by the additive via accelerating the zinc growth in the orientations of (100) and (110).[35]
Furthermore, the polarization measurements of the Zn−Zn symmetric batteries in the hybrid electrolyte with/without additive were conducted at a constant current density of 0.5 mA cm$^{-2}$ to investigate the dynamical stability of the Zn/electrolyte interface (Figure 4.7b). The over-potential of Zn stripping/plating in the symmetric cell without additive is approximately 50 mV at the beginning and almost keep this value in following cycles. After 900 h striping/plating, a large and irreversible voltage drop was detected, indicating a battery failure of short circuit induced by the growth of Zn dendrite. On a striking contrary, the Zn-Zn battery with additive displays an outstanding cycling stability under the same conditions, despite the relatively high-voltage polarization in the initial cycles for the electrode activation and formation of SEI layer. Figure 4.7c shows the over-potential of Zn
stripping/plating with additive is only around 45.1 mV, lower than without additive (69.1 mV), which indicates a low energy barrier for generation of Zn metal nucleation and then promotes a relatively uniform Zn plating process. More importantly, the Zn–Zn cell with additive still maintains an extremely low and stable polarization without short circuiting even after 1500 h cycling, demonstrating highly stable Zn plating/stripping cycling reversibility.

On the other hand, the wettability of electrode material is of great importance for the ion exchange at the electrolyte/electrode interface. To learn the impact of additive on wettability of the LFP cathode, the sessile drop contact angle technique was employed, as illustrated in Figure 4.8a,b. The contact angle of the LFP electrode with the pure electrolyte was measured to be 84.4°, demonstrating the limited hydrophilic of LFP electrode. Introducing electrolyte additive notably strengthens the absorbability of the LFP electrode surface with a small contact angle of 50.1°, as further supported by the insert images. According to S. Manne, the surfactant molecules will be adsorbed on the electrode surface, rendering the surface of LFP electrode more hydrophobic, which favours the electrochemical reaction at the interface of electrode/electrolyte. Based on the contact angle, the wetting free energy of electrode material was also evaluated. According to the simple model built by Extrand, the change of the wetting free energy with/without additive media was calculated by the following equation:

$$\Delta G = \frac{RT}{3} \ln \left( \frac{(1 - \cos \theta_A)^2(2 + \cos \theta_A)}{4} \right)$$

in which R is the ideal gas constant, T is absolute temperature and $\theta_A$ is the contact angle. Similar to surface energies, the absolute magnitude of $\Delta G$ values was small for large contact angles. The calculation results show that the wetting free energy of LFP electrode surface without surfactant additive is $-4.6 \text{ J mol}^{-1}$. The value of $-\Delta G$ increases to $7.33 \times 10^3 \text{ J mol}^{-1}$
in the additive media, indicating that the surfactant additive increases the hydrophilicity of LFP electrode and facilitates the Li\(^+\) ion diffusion at the electrode/electrolyte interface.\(^{[39]}\) To further investigate the effects of additive on the LFP electrode at atomic scale, the ab into MD calculations was also performed on the interface of LFP (010) and aqueous electrolyte. The simulation snapshots (Figure 4.8c) illustrates the migration of Li\(^+\) ion at the LFP(010)/electrolyte interface without surfactant additive. Initially, the migrating Li ion is located at the top of LFP [010] channel.\(^{[40]}\) As the simulation proceeds, the Li\(^+\) coordinates to water molecules, then water molecules lift the Li\(^+\) ion from its original position, and carry the Li\(^+\) ion to migrate into the bulk of electrolyte. Thus, water molecules are involved into the Li\(^+\) ion migration process rather than acting as the simple adsorbent.\(^{[41]}\) When the additive was added into electrolyte, the LFP surface adsorbs tail group of the surfactants molecules (Figure 4.8d), which helps to reduce the wetting free energy. Therefore, more water molecules adhered to the LFP (010) surface, assisting in the Li\(^+\) migration across the solid/liquid interface.
Figure 4.8 The effect of surfactant additive on LFP cathode. a, b) The contact angle measurements at the LFP electrode/electrolyte interface with/without additive. c, d) The molecular dynamics calculations conducted at the LFP (010)/electrolyte interface with/without additive to study the Li-ion migration. Note: H in H$_2$O and SDBS (white); C in SDBS (brown); O ions in H$_2$O (red) and LiFePO$_4$ (red); Li ions (green); Na in SDBS (yellow); PO$_4$ (purple); FeO$_6$ (brown). e) GITT measurements of LFP/Zn batteries with/without additive.

Additionally, to verify the additive accelerating the Li$^+$ ion transfer, the electrochemical reaction kinetics of both systems were compared using the galvanostatic intermittent titration technique (GITT) During GITT measurements, the LFP electrodes with/without surfactant additive were intermittently charged/discharged using the current pulses at 0.1 C with the
equal duration of 0.5 h. Following each pulse, the batteries were left on open circuit for 1 h to reach equilibrium potentials, as illustrated in Figure 4.8e. Two potential plateaus can be observed on the curves, corresponding to the Li$^+$ ion extraction and insertion process.$^{[42]}$ The insert of Figure 4.8e shows the LFP electrode without additive suffers from a large over-potential of $\sim$153 mV, almost twice larger than that with additive ($\sim$68 mV), demonstrating that the electrochemical reaction resistant is lower in the additive media.

**Figure 4.9** The electrochemical performance of LFP/Zn pouch-cell with additive. a) The charge-discharge profiles at 0.5 C, insert shows the LFP/Zn cells provide the power for 5 LEDs with different colours. b) The cycling stability.

The encouraging performance of LFP/Zn coin-cells with additive has motivated us to further assess the performance in soft-packed full-cells, which could be facilely assembled in ambient air without complicated procedures. The galvanostatic discharge-charge measurements of the pouch-cell were carried out at a current rate of 0.5 C, as illustrated in Figure 4.9a. One pair of redox plateaus was found with a reversible capacity of 136.2 mA h g$^{-1}$. The full-cell delivers an energy density of $\sim$113.2 Wh kg$^{-1}$ based on the total weight of the active materials (including both cathode and anode), which far exceeds that of other aqueous batteries, such as aqueous LIBs ($\sim$50–90 Wh kg$^{-1}$)$^{[43]}$ and aqueous Na-ion batteries ($\sim$30–40 Wh kg$^{-1}$)$^{[44,45]}$. The insert of Figure 5a shows the pouch cells light the five LED lights with different colours (two yellows, 2.0 V, two red, 2.0 V and one green, 3.0 V). The
cycle life of the aqueous pouch-cell was evaluated at 1 C, as shown in Figure 4.9b. It exhibited an encouraging cycling stability, showing a discharge capacity of 102.1 mA h g\(^{-1}\) after 150 cycles at 1 C for \(~80\%\) capacity retention and a CE of about 100%.

In order to assess the feasibility of SDBS additive in other aqueous batteries, the MnO\(_2\)/Zn battery was assembled, where the electro-deposited MnO\(_2\), Zn foil, and 1 M Zn(SO\(_3\)CF\(_3\))\(_2\) + 0.5 M Mn(SO\(_3\)CF\(_3\))\(_2\) solution service as cathode, anode, and electrolyte, respectively. Since the MnO\(_2\)/Zn system is the most commonly used aqueous Zn-based battery.\(^{[46-47]}\) The morphology of Zn foils stripped out from the MnO\(_2\)/Zn batteries after 700 cycles were compared. Clearly, the Zn foil suffers from the serious corrosion on its surface without additive (Figure 4.10). In contrast, the corrosion on the Zn surface was alleviated with the assistance of additive, which contributes to enhancing the cycling performance of aqueous MnO\(_2\)/Zn system.

![Figure 4.10](image)

**Figure 4.10** The photos of Zn foil anodes stripped from the MnO\(_2\)/Zn batteries with additive, a) and without additive after 700 cycles, b), respectively.

### 4.4 Conclusion

In this work, the hybrid working mechanism of aqueous LFP/Zn battery was confirmed by operando synchrotron tests. Based on this hybrid system, a surfactant additive was developed and comprehensively studied. By modifying the intrinsic pattern of Zn electro-deposited, the
formation and growth of Zn dendrites were effectively suppressed, which in turns enhanced the CE and eliminated the potential safety hazard. Moreover, this surfactant additive accelerated the surface wettability of the electrode, facilitating the Li-ion diffusion at the interface of LFP electrode/electrolyte. Consequently, the Li-ion diffusion coefficient of LFP cathode was increased from $1.78 \times 10^{-11} \text{cm}^2\text{s}^{-1}$ to $8.22 \times 10^{-11} \text{cm}^2\text{s}^{-1}$. The rapid Li-ion diffusion at the solid/liquid interface was also confirmed by the MD calculation. Benefiting from the Zn dendrite-free anode and the rapid Li-ion diffusion kinetics of cathode, the hybrid LFP/Zn coin-cell with additive displays a high initial CE of 94.5% at 0.5 C, a high rate capability with a capacity of 57.8 mA h g$^{-1}$ remaining at even 20 C. An encouraging cycling stability over 150 cycles was still achieved even in an LFP/Zn pouch-cell. Importantly, this additive was also applied in MnO$_2$/Zn battery, assisting in enhancing its cycling stability. The obtained promising electrochemical results and scientific understanding suggest that developing additive could be a viable strategy for advanced aqueous systems and encourage more relevant research on new additives for high-performance Zn-based batteries towards practical applications.

4.5 References


Chapter 5

Ex-situ building artificial layer on Zn metal towards advanced aqueous Zn batteries

5.1 Introduction

Aqueous rechargeable batteries, as highly promising candidates for grid-scale energy storage, have recently received great attention due to their advantages of high safety, high ionic conductivity, low cost, and environmental benignity.\cite{1-4} Among these aqueous batteries, Zn metal batteries have been intensively investigated, because the Zn anode has the advantages of high theoretical capacity (gravimetric capacity of 820 mA h g$^{-1}$ and volumetric capacity of 5855 mA h cm$^{-3}$), a low reduction potential ($-0.76$ V vs. SHE), and high over-potential for hydrogen evolution in aqueous media.\cite{5-8}

Although aqueous Zn batteries, including the Zn-air battery and the Zn-MnO$_2$ battery, have achieved great progress in recent years,\cite{9-11} state-of-the-art Zn batteries with alkaline electrolyte still suffer from several critical challenges, such as Zn dissolution, shape change, passivation, dendrite growth, etc.\cite{12, 13} Zn electrode issues are mitigated to some extent in mild electrolyte, but it is well known that dendrite growth still exists in mild Zn systems.\cite{14}

Although the dendrite growth does not result in the same hazardous situations as in organic lithium-ion or sodium-ion batteries, such as fire or even explosion,\cite{15, 16} it causes unceasing water/electrolyte decomposition and further degrades the lifespan of the battery.\cite{17} To enhance the reversibility of Zn anode in neutral electrolyte, great efforts have recently been spent on the inhibition of Zn dendrite growth, including the introduction of different electrolyte additives,\cite{18-21} designing porous Zn metal architectures,\cite{22} guiding Zn backside plating,\cite{23} employing high concentration electrolytes,\cite{24, 25} and building artificial inorganic layers.\cite{17, 26, 27} Yet, the side reactions between Zn metal and mild electrolyte have often been
neglected. These reactions between Zn metal and electrolyte not only dramatically reduce the CE of the Zn battery, but also constantly consume the Zn anode, which leads to a limited battery lifespan. Thus, achieving an in-depth understanding of the side reactions in slightly acidic electrolyte as well as their by-products is highly desirable for further improving the CE and cycling stability of Zn batteries.

In this work, the stability has been studied of pure Zn metal electrode in 1 M ZnSO₄ electrolyte. The results reveal that Zn electrode is highly unstable in slightly acidic electrolyte because it generates a loose Zn₄SO₄(OH)₆·xH₂O layer. Unfortunately, this loose layer cannot effectively block the electrolyte from coming into contact with the Zn surface, so it cannot terminate the corrosion reactions by passivating the fresh Zn. In addition, Zn plating in 1 M ZnSO₄ electrolyte was studied in a transparent cell, demonstrating that Zn dendrites with a palm-leaf-like morphology grew on the surface of the Zn anode. After ~260 h and ~750 h of plating/stripping at 0.5 mA cm⁻², the separators in the coin cells, with thicknesses of 0.24 mm and 0.96 mm, were pierced by Zn dendrites, leading to battery failure. To effectively inhibit the side reactions and Zn dendrite growth, a polymer film of PVB as an artificial SEI layer was deposited on the surface of the Zn anode via a facile spin-coating strategy. The PVB layer can effectively remove the Zn solvated water during Zn plating/stripping, significantly suppressing the side reactions and enhancing the CE. Moreover, this polymer film also exhibits strong adhesion to the Zn surface with excellent flexibility and encouraging hydrophilicity, rendering the electrolyte distribution on the Zn surface highly homogeneous, which contributes to even Zn plating/stripping underneath the artificial SEI layer, as confirmed by in-situ optical microscopy. Consequently, the PVB protected Zn (PVB@Zn) electrode delivered an extended plating/stripping cycling life of 2200 h in symmetric cells at 0.5 mA cm⁻². To further evaluate its practical implementation, a MnO₂/PVB@Zn battery was assembled, and it showed excellent cycling stability with a
capacity retention of ~86.6% at 5 C over 1500 cycles, much higher than that of the battery with bare Zn electrode (where the capacity retention was only 31.8%). Additionally, this artificial layer protecting the Zn anode also enhanced the CE and long-term cycling performance of a hybrid LFP/PVB@Zn cell.

5.2 Experimental section

5.2.1 Material synthesis

The artificial PVB film coated on the surface of Zn foil was obtained via a spin-coating method. Specifically, the bare Zn foil was polished using abrasive paper to remove the oxidation layer. The PVB powder was dissolved in ethanol to prepare a 10 mg ml\(^{-1}\) PVB solution. Subsequently, the PVB was homogeneously coated on the fresh Zn foil using a spin-coater at a spin-speed of 400 rpm for 5 min.

5.2.2 Materials characterization

The morphologies of the Zn foil and PVB@Zn foil before and after electrodeposition were observed by SEM, operated at 5 kV and 10 mA, along with energy dispersive X-ray spectroscopy (EDX) mapping. The crystalline structure of the bare Zn electrode, PVB, PVB@Zn electrode, and LFP electrode was investigated by XRD with Cu K\(\alpha\) radiation and a scanning rate of 1° min\(^{-1}\). XPS was conducted on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al K\(\alpha\) radiation under vacuum at 2 × 10\(^{-6}\) Pa. All of the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. FTIR spectra were acquired in duplicate in the range of 4000–600 cm\(^{-1}\) using a PerkinElmer Frontier FTIR spectrometer with a resolution of 2 cm\(^{-1}\) and averaging 8 scans for each spectrum. The dynamic contact angles of the bare Zn and PVB@Zn electrode were measured on Dataphysics OCA15 optical contact angle system with 1 \(\mu\)L of electrolyte for each test at the temperature of 25 °C.

5.2.3 Electrochemical measurements
Electrochemical characterization of symmetrical cells was conducted using both transparent cells and 2032-type coin-cells with 1 M ZnSO$_4$ as electrolyte. All the bare Zn anodes were polished using abrasive paper. The electrodeposition of Zn was performed in a standard two-electrode system consisting of the clean Zn foil as working electrode and a Pt plate counter electrode. Electrochemical impedance spectroscopy (EIS) of the Zn-Zn cells was conducted on a VMP-3 electrochemical workstation over the frequency range of 100 kHz to 1 Hz. The hybrid LFP/Zn batteries were tested by using 2032-type coin-cells with 1 M ZnSO$_4$ and 1 M Li$_2$SO$_4$ as electrolyte. LFP electrode was made from a mixture of 75% active material, 15% acetylene black, and 10% PTFE binder. The mixture was rolled out into a thin sheet, and then was cut into 8.0 mm pellets and pressed on stainless steel (10 mm). Subsequently, the electrode was dried at 80 °C for 12 hours in a vacuum oven. The cells were galvanostatically charged/discharged in the voltage range of 0.9–1.35 V vs. Zn/Zn$^{2+}$ at different current densities on a Land CT2001A battery tester, and the specific capacities were calculated based on the active mass of LFP cathode. For the MnO$_2$/Zn batteries, the MnO$_2$ electrode was prepared by electrodeposition on a piece of carbon cloth in a 0.1 M ZnSO$_4$ solution, using the SCE electrode as the reference electrode and Pt foil as counter electrode. The area of the electrode surface was ~0.71 cm$^2$, and the mass loading was about ~0.8 mg.

5.3 Results and discussion

The issues of Zn anode in 1 M ZnSO$_4$ electrolyte

To explore the side reactions between Zn metal and electrolyte, commercial Zn foil was soaked in 1 M ZnSO$_4$, as illustrated in Figure 5.1a. After 7 days, the Zn surface was seriously corroded, with the color changing from bright to gray (Figures 5.1b, c), indicating that Zn metal is highly unstable in 1 M ZnSO$_4$ electrolyte. The morphology of bare Zn before/after immersion in electrolyte was investigated by SEM. A rough and uneven surface was observed for the bare Zn foil (Figure 5.1d), which is mainly generated during its
manufacturing process. In comparison, the Zn surface was damaged after soaking in electrolyte, and regular hexagonal flakes overgrew the whole surface (Figure 5.1e). Even worse, these flakes were piled up loosely on the fresh Zn surface with plenty of open space. Thus, this by-product layer could not effectively block the electrolyte and terminate the corrosion reaction, unlike the SEI layer generated on Li metal in organic electrolyte. To determine the composition of the side-products, XRD and FTIR measurements were conducted. Figure 5.1f shows the XRD patterns of the Zn foil before/after soaking in electrolyte. Several new peaks clearly located at 9.5, 19.1, and 28.9 emerged after the side-reactions of the Zn foil with electrolyte, corresponding to the (002), (004), and (006) planes of Zn₄SO₄(OH)₆·3H₂O (PDF.#04-012-8190), respectively. Compared with the bare Zn foil, the corroded Zn foil also showed several new conspicuous absorption peaks in its FTIR spectrum (Figure 5.1g). The broad absorptions at ~3230 cm⁻¹ and ~1630 cm⁻¹ are assigned to the stretching vibrations of O-H and the bending vibrations of H₂O molecules, respectively. The absorptions at ~1160 cm⁻¹, 1100 cm⁻¹, 1000 cm⁻¹, and ~600 cm⁻¹ are attributed to the asymmetric and symmetric S–O stretching vibrations of SO₄²⁻ and the O–S–O bending vibrations of SO₄²⁻. The ~520 cm⁻¹ and ~417 cm⁻¹ peaks reflect the stretching of the Zn–O bonds, combined with librational vibrations of H₂O molecules. All the absorptions on the FTIR spectrum are well matched with Zn₄SO₄(OH)₆·xH₂O crystal, which is also consistent with the XRD results. Figure 5.1h illustrates the crystal structure of Zn₄SO₄(OH)₆·xH₂O with the space group PIFT (a = 8.367, b = 8.393, c = 18.569 Å, α = 90.29°, β = 89.71°, γ = 120.53°), in which the Zn ions coordinate with oxygen ions, forming ZnO₄ tetrahedra and ZnO₆ octahedra. The Zn ion layered structure consists of the edge-sharing ZnO₆ octahedra as well as the corner-sharing ZnO₄ tetrahedra with the H₂O molecules.
between the layers. Overall, the side reactions of Zn electrode with electrolyte can be expressed as follows:

\[
\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e^- \quad (5-1)
\]

\[
4\text{Zn}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} + x\text{H}_2\text{O} \leftrightarrow \text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O} \quad (5-2)
\]

\[
2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 \uparrow + 2\text{OH}^- \quad (5-3)
\]

**Figure 5.1** The stability of Zn metal in mild electrolyte. a) Zn foil soaked in 1 M ZnSO\textsubscript{4} electrolyte. b) Digital image of the bare Zn foil. c) Digital image of Zn foil after soaking in electrolyte for 7 days. SEM image of bare Zn foil (d) and soaked Zn foil (e). f) XRD patterns of Zn foil before/after soaking in the electrolyte. g) FTIR spectra of Zn foil before/after soaking in the electrolyte. h) The crystal structure of Zn\textsubscript{4}SO\textsubscript{4}(OH)\textsubscript{6}\cdot3\text{H}_2\text{O} by-product.

Unlike Li metal in organic electrolyte, Zn metal in mild electrolyte cannot form a dense SEI film to protect the fresh Zn, since the Zn\textsubscript{4}SO\textsubscript{4}(OH)\textsubscript{6}\cdot3\text{H}_2\text{O} layer is loose and porous. Moreover, this by-product layer also increases the interphase impedance between the Zn metal electrode and the electrolyte, seriously affecting the electronic/ionic diffusion at the interphase. The side-reaction responsible for this and its loose by-product layer not only
severely fades the CE of the Zn plating/stripping, but also shortens the cycle life of Zn batteries. Therefore, studying how to suppress the side-reactions is definitely promising for further enhancing the performance of the Zn battery.

![Figure 5.2](image)

**Figure 5.2** a) Photograph of the Zn-Zn transparent battery, which was built to observe the Zn dendrite growth. b) Enlarged photograph of the battery.

Zn plating on Zn foil in 1 M ZnSO₄ electrolyte was investigated using a transparent symmetrical cell at 10 mA cm⁻² (Figure 5.2). After 0.5 h of plating, the protrusions/dendrites grown on the Zn surface were observed with an optical microscope equipped with a digital camera, as shown in Figure 5.3a. Zn dendrites, resembling Palma leaves in their morphology (Figure 5.3b), grow in the perpendicular direction to the Zn metal. To study the influence of Zn dendrites on the cycling stability of Zn batteries, Zn plating/stripping in symmetric bare Zn coin-cells using separators with different thicknesses (0.24 mm and 0.96 mm, respectively) was investigated at 0.5 mA cm⁻² (Figure 5.3c). After cycling for ~260 h, a sudden and profound polarization increase (~4.5 V) was detected in the symmetric Zn cell with the 0.24 mm separator, indicating battery failure. On the contrary, after ~750 h of stripping/plating, an arresting polarization was observed in the cell with the separator that was 0.96 mm thick, suggesting that the thick separator could prolong the battery life.
Chapter 5 *Ex-situ* Building artificial layer on Zn metal towards advanced aqueous Zn batteries

Figure 5.3 Zn dendrite morphology and schematic illustration of Zn plating/stripping. a) Optical microscope image of Zn dendrites on a cross-section of Zn foil. b) Photograph of a palm leaf, similar to the morphology of Zn dendrites. c) Plating/stripping measurements of bare Zn symmetric coin-cells using separators with different thicknesses (0.24 mm and 0.96 mm) were conducted at a current density of 0.5 mA cm\(^{-2}\).

To further understand the effects of Zn dendrites on the cycling stability, the Zn foil electrodes and separators were stripped out of the cells after 100 h, 200 h, and 300 h of cycling, as shown in Figure 5.4. Severe Zn corrosion with the formation of a thick resistive layer of Zn\(_4\)SO\(_4\)(OH)\(_6\)·\(x\)H\(_2\)O had occurred on the Zn foil electrodes after 100 h of cycling, regardless of which separator was used. Zn corrosion also became worse with further cycling. Such serious corrosion and dendrite growth triggered battery failure by impaling the thin separator after 260 h of cycling. The results confirm that Zn dendrite growth perpendicular to the Zn foil surface is a huge potential hazard for battery failure, even in a mild electrolyte.

Furthermore, the growth of Zn dendrites promotes side-reactions between the Zn metal electrode and the electrolyte. This is because the fresh plated Zn deposited in the form of dendrites has a higher surface area in contact with the electrolyte, contributing to reaction of the Zn metal with the electrolyte. In turn, the side-reactions also aggravate the inhomogeneity of the Zn electrode surface and the Zn\(^{2+}\) concentration polarization in the
electrolyte, which provides more nuclei for deposition and a stronger driving force to form the Zn dendrites. Therefore, developing a new strategy to effectively suppress both side-reactions and Zn dendrite growth in such an electrolyte is a matter of top priority to enhance the electrochemical properties of Zn-based batteries.

**Figure 5.4** a) Photographs of Zn foil electrodes stripped out of the Zn-Zn batteries containing the thin separators after different numbers of cycles. b) Photographs of Zn foil electrodes stripped out of the Zn-Zn batteries containing the thick separators after different numbers of cycles.

**The suppression of side-reactions and dendrite growth by PVB coating**

Similar to Li-ion batteries, the side-reactions and dendrite growth are self-enhancing in aqueous Zn-ion batteries.\[34-36\] To develop a side-reaction-free and dendrite-free Zn electrode, building an dense artificial layer on the Zn metal surface is quite promising.\[27\] Theoretically, the ideal artificial layer should meet the following criteria. First, it should be water-insoluble, which helps to block the aqueous electrolyte from encountering the Zn electrode surface. Second, it should feature a high ionic conductivity and a low electronic conductivity, promoting uniform Zn\textsuperscript{2+} deposition underneath the artificial layer. Third, it should have
strong and also flexible mechanical properties to accommodate the volumetric changes of Zn electrode during cycling. Fourth, it should have good adhesion to the Zn metal surface, so that this layer would not be detached from the Zn surface during cycling. Based on the above conditions, the PVB polymer seems appropriate. PVB is the random ternary polymer poly(vinyl butyral, vinyl alcohol, and vinyl acetate), the structure of which is shown in Figure 5.5a. This PVB polymer is insoluble in an aqueous solution and has been intensively applied in laminated safety glass for automobile windshields and gel electrolytes due to its strong adhesion, superior flexibility, high ionic conductivity, good mechanical stability, and favourable hydrophilic property.\textsuperscript{[37]} Due to these advantages, this PVB polymer was selected for the artificial SEI layer and deposited on the Zn metal surface using a facile spin-coating method, which not only retarded side-reactions by blocking contact with the electrolyte, but also inhibited dendrite growth by promoting even Zn-ion plating/stripping.

\textbf{Figure 5.5} a) Schematic illustration of morphology evolution for both the bare Zn-Zn cell and the PVB@Zn-PVB@Zn cell during repeated cycles of stripping/plating. d) Cycling stability of Zn
plating/stripping in both bare Zn and PVB@Zn symmetric cells, with the inset showing the initial voltage profiles of both cells.

The effectiveness of the PVB layer for enhancing the stability of PVB@Zn foil was evaluated in 1 M ZnSO$_4$ electrolyte. After 7 days, the PVB@Zn foil still maintains a bright surface without obvious corrosion, which is mainly because the electrolyte is isolated by the protective PVB film. The electrochemical performance of PVB@Zn electrode was investigated in the symmetrical PVB@Zn cells by repeated plating/stripping measurements at 0.5 mA cm$^{-2}$ (Figure 5.5b). As was discussed above, the bare Zn-Zn symmetrical cell with a thin separator failed after nearly 260 h of cycling due to an internal short circuit. In strong contrast, the PVB@Zn symmetrical cell with the same thin separator displayed much smaller polarization and maintained smaller polarization curves for more than 2200 h of cycling without any internal short circuit, benefiting from the dendrite-free Zn anode. That is to say, the PVB-coating effectively inhibits the Zn dendrites and prolongs the cycle life of the Zn symmetrical cell. In addition, the polarization curves of both cells after different cycling times are compared in the inset of Figure 5.5b and Supplementary Figure 5.6. At the first plating/stripping, the PVB@Zn cell shows polarization of 108.5 mV, lower than that of the bare Zn (~200 mV). Importantly, the low polarization indicates a low energy barrier for metal nucleation, which promotes a relatively uniform metal plating process.$^{[38]}$ After 125 cycles, a sharp increase was found in the curves for the bare Zn cell, essentially because the separator was pierced (Figure 5.6a). In comparison, the PVB@Zn cell still features the low polarization value of 84.5 mV, which is also maintained in the following cycles, as evidenced by the value after 500 cycles (~84.3 mV) (Figure 5.6b).
Figure 5.6 Cycling stability of Zn plating/stripping in both bare Zn and PVB@Zn symmetric cells. a and b) High-resolution voltage profiles for the 125th and the 500th cycles, respectively.

To intuitively understand the protection of Zn foil provided by the PVB layer, Zn foil electrodes with/without PVB protection were stripped out of the symmetrical cells after different numbers of cycles. The symmetrical cells were cycled at a current density of 2 mA cm$^{-2}$ with 10 min of intermittence. After 50 cycles, the digital image of PVB@Zn anode shows a bright and smooth surface (Figure 5.7a), although corrosion had occurred on the edge and surface of the bare Zn foil (Figure 5.7b). In the following cycles, the corrosion was aggravated, which had a serious impact on the CE and cycling stability of the Zn-based battery. In contrast, only slight corrosion at the edge of the PVB@Zn electrode was found, even after 800 cycles, which directly confirms that Zn foil was protected by PVB film during the electrochemical tests.
Figure 5.7 The morphology of cycled Zn anodes, optical microscopy study of Zn plating/stripping chemistry, and CEs of the Zn plating/stripping. a) Digital images of Zn electrodes that were stripped out of the cells after 50, 100, 200, 300, 400, and 800 cycles. b) Digital images of PVB@Zn electrodes stripped out after the same cycle numbers. In-situ optical microscope images of the front surfaces of Zn electrodes (c) and PVB@Zn electrodes (d) in symmetric transparent cells, along with the specified numbers of plating/stripping cycles. e) CEs of the Zn plating/stripping on Cu foil with/without PVB at 4 mA cm\(^{-2}\). Voltage profiles of the bare Cu foil (f) and PVB coated Cu foil (g).

In order to further evaluate the inhibition of Zn dendrite growth by the PVB film, an optical microscope equipped with a digital camera was used for in-situ monitoring of Zn
plating/stripping on Zn foil in a transparent symmetrical cell. A high current density of 4 mA cm\(^{-2}\) with 10 min of intermittence was applied to repeatedly conduct the plating/stripping measurements on the transparent cells. Figure 5.7c illustrates the nucleus formation as well as Zn dendrite growth at different plating/stripping cycles in the bare Zn symmetric cell. Before cycling, the Zn surface was found to be uneven, which induces the generation of nuclei. After 50 cycles, nuclei or protrusions were observed at the edges and on the surface, which is evidence of inhomogeneous Zn plating. Under further repeated plating/stripping, some nuclei evolve into Zn dendrites on the edge. Simultaneously, severe corrosion can be observed on the surface of the Zn foil, which distorts the electrochemical performance of Zn-based batteries. The PVB-film-protected Zn foil was also tested under the same conditions. Before cycling, the surface of the PVB@Zn foil was smooth. In the following plating/stripping process, the PVB-protected Zn electrode exhibited smooth Zn deposition with no sign of dendrites or pulverization during cycling (Figure 5.7d). In addition to suppressing the Zn dendrites, the impact of the PVB layer on the CE of the Zn plating/stripping behaviour was also evaluated at 4 mA cm\(^{-2}\), respectively. Fluctuating CEs with an average value of 93.8% were obtained for the bare Cu-Zn cell (Figure 5.7e). In contrast, the PVB@Cu-Zn cell still presented stable CEs with the average value of 99.4%. The increased CE is mainly because the PVB film inhibits the side-reactions as well as facilitating the formation of even nuclei and reversible Zn plating/stripping, as we mentioned above. Moreover, the initial voltage hysteresis in the PVB@Cu-Zn cell is \(~133\) mV, which is much smaller than that in the bare Cu-Zn cell (\(~170\) mV) (Figure 5.7f, g).

**Zn dendrite suppression mechanism by PVB coating**
Figure 5.8 Characterization of bare Zn and PVB@Zn foils. a) SEM image of bare Zn foil. b) Cross-sectional SEM image of PVB@Zn foil with EDS mappings of Zn, C, and O elements, respectively. c) XRD patterns of bare Zn foil, PVB@Zn foil, and PVB. d) FTIR spectrum of PVB film on the surface of Zn foil. e) Schematic illustration of PVB@Zn foil. f) XPS analysis of PVB film, with the top panel showing the high-resolution C 1s spectrum, while the bottom panel contains the high-resolution O 1s spectrum.

First, the morphology of PVB@Zn foil was studied by SEM. After spin-coating, the rough and uneven surface of Zn foil was coated by a dense and uniform PVB film (Figure 5.8a), as evidenced by the cross-sectional images with energy dispersive spectroscopy (EDS) mappings of Zn, C, and O elements (Figure 5.8b). PVB powders have an amorphous structure, as evidenced by the broad peak in the XRD pattern of the PVB powder (Figure 5.8c). FTIR spectra of this artificial PVB SEI film exhibit several characteristic peaks. The peak located at ~3309 cm\(^{-1}\) is attributed to the symmetrical stretching vibration of O-H, as labelled in Figure 5.8d.\(^{[39]}\) The absorption at ~1726 cm\(^{-1}\) and 1129 cm\(^{-1}\) is related to the stretching vibrations of C-H and C=O bonds, respectively.\(^{[40]}\) Then, the surface
characteristics of the PVB layer (Figure 5.8e) were also investigated by XPS. Figure 5.8f presents the C 1s and O 1s spectra, which could be decomposed into several Lorentzian peaks. The curve fitting results for C 1s and O 1s clearly illustrate that this artificial PVB layer has abundant oxygen-containing functional groups, which not only enhance its adhesion to the Zn metal, but also greatly boost its hydrophilicity in aqueous media. The excellent adhesion between the PVB layer and the Zn foil was confirmed by rolling and twisting experiments (Figure 5.9).

![Figure 5.9](image)

**Figure 5.9** Rolling and twisting experiments: a) Photograph of the initial PVB@Zn foil. b and c) The rolling and twisting experiments. d) Photograph of PVB@Zn foil after rolling and twisting experiments. The results demonstrate that the PVB film has strong adhesion to the Zn surface.

The hydrophilicity of the PVB film with respect to the electrolytes was evaluated by measuring the dynamic contact angle of Zn with/without the PVB coating at ambient temperature of 25 °C, as illustrated in Figure 5.10a,b. The initial contact angle of the bare Zn was approximately 88.7°, and it remained unchanged in the following 4 min. Even after 20
min, a large contact angle of 51.8° still remained, indicating the limited hydrophilicity of the Zn metal surface in aqueous media. In striking contrast, the initial contact angle of PVB@Zn foil was found to be 72.2°, smaller than that on the bare Zn foil. In the ensuing 20 min, it was gradually reduced to 14.5°, suggesting that the artificial PVB film dramatically enhances the hydrophilicity due to its rich polar functional groups. Thermodynamically, the enhanced hydrophilicity will reduce the interfacial free energy between the Zn substrate and the electrolyte, contributing to the formation of homogeneous plating and nucleation, which plays a crucial role in the final Zn plating pattern. Then, SEM was employed to investigate the electrodeposition behavior of Zn-ions with/without the PVB layer (Figures 5.10c-e). Before plating, the cross-sectional view of the PVB@Zn foil reveals that the bare Zn surface was tightly coated by the PVB film, which had a thickness of approximately 1 μm (Figure 5.10c). After 0.5 mA h cm⁻² of plating, the Zn was evenly plated under the artificial protective layer, as shown in Figure 5.10d.

Figure 5.10 Hydrophilicity results and morphology of Zn foils before and after plating. a and b) in-situ contact angle measurements of bare and PVB@Zn foil, respectively. c, d, and e) Cross-sectional...
SEM images of PVB@Zn foil, PVB@Zn foil after Zn plating, and bare Zn foil after Zn plating, respectively.

The protective PVB layer functions as an artificial SEI and serves to prevent water from reaching the Zn surface, suppressing Zn dendrites and enhancing the CE. PVB is an electronic insulator, as verified by an electrical conductivity measurement. The electrical resistivity was estimated as $\sim 2.4 \times 10^5 \, \Omega \cdot \text{cm}$ (the conductivity, $\sigma = \sim 4.17 \times 10^{-6} \, \text{S cm}^{-1}$). The high potential gradient in the PVB film due to the high electronic resistance of the insulating PVB film could drive $\text{Zn}^{2+}$ diffusion through the PVB film, but prevented the reduction of solvated water and anions, thus increasing the transference number. Moreover, the PVB film features good ionic conductivity ($\sim 6.67 \times 10^{-5} \, \text{S cm}^{-1}$), as reported elsewhere, which facilitates the $\text{Zn}^{2+}$ diffusion through this protective film.
Figure 5.11  *In-situ* FTIR measurements conducted at the interface of the electrolyte and the Zn electrode in the bare Zn cells. a) Before cycling. b) After 2 min charging at 2 mA cm$^{-1}$. c) After 4 min charging at 2 mA cm$^{-1}$. d) Attenuated total reflectance (ATR) FTIR spectra collected at the testing point at various states. *In-situ* FTIR measurements conducted at the interface of the electrolyte and the PVB@Zn electrode. e) Before cycling. f) After 2 min charging at 2 mA cm$^{-1}$. g) After 4 min charging at 2 mA cm$^{-1}$. h) FTIR spectra collected at the testing point at various states.

The transference number ($t_{\text{Zn}^{2+}}$) was further calculated to quantitatively describe the Zn$^{2+}$ conducting ability of the PVB layer. A rather low $t_{\text{Zn}^{2+}}$ of 0.34 was obtained in the pure Zn symmetric cell, owing to the faster migration speed of the anions than solvated Zn$^{2+}$, which is consistent with a previous report.\textsuperscript{[49]} $t_{\text{Zn}^{2+}}$ can be dramatically improved to 0.68, however,
after introducing the PVB layer, because the poly(vinyl alcohol) groups in PVB provide the active sites or solvating groups for ion transfer, and the dense PVB can block solvated water and anions from diffusing through the PVB. To further confirm the enhanced $t_{Zn^{2+}}$ in the PVB@Zn cells, we designed a special device to conduct in-situ FTIR measurements at the electrolyte/Zn anode interface with/without the PVB film. In the bare Zn cell, the absorption intensity of $SO_4^{2−}$ at about 1100 cm$^{-1}$ (due to the triply degenerate asymmetric stretching vibration) clearly decreased after Zn$^{2+}$ plating (Figure 5.11a-d), demonstrating that a great many anions had moved during this period, which led to the limited $t_{Zn^{2+}}$. In strong contrast, the absorption intensity of $SO_4^{2−}$ almost retained a similar value when Zn$^{2+}$ plating was conducted in the PVB@Zn cells, indicating that anion migration is much weaker at the electrolyte/Zn interface (Figure 5.11e-h). The high $t_{Zn^{2+}}$ also contributes to eliminating the large Zn$^{2+}$ concentration gradient and facilitating uniform ion distribution, resulting in homogeneous Zn plating.

![Figure 5.12](image.png)

**Figure 5.12** Mechanical strength of the PVB film, tested by Young’s modulus mapping on an atomic force microscope (AFM).

Moreover, the dense PVB film shows excellent mechanical strength. The Young’s modulus of the PVB@Zn electrode was tested using the peak force tapping (PFT) mode of AFM.
(Figure 5.12). The value of the Young’s modulus of PVB film is approximately 220-260 MPa, which helps to suppress the Zn dendrite growth. Hence, due to the limited electrical conductivity, good ionic conductivity, and excellent mechanical stability of the PVB film, the Zn nuclei are generated on the Zn surface instead of on the PVB film. In comparison, the Zn foil without the PVB protective film suffered from serious dendrite growth after electrodeposition (Figure 5.10e). These dendrites would be a potential hazard, leading to an internal short circuit of the battery.

**Electrochemical performance of LFP/PVB@Zn and MnO₂/PVB@Zn full cells**

**Figure 5.13** Electrochemical performance of Zn-based full cells. a) The first cycle charge-discharge profiles of LFP/Zn and LFP/PVB@Zn batteries at the current rate of 0.5 C. b) Long-term cycling stability of both batteries at 5 C with the corresponding CEs.

Hybrid LFP/PVB@Zn and MnO₂/PVB@Zn batteries were assembled to further study the impact of the PVB protective film on Zn on the performance of the full-cells. Galvanostatic charge-discharge of hybrid LFP/PVB@Zn cells at 0.5 C (where 1 C is equal to 170 mA g⁻¹,[52, 53] Figure 5.13a) shows a flat potential plateau, corresponding to the Li⁺ ion extraction/insertion from/into the LFP cathode.[54] Remarkably, an initial CE of 96.3% was obtained from the LFP/PVB@Zn battery (capacity of ~153.5 mA h g⁻¹), higher than that of the battery with bare Zn electrode (an initial CE of 93.1% with a capacity of ~149.2 mA h g⁻¹). After 500 cycles at 5 C, the LFP/PVB@Zn battery still delivered a reversible discharge
capacity of 108.4 mA h g\(^{-1}\) and maintained a high capacity retention of 87.6\%, with only 0.025\% capacity fading per cycle (Figure 5.13b), which is much higher than that of the LFP/Zn battery with capacity retention of only 60\% after 500 cycles. The morphology of Zn anodes after 500 cycles was studied by SEM. The bare Zn electrode shows serious corrosion and dendrite growth (Figure 5.14), which is likely to be the main reason for its poor CE and limited cycling stability.\[55\] The PVB@Zn electrode is still even and smooth, however, and no serious corrosion or dendrites can be found (Figure 5.15). It shows that our LFP/PVB@Zn battery is superior to those other hybrid Zn-based batteries.

**Figure 5.14** a and b) SEM images of the bare Zn electrode stripped out of the hybrid LFP/Zn battery after 500 cycles. Serious corrosion has occurred on the bare Zn foil surface along with the growth of Zn dendrites after 500 cycles, which causing fading of the Coulombic efficiency and cycling performance.
Figure 5.15 a and b) SEM images of the PVB@Zn electrode stripped out of the hybrid LFP/PVB@Zn battery after 500 cycles. Only some glass fibres without Zn dendrites can be observed on the Zn surface.

To further demonstrate the versatility of our PVB SEI film on Zn anode, MnO$_2$/PVB@Zn batteries were assembled as well, as the MnO$_2$/Zn battery is one of the most commonly used systems in mild aqueous electrolyte.\[56\] The MnO$_2$ was \textit{in-situ} synthesized on a carbon cloth by a chronoamperometric electrodeposition process, and its nanoflower morphology was characterized by SEM. MnO$_2$/PVB@Zn batteries were tested in an electrolyte composed of 1 M ZnSO$_4$ and 0.1 M MnSO$_4$, in which MnSO$_4$ serves as an electrolyte additive to suppress the Mn$^{2+}$ dissolution from the cathode material. The typical charge-discharge curves of MnO$_2$/Zn battery at 1 C are presented in Figure 5.16a. Our PVB coated Zn anode helps to enhance the CE and cycling stability of the MnO$_2$/Zn system, as shown in Figure 5.16b. After 1500 cycles, the capacity retention of the MnO$_2$/PVB@Zn battery is approximately 86.6%, much higher than that of the MnO$_2$/Zn battery (31.8%).

Figure 5.16 a) Charge-discharge profiles of MnO$_2$/Zn batteries in electrolyte composed of 1 M ZnSO$_4$ and 0.1 M MnSO$_4$ solution at the rate of 1 C. b) Long-term cycling stability of MnO$_2$/Zn and MnO$_2$/PVB@Zn batteries at 5 C with the corresponding CEs.

5.4 Conclusion

In this work, the Zn surface chemistry in slightly acidic electrolyte as well as the influence of Zn dendrite growth on the electrochemical performance of Zn-based batteries were
comprehensively investigated. The results reveal that Zn metal shows poor thermodynamic stability even in mild electrolyte. A by-product layer of Zn₄SO₄(OH)₆·xH₂O was generated at the interphase between the Zn surface and the electrolyte, although it could not block the electrolyte due to its loose structure. In addition, Zn dendrites that formed on the bare Zn electrode would pierce the thin separator (0.24 mm) and generate an internal short circuit after prolonged plating/stripping. Although a thick separator (0.96 mm) extended the cycle life of the symmetric Zn cell, it could not fundamentally address the issues caused by the Zn dendrites. To effectively suppress the side reactions and Zn dendrite growth, an even and dense PVB SEI film was deposited on the surface of the Zn metal using the spin-coating method. Benefiting from the abundant polar functional groups of the PVB chains, this insulating polymer shows good hydrophilicity and ionic conductivity, inhibiting the side-reactions and Zn dendrite growth. The side-reaction-free and dendrite-free PVB@Zn anode facilitated repeated plating/stripping over 2200 h in the symmetrical Zn cell, much longer than for the bare Zn cells. Importantly, both the commonly-used MnO₂ system and the hybrid LFP system displayed higher initial CE and longer lifespan when coupled with PVB@Zn anode compared to the batteries with bare Zn anode. Our findings can help to elucidate the side-reactions between Zn metal electrode and mild electrolyte, as well as Zn dendrite growth. We provide a simple and inexpensive strategy to manipulate the Zn electrodeposition behaviour from dendritic to non-dendritic, which paves the way to rejuvenated prospects for Zn-based batteries in large-scale applications.

5.5 References


Chapter 6

An in-depth study on Zn metal surface chemistry

6.1 Introduction

Zn metal batteries have gained extensive attention due to its high abundance, low toxicity, low reduction potential, high hydrogen evolution over-potential, and high theoretical capacity (gravimetric capacity of 820 mA h g$^{-1}$ and volumetric capacity of 5855 mA h cm$^{-3}$).[1-3] Nevertheless, Zn metal anode in mild electrolyte still faces severe inherent problems of dendrite growth, Zn corrosion, and hydrogen evolution, which significantly compromise the CE, cycling stability, and practical implementation of Zn metal batteries.[4-7] According to our previous study,[8] the fresh Zn metal is highly unstable in slightly acidic electrolyte and generates a loose Zn$_4$SO$_4$(OH)$_6$·xH$_2$O layer that cannot block the electrolyte to protect Zn electrode, and simultaneously produces hydrogen gas which easily causes the battery swelling. However, it is well-known that there is a dense Zn$_5$(CO$_3$)$_2$(OH)$_6$ passivation layer on commercial Zn metal surface due to Zn oxidation by contacting with oxygen and moisture in air.[9] This layer is homogeneous and dense enough to effectively reduce the Zn corrosion rate in air.[10] Could this layer protect the fresh Zn in mild electrolyte by termination of side reactions? Does the existence of this layer have an impact on the Zn stripping/plating behaviors during Zn battery operation? Up to now, little attention has been spent on achieving an in-depth understanding of this dense passive film in Zn metal batteries. To date, most efforts have been spent on suppressing Zn dendrite growth to enhance the CE of Zn metal, such as designing three-dimensional Zn metal architectures,[11] developing new/highly concentrated electrolytes,[1, 12-14] introducing different electrolyte additives,[15, 16] and controlling the Zn growth.[17-19] Although these strategies could stabilize Zn metal to some extent, the battery performance is still far from satisfactory to industrial application.
resulting from the persistent existence of side reactions.\textsuperscript{[20]} Because Zn electrode would continuously react with the electrolyte during the transportation, and shelf time after the battery assembling but before the customer use, which seriously limits the practical application of Zn batteries. Building artificial solid-electrolyte interphase (SEI) layers should be a good alternative, which not only effectively inhibits Zn dendrite growth, but also stops the side reactions.\textsuperscript{[21-23]} However, the inhomogeneous and uncompacted artificial layers built by \textit{ex-situ} techniques are unlikely to effectively block electrolyte from Zn metal surface, thus the side reactions including Zn corrosion and hydrogen evolution would occur when the uncovered Zn contacts with the electrolyte. Even worse, they features a poor adhesion and easily detached from Zn metal surface due to the volume change during cycling, so that they cannot fully protect the interior fresh Zn metal. Moreover, most artificial layers still suffer from the low transference number ($t_{Zn^{2+}}$), which may discount the inhibition of dendrite growth. Because the divalent Zn$^{2+}$ (radius, 0.74 Å) has a much higher electric charge density compared to the monovalent Li$^+$ and Na$^+$ (radii, 0.76 and 1.02 Å, respectively)\textsuperscript{[24]}, which creates a huge energy barrier for Zn$^{2+}$ transfer in these artificial layers. Therefore, \textit{in-situ} developing a dense and homogeneous artificial SEI with a strong adhesion and high $t_{Zn^{2+}}$ is still challenging for Zn metal anode.

Here, the protective function of the oxidation layer on Zn metal is studied in-depth in 1 M ZnSO$_4$ electrolyte, indicating that this dense Zn$_5$(CO$_3$)$_2$(OH)$_6$ oxidation layer is thermodynamically unstable in slightly acidic electrolyte, and cannot act as an effective barrier against electrolyte. Because it was gradually transformed into a loose Zn$_4$SO$_4$(OH)$_6$·xH$_2$O layer after soaked in 1 M ZnSO$_4$ electrolyte. To effectively suppress the Zn dendrite growth and the side reactions, a compact artificial ZnS layer has been elaborately built on the Zn metal surface by an \textit{in-situ} vapour-solid strategy. The different
temperatures were conducted, suggesting that the homogeneous ZnS coating on Zn metal surface was realized at 350 °C (ZnS@Zn-350). At the interphase of ZnS and Zn metal, S atoms have the bonding interaction with the Zn atoms in the Zn metal due to the occurrence of charge migration, as confirmed by the density functional theory (DFT) calculation. The unbalanced charge distribution not only enhance the Zn\(^{2+}\) diffusion at the ZnS@Zn interphase but also increases the adhesion ZnS film to the Zn surface. Importantly, it is highly stable in aqueous electrolyte, which contributes to enhancement of the Zn reversibility by avoiding the side reactions. Benefiting from the good mechanical strength and high ionic conductivity, ZnS coating film facilitates the dendrite-free Zn plating/stripping underneath the protective layer, which was confirmed by in-situ optical microscopy. With this strategy, the high cycling stability (>2500 cycles) and high CE (>99.8%) were realized in both symmetric cells and full-cells when coupled with MnO\(_2\) cathode.

### 6.2 Experimental section

#### 6.2.1 Material synthesis

Zn foil was cut into Zn ribbon (5 cm × 2 cm), then the one side of Zn ribbon was polished. Two polished Zn ribbons were put in a specially designed tube with 100 g sulfur powder below it. Then, the tube was evacuated and sealed. After that, a high-temperature treatment was carried out with a given heating rate of 5 °C min\(^{-1}\) at target temperature of 300, 350, and 400 °C for 2 h in a Muffle Furnace (151H1TN). Finally, the ZnS coated Zn foils were obtained, which were denoted as ZnS@Zn-300, ZnS@Zn-350, and ZnS@Zn-400, respectively.

#### 6.2.2 Materials characterization

The microstructure/morphology of the as-prepared Sb\(_2\)S\(_3\) bulks and nanosheets was investigated by XRD (GBC MMA) with Cu K\(\alpha\) radiation, field-emission scanning electron microscopy (FESEM) (JEOL 7500), TEM (JEOL ARM-200F) with high-resolution TEM
(HRTEM), and Raman spectroscopy (Jobin Yvon HR800) employing a 10 mW helium/neon laser at 632.8 nm. A commercial AFM (Asylum Research MFP-3D) was used to measure the morphology and thickness of the SBS nanosheets in trapping mode. An Al coated n-silicon probe with resonance frequency of 204-497 kHz and force constant of 10-130 N m⁻¹ was used in the AFM measurements. For synchrotron X-ray powder diffraction, a specially modified CR2032 coin cell was used with holes on both sides. In-situ synchrotron XRD measurements were then performed at the Powder Diffraction beamline (Australian Synchrotron), and the XRD patterns were conducted at 0.688273 Å (determined using LaB₆, NIST SRM 660b).

### 6.2.3 Electrochemical measurements.

The crystalline structure of the bare Zn foil and ZnS@Zn foils obtained at different temperatures was investigated by X-ray diffraction (XRD, GBC MMA diffractometer) with Cu Kα radiation and a scanning rate of 1° min⁻¹. The morphologies of the Zn foil, ZnS@Zn foils, and the Zn plating on bare Zn and ZnS@Zn-350 were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7500FA), operated at 5 kV and 10 mA, along with energy dispersive X-ray spectroscopy (EDX) mapping. X-ray photoelectron spectroscopy (XPS) measurements of bare Zn foil and ZnS@Zn-350 were performed on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using monochromatic Al Kα radiation under vacuum at 2 × 10⁻⁶ Pa, in which the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. FTIR spectra of bare Zn and polished Zn foil were acquired in duplicate in the range of 4000–600 cm⁻¹ using a PerkinElmer Frontier FTIR spectrometer (PerkinElmer, Boston, MA, USA) with a resolution of 2 cm⁻¹ and averaging 8 scans for each spectrum.

The ionic conductivity of ZnS film was tested using two blocking electrodes (Ti foil). First, the ZnS film was coated on the Ti foil using the doctor blading method, and then the ZnS
coated Ti foil was fixed in a plastic splint cell with a wetted glass fiber (wetted by 1 M ZnSO$_4$ solution). The ionic conductivity of the ZnS film was evaluated according to the following equation:

$$\sigma = \frac{L}{R_b S} \quad (6-1)$$

where $R_b$ represents the resistance according to the EIS measurement, $L$ represents the thickness of the ZnS film, and $S$ is the contact area. The testing was conducted at the temperature of 25 °C.

The transference number of Zn$^{2+}$ ($t_{Zn^{2+}}$) was based on measurements in a symmetrical Zn (or ZnS@Zn-350) battery with the help of EIS before and after the contact angle (CA) tests and determined by the following equation:

$$t_{Zn^{2+}} = \frac{i_s(\Delta V - i_0 R_0)}{i_0(\Delta V - i_s R_s)} \quad (6-2)$$

where $\Delta V$ is the applied voltage, $I_0$ and $R_0$ are the initial current and resistance, and $I_s$ and $R_s$ are the steady-state current and resistance, respectively.

### 6.2.4 Theoretical calculations

All calculation tasks were executed by first principle program package the Cambridge Serial Total Energy Package (CASTEP). As experimentally determined, the cubic ZnS exhibits the orthorhombic structure with the space group of F-43m. Its unit cell contains four formula units with the lattice constants of $a = 5.4053$, $b = 5.4053$, and $c = 5.4053$ Å. As experimentally determined, Zn metal presents the monoclinic structure with space group of P63/mmc, and the unit cell contains two formula units with the lattice constants $a = 2.6587$ Å, $b = 2.6587$ Å, and $c = 4.8666$ Å. To simulate the interface of ZnS(002)/Zn(002), an ZnS(002) slab model with 14 atoms and Zn metal (002) slab model with 16 atoms layers, and the distance between ZnS(002) and Zn(002) layers was set 3 Å. A vacuum thickness of
10 Å was set. The average lattice constants of the constructed ZnS(002)/Zn(002) heterointerface are $a = 5.3174$ Å and $b = 18.6109$ Å.

### 6.3 Results and discussion

#### Fundamental study on Zn metal

![Figure 6.1](image)

**Figure 6.1** Characterization of passivation layer on Zn metal. a) SEM image of bare Zn foil without polishing. Digital images of Zn metal. b) Zn metals soaked in the electrolyte for one week. c) Bare Zn metal before (top) and after soaking in electrolyte (bottom). d) Polished Zn metal before (top) and after soaking in electrolyte (bottom). e) SEM image of bare Zn foil after soaking in electrolyte for one week.

A dense zinc hydroxycarbonates (i.e. $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ or $\text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O}$) passivation layer forms on Zn metal surface once exposed to the air, which can significantly retard the corrosion process by keeping out moisture and oxygen.$^{[25]}$ Can this passive film protect the Zn metal in 1 M $\text{ZnSO}_4$ electrolyte? Does this film influence the Zn plating/stripping behavior? These fundamental issues are still unclear. To address these problems, the stability
of this oxidation layer was first studied in 1 M ZnSO₄. A scanning electron microscope (SEM) image of bare Zn metal without polishing shows a flat surface with some holes (Figure 6.1a). After deep cleaning, the oxidation layer was removed, with many scratches remaining on the polished Zn metal.[26] No obvious absorption can be observed after polishing, indicating that Zn₅(CO₃)₂(OH)₆ layer was thoroughly removed. Both bare Zn metal and polished Zn were soaked in 1 M ZnSO₄ electrolyte. After one week, the surfaces of both bare and polished Zn metal occurred the severe corrosion reaction with significant colour change (Figure 6.1b-d). SEM image shows by-products with the morphology of regular hexagonal flakes that cover the whole surface of bare Zn (Figure 6.1e), which is similar to the polished Zn, demonstrating that the Zn₅(CO₃)₂(OH)₆ layer is highly active in the electrolyte.

**Figure 6.2** XRD patterns of different Zn metal. a) Bare Zn metal and bare Zn metal after soaked in electrolyte for one week. b) Polished Zn metal and polished Zn metal after soaked in electrolyte for one week. The results indicated that the by-product generated on both bare Zn and polished Zn metal was Zn₅SO₄(OH)₆·xH₂O.

XRD (Figure 6.2) and FTIR measurements were conducted to identify the by-products of both samples. The results indicated that the by-product generated on both bare Zn and polished Zn metal was Zn₅SO₄(OH)₆·xH₂O, as further confirmed by the energy dispersive...
spectroscopy (EDS) mapping of S and Zn elements (Figure 6.3a-c). Accordingly, Zn$_5$(CO$_3$)$_2$(OH)$_6$ passivation layer cannot function as a protective layer in electrolyte due to its high thermodynamic activity. The corrosion reaction of bare Zn with a Zn$_5$(CO$_3$)$_2$(OH)$_6$ passivation layer can be expressed as following:

\[
\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 + \text{SO}_4^{2-} + 4 \text{H}^+ + (x - 2)\text{H}_2\text{O} \rightarrow \text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O} + 2\text{CO}_2 + \text{Zn}^{2+}
\] (6-3)

\[
\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2e^-
\] (6-4)

\[
4\text{Zn}^{2+} + 6\text{OH}^- + \text{SO}_4^{2-} + x\text{H}_2\text{O} \leftrightarrow \text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}
\] (6-5)

Figure 6.3 a-c) EDS mapping of the plates generated during the side reactions, showing the uniform distribution of S and Zn elements. d) Initial charge/discharge voltage profiles of bare Zn symmetric cell and polished Zn symmetric cell, with an enlargement in the inset.

The electrochemical performance of symmetrical Zn cells with/without polishing was tested to investigate the influence of the Zn$_5$(CO$_3$)$_2$(OH)$_6$ layer on Zn electrodeposition behaviour. Figure 6.3d compares the initial charge/discharge voltage profiles of both cells. Remarkably, the bare Zn cell displays a higher voltage hysteresis compared to the polished Zn cell at the
start of charge, indicating its higher energy barrier for Zn striping/plating due to the passivation layer.[27] As the charge proceeds, the voltage hysteresis of the bare Zn cell decreases, probably due to the dissolution of the passivation layer in ZnSO₄ electrolyte, but it increases in the polished Zn cell, indicating the enhanced impedance due to the by-product layer formation. Electrochemical impedance spectroscopy (EIS) measurements of Zn cells were conducted after different numbers of cycles (Figure 6.4a,b). Both bare and polished Zn cells show two different charge transfer steps after one cycle and after 50 cycles, manifesting the additional by-product layer generated during the charge-discharge process.

Figure 6.4 Electrochemical impedance spectroscopy measurements of Zn cells at different numbers of cycles. a) Bare Zn symmetrical cell before cycling, after one cycle, and after 50 cycles. b) Polished Zn symmetrical cell before cycling, after one cycle, and after 50 cycles. The results manifest the additional by-product layer generated during the charge-discharge process. Digital images of Zn metal electrodes stripping out from the Zn cells at different states. c) Bare Zn electrode before cycling, after one cycle, and after 50 cycles. d) Polished Zn electrode before cycling, after one cycle, and after 50 cycles. The results reveal that the two kinds of Zn electrodes suffered from surface corrosion with obvious a colour change during cycling.
Digital images of bare and polished Zn metal electrodes reveal that the two kinds of Zn electrodes suffered from serious surface corrosion with obvious a colour change during cycling (Figure 6.4c,d), as further confirmed by XRD patterns. Before cycling, only the characteristic peaks of Zn metal located at 36.4°, 39.1°, and 43.3° can be found for the bare Zn electrode, which suggests that the Zn₅(CO₃)₂(OH)₆ layer is hard to identify.[28] After one cycle, a small peak at 8.5° can be detected, corresponding to (002) facets of Zn₄SO₄(OH)₆·xH₂O by-product, and the intensity increases with the further cycling (50 cycles), indicating the aggravated side reactions during battery operation, which is similar to XRD patterns of the polished Zn after different cycles. Although removal of the Zn₅(CO₃)₂(OH)₆ reduces the energy barrier for Zn stripping/plating and prolongs the cycling lifespan from ~100 h to ~250 h at 2 mA cm⁻² (Figure 6.5), the performance of the polished Zn cell is still far from satisfactory due to the notorious Zn dendrite growth and side reactions.

Figure 6.5 Cycling stability of bare Zn symmetrical cell and polished Zn symmetrical cell at a current density of 2 mA cm⁻² with the capacity of 2 mA h cm⁻². Although removal of the Zn₅(CO₃)₂(OH)₆ reduces the energy barrier for Zn stripping/plating and prolongs the cycling lifespan from ~100 h to

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~250 h, the performance of the polished Zn cell is still far from satisfactory due to the notorious Zn dendrite growth and uninterrupted side reactions.

**In-situ building ZnS film**

![Diagram of in-situ building ZnS film](image)

**Figure 6.6** Schematic illustration of the artificial ZnS layer and Zn plating behaviour with/without ZnS. a) Introducing ZnS layer on the surface of Zn metal substrate by an *in-situ* strategy. b) Zn plating on the bare Zn foil with a Zn$_5$(CO$_3$)$_2$(OH)$_6$ passivation layer, leading to side reactions and dendritic Zn deposition (up), after incorporating the artificial ZnS layer on Zn surface, uniform and compact Zn plating behaviour without side reactions can be obtained (bottom).

Building a dense and homogeneous SEI layer is an effective strategy to enhance the Zn reversibility.$^{29}$ Based on the phase diagram of sulfur, we have elaborately grown an artificial ZnS film on Zn metal surface by *in-situ* vapour-solid reaction, as illustrated in Figure 6.6a. Specifically, sulfur will be vaporized at ~200 °C under the pressure of ~1 × 10$^{-3}$ atm, and the sulfur vapour will react with Zn metal by generating ZnS at high temperatures. Accordingly, Zn foil was put in a specially designed tube with 100 g sulfur powder below it. Then, the tube was evacuated and sealed. At the high temperature, the gaseous sulfur vapour spread to the Zn metal surface and reacted with Zn metal by generating a dense and
uniformed ZnS layer. As aforementioned, Zn electrode, whether with/without a ZnS(CO_3)_2(OH)_6 layer, is highly unstable, and suffers from side reactions and dendrite growth during battery operation (Figure 6.6b), which not only fades the CE and reversible capacity, but also shortens the cycling lifespan of Zn batteries. In striking contrast, the ZnS protective layer on the Zn surface not only effectively inhibits the corrosion reactions by blocking the electrolyte, but also suppresses the Zn dendrite formation and growth by guiding the Zn^{2+} stripping/plating underneath, enhancing the reversibility of Zn metal (Figure 6.6b).

Figure 6.7 Characterization of Zn foil protected by ZnS layer and the charge density distribution at the interface of ZnS layer and Zn metal. a) XRD patterns of ZnS@Zn foils obtained at different temperatures. b) SEM image of ZnS@Zn-350 foil (top-view). c) Cross-sectional image of ZnS@Zn-350 foil, showing that the thickness of ZnS is approximately 0.5 µm. d) EDS mapping of Zn element (top) and S element (bottom). XPS characterizations of bare Zn and ZnS@Zn-350 foil: e) Zn 2p spectra, f) S 2p spectra. g) Schematic representation of the ZnS@Zn interphase of ZnS@Zn-350 electrode. h) Electron density difference map at the ZnS@Zn interphase. i) The slice of electron density difference to view the unbalanced charge distribution.
The heating temperature is of great importance for fabricating the high-performance ZnS functional film on Zn metal. Therefore, different operating temperatures of 300, 350, and 400 °C were conducted to prepare the ZnS protective film. From the XRD patterns of ZnS@Zn electrodes (Figure 6.7a), the sample obtained at 300 °C (ZnS@Zn-300) only shows the characteristic peaks belonging to Zn metal, indicating no obvious formation of ZnS film at this temperature, as further confirmed by EDS mapping. No clear S element layer can be found on Zn metal surface, suggesting the improper operating temperature. When the temperature was increased to 350 °C, the XRD pattern displayed new peaks at 28.6°, 47.5°, and 56.3°, corresponding to the (111), (220), and (311) planes of ZnS (PDF # 00-005-0566), respectively. The intensity of these peaks increased when the temperature was increased to 400 °C. SEM images show that Zn surface was evenly covered by ZnS at 350 °C (Figure 6.7b). The cross-sectional image (Figure 6.7c) reveals a homogeneous ZnS coating layer with the thickness of ~0.5 µm, as further confirmed by the EDS mapping (Figure 6.7d). X-ray photoelectron spectroscopy (XPS) spectra of bare Zn and ZnS@Zn-350 were collected (Figure 6.7e-f), where bare Zn electrode only shows the binding energies of Zn 2p\( _{1/2} \) and Zn 2p\( _{3/2} \) at 1045.1 and 1021.9 eV, respectively. Whereas, ZnS@Zn-350 displays the S signals of S 2p\( _{3/2} \) and S2p\( _{1/2} \) located at 161.9 and 163.2 eV. Importantly, a small binding energy shift in the Zn 2p\( _{3/2} \) region mainly due to the formation of the Zn-S polar bond at the interphase of ZnS and Zn metal, which enhances the adhesion of ZnS film to Zn metal. According to the previous report, the Zn (002) face transfers into ZnS (002) at the interphase of ZnS@Zn, as illustrated in Figure 6.7g. DFT calculation reveals that the bonding interaction occurred at the S atoms and Zn atoms in the Zn metal, which modifies the charge distribution (Figure 6.7h) and further leads to an unbalanced charge distribution at the interphase (Figure 6.7i). The unbalanced charge distribution not only accelerates the Zn\(^{2+}\) diffusion at the ZnS@Zn interphase but also enhance the adhesion of ZnS layer to the Zn metal.
presents digital images of ZnS@Zn electrodes obtained at different temperatures, with ZnS@Zn-300 foil showing almost no changes in colours or luminosity. Remarkably, the surfaces of ZnS@Zn-350 and ZnS@Zn-400 foils changed significantly due to the sulfur-vapour reaction. Unfortunately, ZnS@Zn-400 foil suffered from the serious distortion due to the deformation of Zn metal at the high temperature, indicating that the high temperature of 400 °C is unsuitable either.

![Figure 6.8](image)

**Figure 6.8** Digital images of Zn and ZnS@Zn foils obtained at different temperatures. a) Pure Zn foil. b) ZnS@Zn-300 foil. c) ZnS@Zn-350 foil. d) ZnS@Zn-400 foil. Clearly, the ZnS@Zn-400 foil suffers from the serious distortion due to deformation of the Zn metal at the high temperature, indicating that 400 °C is also unsuitable for fabricating the ZnS layer on Zn metal.

**Blocking electrolyte and suppressing dendrite growth**
Figure 6.9 Digital images of ZnS@Zn-350 foil. a) ZnS@Zn-350 foil soaked in the electrolyte for 10 days. b) ZnS@Zn-350 foil before (top) and after soaking in electrolyte (bottom), which show similar surfaces before and after soaking in electrolyte for 10 days. c) XRD patterns of ZnS@Zn-350 foil before and after the soaking in electrolyte for 10 days.

In order to study the stability of ZnS layer, ZnS@Zn-350 foil was soaked in 1 M ZnSO$_4$ electrolyte for one week. The digital images of ZnS@Zn-350 foil show the similar surfaces before and after soaking in electrolyte for 10 days (Figure 6.9a,b), demonstrating that this layer is highly stable. XRD pattern was collected after the soaking in electrolyte (Figure 6.9c), which is similar to that of ZnS@Zn-350 foil before soaking and without any peaks of Zn$_4$SO$_4$(OH)$_6$·xH$_2$O by-product, indicating that the side reactions between Zn metal and electrolyte were interrupted.\textsuperscript{35, 36} In addition to inhibiting the side reactions, ZnS layer also functions as a robust artificial SEI to supress Zn dendrite growth due to its poor electronic conductivity, but high ionic conductivity and high $t_{Zn^{2+}}$. It is well-known that the cubic ZnS has been widespread used as the semiconductors due to its wide-band-gap properties.\textsuperscript{37} The electrical resistivity of ZnS protective film was also evaluated using the blocking electrodes (Figure 6.10). According to the following formula $\rho = \frac{R \times S}{L} = \frac{U \times S}{I \times L}$, the value was estimated as $\sim 1.5 \times 10^5 \, \Omega \cdot \text{cm}$ ($\sigma \approx 6.5 \times 10^{-6} \, \text{S cm}^{-1}$). The high resistance introduced by the insulating ZnS layer is critical for establishing the necessary potential gradient across the artificial film.
to drive Zn\(^{2+}\) diffusion through the layer.\[^{38}\] In addition, ZnS film features good ionic conductivity (evaluated as \(\sim 1.3 \times 10^{-5} \text{ S cm}^{-1}\), Figure 6.10b-c), which facilitates Zn\(^{2+}\) diffusion through this protective film. Furthermore, the \(t_{\text{Zn}^{2+}}\) was further calculated to quantitatively describe the Zn\(^{2+}\) conducting ability of the ZnS protective layer. In a bare Zn symmetric cell, a rather low \(t_{\text{Zn}^{2+}}\) of 0.33 was obtained (Figure 6.10d-e), which is mainly due to the strong preferential solvation of Zn\(^{2+}\) over the anions, leading to a bulky solvation shell around Zn\(^{2+}\). SO\(_4^{2-}\) anions tend to migrate in the opposite direction from Zn\(^{2+}\) and eventually accumulate at the electrode surface, resulting in a build-up of the concentration gradient. This concentration gradient not only limits the rate at which the battery may be charged or discharged, but also creates a concentration overpotential that limits the operating voltage of the battery, thus limiting the power and energy density of the battery.\[^{39}\] Notably, \(t_{\text{Zn}^{2+}}\) can be dramatically improved to \(\sim 0.78\) after introducing the ZnS layer (Figure S21b), suggesting that the anions were effectively retarded by this protective layer.
Figure 6.10 a) Conductivity measurements of bare Zn and ZnS@Zn-350 foils using blocking electrodes with an applied current of 5 mA. Nyquist plots tested at open circuit voltage (OCV) over the frequency range of 100 kHz to 1 Hz. b) Ti symmetry cell with the glass fiber as separator (inset: enlargement of indicated range). c) ZnS coated Ti symmetry cell with the glass fiber as separator (inset: enlargement of indicated range). Current-time plots of bare Zn symmetric cell (d) and ZnS@Zn-350 symmetric cell (e) after the polarization of a constant potential (25 mV) for 4000 s. The inserts are the impedance spectra before and after the polarization.

To confirm the suppression of Zn dendrite growth by the ZnS artificial layer, the transparent symmetric cells were assembled to *in-situ* monitor Zn plating/stripping behaviour using an optical microscope equipped with a digital camera. A high current density of 5 mA cm\(^{-2}\) with 10 min of intermittence was applied to repeatedly conduct plating/stripping measurements.
Figure 6.11a presents images of bare Zn electrode after different plating/stripping cycles. Before cycling, bare Zn electrode displays a smooth edge. After 50 cycles, protrusions start to grow along the edge of the bare Zn electrode, which evidences uneven Zn plating. These protrusions gradually turns into Zn dendrites on the Zn electrode with further cycling. In strong comparison, the ZnS@Zn-350 electrode exhibits smooth Zn plating and stripping in Figure 6.11b. There is still no sign of protrusions or Zn dendrite generation, even after 250 cycles.

**Figure 6.11** Optical microscopy and SEM studies of Zn plating behavior: a) Images of the front surface of bare Zn, and b) of ZnS@Zn-350 electrode in a symmetric transparent cell at the specified numbers of plating/stripping cycles. Cross-sectional SEM images of Zn deposition: c) on bare Zn metal at 1 mA cm$^{-2}$ for 1 mA h cm$^{-2}$, d) 1 mA cm$^{-2}$ for 2 mA h cm$^{-2}$; e) on ZnS@Zn-350 foil at 1 mA cm$^{-2}$ for 1 mA h cm$^{-2}$, f) 1 mA cm$^{-2}$ for 2 mA h cm$^{-2}$. g) CEs of Zn plating/stripping in the bare Cu-Zn and ZnS@Cu-Zn cells with the capacity of 1 mA h cm$^{-2}$. Voltage profiles of the bare Cu-Zn cell (h) and the ZnS@Cu-Zn cells (i) at the 1st, 50th, and 100th cycles.
SEM was further conducted to observe the Zn electrodeposition with/without the ZnS protective layer. Zn deposition was conducted under 1 mA cm\(^{-2}\) with the deposition capacity of 1 mA h cm\(^{-2}\) and 2 mA h cm\(^{-2}\), respectively. Figure 6.11c shows the cross-sectional image of bare Zn metal after Zn plating (1 mA h cm\(^{-2}\)). Remarkably, the uneven deposition on Zn surface with serious agglomeration occurred, which easily triggers the dendrite growth. After deposition of 2 mA h cm\(^{-2}\), the agglomeration was aggravated, raising a potential safety issue after further Zn plating (Figure 6.11d). In contrast, no obvious Zn plates or protrusions were generated on the ZnS@Zn-350 surface after 1 mA h cm\(^{-2}\) plating (Figure 6.11e), indicating that the ZnS protective layer helps to guide the humongous Zn deposition underneath the film. Even after 2 mA h cm\(^{-2}\) plating, the uniform deposition under the ZnS layer was still observed in Figure 6.11f, resulting in dendrite-free Zn plating.

**Electrochemical performance of ZnS@Zn electrode**

CE is one of the most important parameters to evaluate the reversibility of Zn plating and stripping.\(^{[40]}\) In a Cu-Zn cell, the CEs were calculated from the ratio of Zn removed from Cu substrate to that deposited during the same cycle. The ZnS protective layer on Cu foil was obtained by the doctor blading method. First, the morphology of Zn deposition on the bare Cu and ZnS@Cu was studied under 2 mA cm\(^{-2}\) with a capacity of 1 mA h cm\(^{-2}\). Clearly, the bare Cu substrate was covered by mossy Zn plates with the obvious protrusions. In comparison, no obvious protrusion was generated on the ZnS@Cu surface, further indicating that the ZnS protective layer guides the Zn deposition. In the Cu-Zn cell, the initial CE is only ~77.6% and gradually increases to ~97.6% after the first 20 cycles (Figure 6.11g). However, such a CE is still low due to the poor reversibility of Zn metal caused by the side reactions and dendrite formation. Notably, the CEs fluctuate greatly after ~120 cycles, which mainly due to short-circuiting of battery. Notably, the ZnS@Cu-Zn cell displays a much higher initial CE of ~88.5% compared to the Cu-Zn cell, and it increases to 99.2% in the
following 10 cycles. Even after 200 cycles, the CE remains stable, mainly benefiting from the suppression of side reactions and dendrite growth. The charge-discharge voltage profiles for different cycles of Cu-Zn cell are shown in Figure 6.11h. The initial voltage hysteresis is ~141 mV for the Cu-Zn cell, much higher than that for the ZnS@Cu-Zn cell (~105 mV, Figure 6.11i), indicating the higher energy barrier for Zn nucleation/dissolution in the phase transition between Zn$^{2+}$ ions and Zn metal.\cite{41}

Figure 6.12 Electrochemical characterization of the samples. a) Comparison of the cycling stability of bare Zn and ZnS@Zn-350 in a symmetric cell at 2 mA cm$^{-2}$ with the capacity of 2 mA h cm$^{-2}$. b) High-resolution voltage profiles for the 1$^{st}$ cycle. c) Rate performances of both cells at current densities from 0.2 to 10 mA cm$^{-1}$. d) Cyclic voltammogram curves for the 2$^{nd}$ cycle of MnO$_2$/Zn batteries using bare Zn and ZnS@Zn-350 anodes. e) Long-term cycling stability of both batteries at 5 C, along with the corresponding CEs (>99.8%).
The stability of Zn metal anode with/without ZnS layer was evaluated by long-term galvanostatic cycling of the symmetrical cells (Figure 6.12a). After cycling for ~100 h at 2 mA cm\(^{-2}\), a sudden reduction of the polarization voltage appeared in bare Zn cell, which might be ascribed to a dynamic dendrite-induced short circuit. In contrast, ZnS@Zn-350 cell displayed a prolonged cycling stability of more than 1100 h. Figure 6.12b compares the first charge-discharge voltage profiles of both cells. Apparently, ZnS@Zn-350 cell delivers a polarization voltage of ~98 mV, much lower than that of bare Zn cell (~153 mV), indicating its low energy barrier for Zn deposition. One of the probable reasons for the high energy barrier is that the accumulation of detrimental by-products may block the conduction of ions.\(^{[42]}\) The rate performance of Zn cells was investigated at various current densities from 0.2 to 10 mA cm\(^{-2}\), as shown in Figure 6.12c, in which the bare Zn cell always exhibits the substantially higher voltage hysteresis than ZnS@Zn-350 cell, suggesting the low polarization and favourable stability in ZnS@Zn-350 cell.

To further prove the application of ZnS@Zn-350 electrode, the MnO\(_2\)/Zn full-cell was assembled by hiring MnO\(_2\) electrode as the cathode, since it is one of the most promising candidates for aqueous Zn batteries.\(^{[43, 44]}\) The full-cells were tested in electrolyte consisting of 1 M ZnSO\(_4\) + 0.1 M MnSO\(_4\), in which MnSO\(_4\) was used as an additive to inhibit the dissolution of Mn\(^{2+}\) from MnO\(_2\) cathode.\(^{[45, 46]}\) The CV curves of the MnO\(_2\)/Zn and MnO\(_2\)/ZnS@Zn-350 batteries were compared in Figure 6.12d. Clearly, the MnO\(_2\)/ZnS@Zn-350 battery shows a smaller of voltage polarization (~20 mV) than that of the MnO\(_2\)/Zn battery, indicating its good reversibility due to the ZnS protection. The long-term cycling stability curves of both batteries at a high rate of 5 C were plotted in Figure 6.12e. The cell with bare Zn foil presents an initial capacity of ~115.6 mA h g\(^{-1}\). The capacity dramatically drops after 1000 cycles, however, mainly because the separator was pierced by Zn dendrites, leading to the short-circuiting of the battery. In contrast, the MnO\(_2\)/ZnS@Zn-350 battery
delivers a higher initial capacity (125.8 mA h g$^{-1}$) compared to the MnO$_2$/Zn battery. After 2500 cycles, a high capacity of 110.2 mA h g$^{-1}$ with a high CE of 99.3 % was retained, corresponding to capacity retention of 87.6%, which is mainly due to the inhibition of Zn corrosion and dendrite growth during the battery operation.

6.4 Conclusion

The protective function of Zn$_5$(CO$_3$)$_2$(OH)$_6$ passive film on Zn metal was explored in 1 M ZnSO$_4$ electrolyte. Although this dense passivation layer could passivate Zn metal in air by blocking oxygen and moisture, it cannot protect Zn metal in mild electrolyte. Accordingly, a homogeneous and dense ZnS protective film was *in-situ* introduced on the Zn metal surface by a high-temperature vapour-solid strategy. Different temperatures were used, with the results suggesting a homogenous ZnS film with a thickness of 0.5 µm was obtained at 350 °C. It was found to be highly stable in mild electrolyte, which contributes to improving the reversibility of Zn metal by avoiding the electrolyte-induced side reactions. Moreover, this robust ZnS coating film shows strong adhesion, good mechanical strength, and high ionic conductivity, which enable even Zn plating/striping underneath the functional layer, as confirmed by *in-situ* optical microscopy. With the artificial layer, ZnS@Zn-350 symmetric cell delivers a smaller voltage polarization and longer lifespan >1100 h at 2 mA h cm$^{-1}$ compared to bare Zn cells. Benefiting from the side reaction-free and dendrite-free ZnS@Zn-350 electrode, the MnO$_2$/ZnS@Zn-350 full-cell displays excellent cycling stability, with 87.6% capacity retention after 2500 cycles. Our fundamental findings offer a better understanding of Zn metal surface chemistry and pave the way to developing the practical Zn metal batteries with mild electrolyte.

6.5 References


Chapter 6 An in-depth study on Zn metal surface chemistry


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Chapter 7

Conclusions and outlook

7.1 Conclusion

Aqueous Zn-based batteries have been regarded as the promising alternative of LIBs for large-scale application due to their advantages of low cost, high performance, inherent safety, and environmental benignity. However, the state-of-the-art aqueous Zn battery is still far from meeting the ever-increasing large-scale energy demands. In this doctoral thesis, recent progress on the aqueous ZIBs and hybrid Zn batteries with mild electrolyte have been comprehensively summarized, including the cathode materials, Zn-ion storage mechanism, electrolyte formulation, and Zn electrode. Zn metal electrode persistently suffer from the poor reversibility and low CE in the mild electrolyte, which seriously restricted further development of Zn-based batteries. To effectively enhance the Zn performance, we proposed different strategies to suppress Zn dendrite and resolve other issues, including adding the electrolyte additive, ex-situ and in-situ building artificial layers on Zn electrode surface.

In this first case, the SDBS additive was added in the hybrid electrolyte. It can be absorbed on the Zn electrode surface by forming a surface passivating film. This film not only increases the competition between the nucleation and crystal growth but also facilitates the hydrophilicity of Zn foil, which promotes the generation of electroplating nucleation on the electrically charged substrate, resulting in dendrite-free Zn plating. In addition, no obvious corrosion was found on the surface of Zn foil, indicating that the additive relieves the Zn corrosion to some extent, which assists in the high CE and long cycling stability of battery. Consequently, the hybrid LFP/Zn coin-cell with additive displays a high initial CE of 94.5% at 0.5 C, a high rate capability with a capacity of 57.8 mA h g\(^{-1}\) remaining at even 20 C. An
encouraging cycling stability over 150 cycles was still achieved even in an LFP/Zn pouch-cell.

In the second case, the side reactions between Zn electrode and mild electrolyte (1 M ZnSO$_4$) were thoroughly studied. The results indicate that Zn metal is thermodynamically unstable in mild electrolyte. Due to the corrosion, the by-product layer of Zn$_4$SO$_4$(OH)$_6$$\cdot$$x$H$_2$O was formed on the Zn metal surface. Unlike the SEI layer on Li metal in organic electrolyte, this by-product layer is loose, which cannot block the electrolyte from the Zn metal surface. Therefore, the loose layer cannot stop the side reaction. To effectively inhibit the side reactions and Zn dendrite growth, a dense PVB layer was built on the Zn electrode surface through a facile spin-coating strategy. The PVB not only blocks the water from Zn surface but also the guides the even Zn plating, resulting in side-reaction-free and dendrite-free Zn electrode. As a result, the dendrite-free and side-reaction-free Zn electrode showed an extended plating/stripping cycling life of 2200 h in symmetric cells at 0.5 mA cm$^{-2}$. When assembled the full cell with MnO$_2$, an excellent cycling stability with a capacity retention of $\sim$86.6% at 5 C over 1500 cycles can be obtained, which is superior to the battery with bare Zn electrode.

In the third case, a homogeneous and dense ZnS protective film was in-situ built on the Zn metal surface by a high-temperature vapour-solid strategy to inhibit the side reactions and dendrite growth. Compared to the PVB layer built on Zn surface by ex-situ strategy, ZnS layer is more homogeneous and compacted, which is more effectively block electrolyte from Zn metal surface. Moreover, this robust ZnS coating film shows strong adhesion, good mechanical strength, and high ionic conductivity, guiding the even Zn plating/stripping with a small voltage polarization and long lifespan $>$1100 h at 2 mA h cm$^{-1}$. The full cell of MnO$_2$/ZnS@Zn-350 also shows excellent cycling stability, with 87.6% capacity retention after 2500 cycles.
7.2 Outlook

**Zn electrode:** Most reported aqueous ZIBs and Zn hybrid batteries directly use commercial Zn foil as the Zn anode. However, it suffers from several irreversibility issues during the cycling process in mild aqueous electrolytes, such as the dendrite growth, corrosion, as well as hydrogen evolution, which will affect the cycling performance of Zn-based systems. Until now, only limited work focused on the optimization of Zn metal and the Zn electrode reversibility behaviour under the aqueous mild electrolytes is not well understood. The effective methods to suppress the dendrite growth and achieve high CE should be building a stable artificial layer on Zn electrode surface and optimizing the electrolyte formulation. Although the behaviour of Zn electrode in mild electrolytes is different with that in alkaline electrolyte, knowledge accumulated in alkaline Zn batteries research to alleviate the dendrite growth and side reactions can be applied to the investigation of AZIBs and aqueous Zn hybrid batteries. Also, more progresses are desired to be achieved by learning from other metal anode protecting technology such as Li/Na metal batteries. Moreover, the strategies for improving the performance of Zn electrode should be demonstrated in full cells towards practical applications.

**Electrolyte:** The optimization of the electrolyte are critical for achieving high performance batteries by enabling highly efficient Zn plating/stripping and stabilizing the cathode materials, which are related to the Zn salts, salt concentrations, and additives. However, development of the mild aqueous electrolytes in Zn-based battery systems is still a fresh topic. Currently, most work adopted ZnSO₄ or Zn(CF₃SO₃)₂ as Zn salt for preparing the aqueous electrolyte. However, batteries using ZnSO₄ electrolyte still suffer from the rapid capacity decay due to the formation and growth of Zn dendrites and electrode dissolution. In addition, the formation and dissolution of hydroxide sulphate (Zn₄(OH)₆SO₄·xH₂O) associated with ZnSO₄ electrolyte still needs to be understood, as well as the effect on the
electrochemical performance. Batteries employing the Zn(CF$_3$SO$_3$)$_2$ electrolyte show superior electrochemical properties compared to those using ZnSO$_4$ electrolyte, the high price of Zn(CF$_3$SO$_3$)$_2$ severely retards its wide application on a large scale, however. Thus, exploring the new Zn salts with affordable price will be worthwhile to unlock the potential of Zn-based systems by enhancing the CE, cycling stability and rate performance, and more importantly suppressing Zn dendrite growth. In addition, most of the aqueous Zn salt electrolytes are actually the mild acidic electrolyte, where the issues of corrosion of the metal and current collector should be considered and resolved. Moreover, the narrow electrochemical window of aqueous electrolyte would trigger the water-based side reactions and limit the operating voltage of cathode materials. Efforts are still highly desirable to research the new additives or electrolyte concentration, aiming to expand the stability window of electrolyte and bring more potential materials into Zn-based aqueous systems.

**Configuration:** Currently, the vast majority of work about ZIBs and hybrid Zn batteries are still conducted in the coin cell or pouch cell. To meet the different demands at the future market, the different types of aqueous Zn-based technologies should be available in parallel, including coin cell, pouch cell, cylindrical cell (18650), and prismatic cell. An additional challenge is whether strategies suitable for coin cells will work in large-scale cells, for practical application, materials should be demonstrated in large-scale cells. In addition, wearable and flexible electronics with high flexibility and reliable electrochemical properties is a vibrant and active research area for the large demand of portable applications. Benefiting from its green and sustainable features, flexible aqueous Zn-based devices may be a good choice for practical wearable applications. However, only few works focused on flexible Zn-based batteries in neutral or mild acidic media was proposed until now due to the limitations of stable electrode materials and appropriate electrolyte. Therefore, new strategies are highly needed to develop new materials and electrolyte with both excellent electrical conductivity
and outstanding flexibility for the further development of well-designed and safe Zn-based batteries.
Appendix A: Publications


7. **Junnan Hao**, Tao Meng, Dong Shu*, Xiaona Song, Honghong Cheng, Bo Li, Xiaoping


13. Hanna He, Dan Huang, Qingseng Gan, Junnan Hao, Sailin Liu, Zhibin Wu, Wei Kong Pang, Bernt Johannessen, Yougen Tang, Jing-Li Luo, Haiyan Wang*, Zaiping Guo*. 147


Appendix B: Conferences & Activities

1. International Conference on Nanoscience and Nanotechnology, Wollongong, Australia, Jan. 29th – Feb. 2nd, 2018


Appendix C: Scholarships & Awards

1. 2018 ISEM Postgraduate Student Excellence Award

2. 2017 International Postgraduate Research Scholarships, Faculty of Engineering & Information Sciences, University of Wollongong.

3. 2017 International Postgraduate Tuition Award (IPTA), University of Wollongong.