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**SINGAPORE**

**CELLULOSE-BASED AQUEOUS ZINC ION BATTERIES FOR  
FLEXIBLE ENERGY STORAGE APPLICATIONS**

**JIAWEN WU**

**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES**

**2025**

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**JIAWEN WU**

**SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES**

A thesis submitted to the Nanyang Technological  
University in partial fulfilment of the requirement for the  
degree of Doctor of Philosophy

**2025**

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Hong Jin Fan

## Authorship Attribution Statement

This thesis contains material from 2 papers published in which I am listed as an author.

Chapter 3 is published as J. Wu, J. L. Yang, B. Zhang, and H. J. Fan. Immobilizing Polyiodides with Expanded Zn<sup>2+</sup> Channels for High-Rate Practical Zinc-Iodine Battery. *Advanced Energy Materials* **14**, 2302738 (2024). DOI: 10.1002/aenm.202302738.

The contributions of the co-authors are as follows:

- Prof Fan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Zhang and Mr. Yang.
- I co-designed the study with Dr Zhang and Mr. Yang, and performed all the laboratory work at the School of Physical and Mathematical Sciences. I also analyzed the data.
- TEM, SEM and XRD, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Zhang assisted in the DFT calculation.

Chapter 4 is published as J. Wu, B. Zhang, H. J. Fan, Asymmetric Kosmotropism-Stabilized Double-Layer Hydrogel for Low-Cost Neutral Zinc-Air Battery. *Small* 2024, 20, 2406484. <https://doi.org/10.1002/sml.202406484>.

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- SEM and XRD, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.

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## **Acknowledgements**

I would like to express my sincere gratitude to my supervisor Prof. Fan Hong Jin for his guidance and patience throughout my Ph.D. program. His guidance in research strategy, data analysis, and English writing skills is an invaluable treasure. And many thanks for his full support in access to lab facilities. I would like to give my deepest gratitude to the Institute of Flexible Electronics Technology of Tsinghua, Zhejiang (IFET-THU), for providing the research scholarship award to support my Ph.D. program. I also would like to express my great gratitude to my co-supervisor Prof. Lian Duan at Tsinghua University for his abundant support and suggestions in my research works.

Many thanks to my collaborators and my group mates, including Prof. Bao Zhang, Dr. Tao Zhang, Dr. Jun Pan, Dr. Yumei Liu, Dr. Hongfei Cheng, Dr. Xinyuan Zhang, Dr Hao Chen, Dr. Hong Li, Jin-Lin Yang, Tao Xiao, Daqian Cai and other group members for the discussions and assistance during my PhD study.

Last but not least, I would like to give my deepest gratitude to my family for their love and support throughout this journey.

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## Abstract

Flexible electronics have been limited by inadequate energy storage solutions. Despite extensive research, the energy efficiency and lifespan of current flexible storage devices fall short of commercial standards. Additionally, the high cost of these solutions hampers the scalability of flexible electronics.

Flexible batteries offer a promising energy storage solution, leveraging the success of commercial batteries. While flexible lithium-ion batteries have been investigated, their intrinsic safety hazards limit their broader adoption, particularly in wearable and medical electronics. Flexible zinc-ion batteries have recently garnered attention for their safety, high capacity, and low cost. However, challenges such as shuttling effects, zinc dendrites, and low energy efficiency remain. Although advancements have been made in electrodes, electrolytes, and separators for flexible zinc-ion batteries, further research is needed before they can achieve commercial viability.

This thesis investigates the materials and structural design of flexible aqueous zinc-ion batteries, focusing on methodologies to enhance reaction kinetics and lifespan for potential industrial applications. We first introduce a hydrogel cellulose paper-based separator that integrates seamlessly with electrode materials, facilitating the rapid and straightforward fabrication of large-area flexible zinc-ion batteries, thus supporting scalable production. The hydrogel-reinforced cellulose paper also provides excellent mechanical durability, addressing the issue of repeated bending and enhancing the overall robustness of paper batteries.

In the next chapter, we introduce a layer-expanding strategy to enhance electrodes for aqueous zinc-ion batteries by increasing active sites and facilitating smooth hydrated zinc ion transport. The insertion of n-butylamine expands the interlayer spacing of  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\alpha$ -ZrP), creating expanded-interlayer ZrP (EI-ZrP). EI-ZrP is also proved to facilitate electron transport. By combining hydrogel cellulose paper (HCP) as the separator, a paper battery with EI-ZrP in the cathode material is fabricated and proved to be efficiently relieved from shuttling effects.

Furthermore, zinc-air batteries, which use atmospheric oxygen at the cathode, reduce material costs and show immense potential for flexible energy storage applications due to their high capacity and low production cost. This thesis introduces an innovative double-layer electrolyte design that leverages the distinct kosmotropism of different anions to induce phase separation, eliminating the need for a separator. This design enhances zinc utilization and

battery lifespan by mitigating side reactions and provides a framework for further advancements in zinc-air batteries and their cost-effective, scalable production.

All proposed solutions for cellulose-based zinc-ion batteries have been demonstrated through integration with practical electronic devices, validating their capability for prolonged use. These experiments offer valuable insights into industrial applications of flexible cellulose-based batteries in wearables, medical devices, and other flexible electronics.

## List of Abbreviations

|                                     |                                   |
|-------------------------------------|-----------------------------------|
| LIB:                                | Lithium-ion Battery               |
| ZIB:                                | Zinc-ion Battery                  |
| FZIB:                               | Flexible Zinc-ion Battery         |
| FAZIB:                              | Flexible Aqueous Zinc-ion Battery |
| ZAB:                                | Zinc-air Battery                  |
| FZAB:                               | Flexible Zinc-Air Battery         |
| FAZAB:                              | Flexible Aqueous Zinc-Air Battery |
| SSB:                                | Solid-State Battery               |
| SSE:                                | Solid-State Electrolyte           |
| SPE:                                | Solid Polymer Electrolyte         |
| HCP:                                | Hydrogel Cellulose Paper          |
| MnO <sub>2</sub> :                  | Manganese dioxide                 |
| ZnCl <sub>2</sub> :                 | Zinc chloride                     |
| ZnSO <sub>4</sub> :                 | Zinc sulfate                      |
| Zn(NO <sub>3</sub> ) <sub>2</sub> : | Zinc nitrate                      |
| Zn(OTf) <sub>2</sub> :              | Zinc trifluoromethylsulfonate     |
| PAAM:                               | Polyacrylamide                    |
| HER:                                | Hydrogen Evolution Reaction       |
| BLE:                                | Bluetooth Low Energy              |
| GPS:                                | Global Positioning System         |
| MCU:                                | Micro-Controller Unit             |
| PET:                                | Polyethylene terephthalate        |
| PC:                                 | Polycarbonate                     |
| PEN:                                | Polyethylene naphthalate          |
| PEO:                                | Polyethylene oxide                |
| PU:                                 | Polyurethane                      |
| PDMS:                               | Polydimethylsiloxane              |
| GPE:                                | Gel Polymer Electrolyte           |
| CNT:                                | Carbon Nanotube                   |

|                       |                                        |
|-----------------------|----------------------------------------|
| HCOONH <sub>4</sub> : | Ammonium formate                       |
| EIS:                  | Electrochemical Impedance Spectroscopy |
| GCD:                  | Galvanostatic Charge-discharge         |
| XPS:                  | X-ray Photoelectron Spectroscopy       |
| UV-vis:               | Ultraviolet-visible Spectroscopy       |
| HER:                  | Hydrogen Evolution Reaction            |
| CVD                   | Chemical Vapor Deposition              |
| PVD                   | Physical Vapor Deposition              |
| OPV                   | Organic Photovoltaic                   |
| SHE                   | Standard Hydrogen Electrode            |

# Chapter 1 Introduction

## 1.1 Flexible electronics

### 1.1.1 Basic concepts

Flexible electronics represent a transformative advancement in the design, fabrication, and application of contemporary electronic devices.<sup>1</sup> Their ability to bend, stretch, and conform to diverse shapes enables innovative applications and enhances the functionality of current electronic technologies.<sup>2</sup>

Flexible electronics are constructed on mechanically compliant substrates that offer significant flexibility. Commonly used polymeric substrates include polyimide (PI), polyethylene terephthalate (PET), polycarbonate (PC), polyethylene naphthalate (PEN), polyurethane (PU), polydimethylsiloxane (PDMS), as well as cellulose paper and cotton textiles.<sup>3</sup> These substrates, however, generally lack intrinsic electrical conductivity. To address this, conductive materials are integrated into flexible electronic designs. Organic conductors, carbon-based materials such as graphene and carbon nanotubes, and flexible metals like silver nanowires and gold nanoparticles are extensively utilized to impart conductivity and facilitate the formation of electronic circuits.<sup>4,5</sup> Moreover, organic semiconductors, metal oxides, and various nanomaterials are employed to ensure flexibility without compromising electronic performance.

Flexible electronics are extensively employed across various industrial applications (Figure 1.1). Among these, wearable devices such as smartwatches have achieved successful commercialization over the past decades. However, other applications, including flexible displays and healthcare devices, necessitate further advancements in both flexible electronics and their fabrication methodologies. Innovations such as flexible OLEDs and micro-LEDs possess significant potential to revolutionize the display industry.<sup>6,7</sup> Additionally, flexible-electronics-based healthcare devices are poised to become integral components of next-generation personal healthcare services.<sup>8</sup>

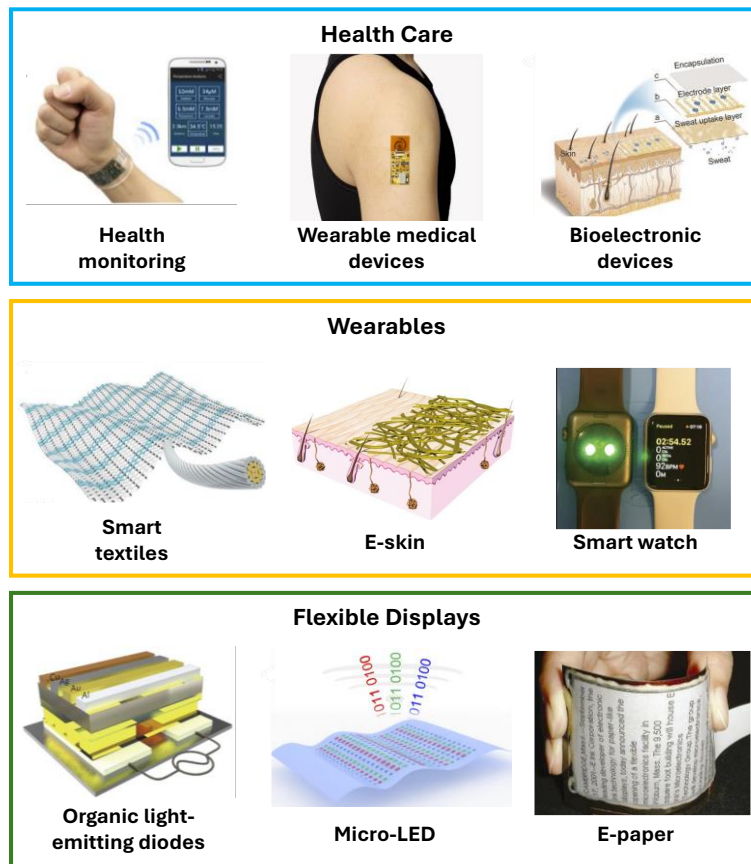


**Figure 1.1** Diverse applications of flexible electronics. The figure is adapted from references.<sup>6-14</sup>

Fabrication methods of flexible electronics include printing, lithography, and deposition techniques (Figure 1.2). Printing technologies, including inkjet printing, screen printing, and roll-to-roll processing, are prevalent due to their suitability for precise, large-area, and cost-effective production of flexible electronics. Soft lithography and photolithography are utilized for patterning circuits on flexible substrates with high resolution. Deposition techniques, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), are employed to deposit thin films of various materials onto flexible substrates, ensuring uniformity and adherence at the microscale level.

While notable advancements have been made in fabrication methods of flexible electronics, several challenges remain unaddressed. Despite the precision, scalability, and cost-effectiveness of printing technologies, there is limited understanding of how material properties and ink formulations impact long-term performance and durability under mechanical stress. Similarly, lithography techniques are not suitable for scalable manufacturing processes for large-area flexible substrates. Deposition techniques including CVD and PVD achieve

excellent uniformity and adherence, but the compatibility with diverse flexible materials needs further exploration. These gaps highlight the need for innovative design and fabrication strategies that combine scalability, cost-efficiency, and material compatibility to advance flexible electronic technologies.

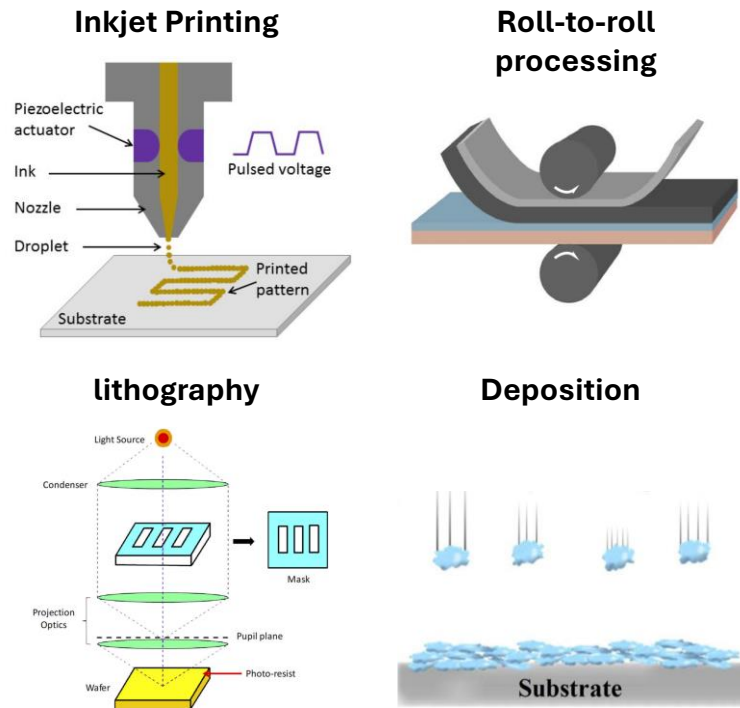


**Figure 1.2** State-of-the-art fabrication methods of flexible electronics. The figure is adapted from references.<sup>15-18</sup>

Flexible electronics are supposed to have high mechanical stretchability and durability to bear continuous bend without breaking or losing functionality. Concurrently, high electrical conductivity and stability are crucial for efficient electronic performance and to mitigate safety risks, particularly in applications such as flexible wearables and medical devices.

Flexible electronics represent a paradigm shift in the design and application of electronic devices. By harnessing advancements in materials science, innovative fabrication techniques, and enhanced mechanical properties, flexible electronics are expanding the horizons of technology, enabling applications that were previously unimaginable. Continued advancements in this field promise to revolutionize sectors ranging from healthcare and consumer electronics to energy and environmental monitoring.

### 1.1.2 Energy storage solutions for flexible electronics

Flexible electronics are extensively utilized across a spectrum of applications, including wearable consumer electronics, medical devices, and industrial equipment. These applications demand long-term operation, high stability, enhanced safety, and low device weight, prompting significant research into efficient and reliable power sources for flexible electronics. Numerous studies have investigated a variety of power sources to meet these stringent requirements.

Flexible batteries rank among the most direct energy storage methods for powering flexible electronics. These batteries are expected to be integrated into devices without compromising their flexibility. Traditional lithium-ion batteries (LIBs) have been adapted to flexible formats through the use of flexible electrodes and advanced encapsulation techniques.<sup>19</sup> As an example of electrode modification, research by Bao et al. reported 3D-printed flexible LFP/LTO electrodes with desirable LIB performance and mechanical durability under large and repeated stretches.<sup>20</sup>

Solid-state batteries (SSBs) represent an alternative to traditional liquid-based batteries by utilizing a solid electrolyte rather than a liquid one. This shift enhances both safety and flexibility, making SSBs particularly suitable for applications in flexible electronics. A study by Liu et al. developed a flexible solid-state battery with flexible composite solid electrolyte membrane composed of argyrodite sulfide  $\text{Li}_6\text{PS}_5\text{Cl}$  and a polar poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) framework, showcasing high lithium-ion conductivity, mechanical ductility, and electrochemical performance.<sup>21</sup>

In addition to flexible batteries, flexible energy harvesting devices provide a sustainable power source by converting ambient energy into electrical power for flexible electronics. Piezoelectric nanogenerators (PENGs) are designed to harvest mechanical energy from movements and vibrations, effectively converting these mechanical stimuli into electrical energy. Cao et al. developed a flexible PENG using ZnO with good piezoelectric properties, grown on the exfoliated  $\text{MoS}_2$  nanosheets through in situ polymerization.<sup>22</sup> Triboelectric Nanogenerators (TENGs) convert mechanical energy into electricity through contact electrification and electrostatic induction and have also been investigated as flexible energy providers.<sup>23</sup>

Research by Yang et al. introduced a flexible TENG based on cellulose nanofibrils (CNFs)/transition metal carbides and nitrides (MXene) composite films, which are capable of

harvesting human movement energy.<sup>24</sup> Thermoelectric Generators (TEGs) generate power from temperature gradients. A study by Yang et al. created a flexible thermoelectric device that achieves an output power density of  $1.5 \text{ mW cm}^{-2}$  using  $\text{Ag}_2\text{Se}$ -based thin films with 3.2 at.% Te doping on Se sites and a protective organic-polymer-based composite layer, demonstrating suitability for wearable electronics that can harness human body heat.<sup>25</sup>

Supercapacitors, known for their high power density and rapid charge/discharge capabilities, are well-suited for flexible devices that require bursts of energy. Graphene-based supercapacitors represent a particularly promising approach due to graphene's exceptional electrical conductivity and mechanical flexibility, which make it highly suitable for integration into flexible electronics. Research by Wang et al. demonstrated a spatial-interleaving supercapacitor (SI-SC) with a prominent liner capacitance increase along with the device thickness and a high energy density achieved on the  $100 \text{ }\mu\text{m}$  thick device.<sup>26</sup> Carbon Nanotube (CNT) supercapacitors offer high surface area and conductivity, also ideal for flexible electronics. An innovative study by Yang et al. developed a flexible supercapacitor using 1D CNT to construct a highly conductive net structure, thus ensuring fast electron delivery and enhanced flexibility.<sup>27</sup>

Apart from the above-mentioned energy storage techniques, flexible solar cells which can convert light into electrical energy, are also considered a renewable power source for flexible electronics. Organic Photovoltaics (OPVs), made from flexible organic materials, hold high potentiality to be applied in flexible electronics. Zheng et al. created an OPV design featuring a top-illuminated structure with ultrathin Ag as the transparent electrode, exhibiting no degradation after 100000 bending cycles.<sup>28</sup> Perovskite solar cells, known for their high efficiency and flexibility, have been a focus of recent research. Zheng et al. developed a flexible perovskite solar cell with pre-buried ammonium formate ( $\text{HCOONH}_4$ ) for cross-layer modification, achieving a power conversion efficiency exceeding 22%.<sup>29</sup>

The advancement of wearable technologies heavily relies on the development of effective energy storage solutions for flexible electronics. Flexible batteries, energy harvesting systems, supercapacitors, and solar cells each offer distinct benefits and face specific challenges. Despite significant progress, the scalable production and commercialization of flexible energy storage devices are still impeded by performance limitations, safety concerns, and high manufacturing costs. Major issues such as inadequate mechanical stability, low energy density, manufacturing complexities, suboptimal electrochemical performance, and inherent safety risks persist.

Addressing these drawbacks requires continued research and interdisciplinary collaboration to unlock the full potential of flexible electronics across diverse applications, including wearable technology and implantable medical devices.

## **1.2 Flexible batteries**

### **1.2.1 Mechanisms of flexible batteries**

The reaction mechanisms of various flexible batteries are diverse, reflecting the wide range of applications and requirements they fulfill. Previously reported metal-ion batteries, including lithium-ion, sodium-ion, and zinc-ion batteries, exhibit significant potential for adaptation into flexible formats. This adaptability renders them suitable for applications in wearable electronics, flexible displays, and portable medical devices, where both flexibility and lightweight design are critical.

In terms of structural designs, solid-state and quasi-solid-state batteries are prominent research areas for flexible battery technologies. Solid-state batteries enhance safety by eliminating liquid electrolytes, which are susceptible to leakage and combustion. They also offer higher energy densities and extended life cycles. However, the development of solid-state batteries is challenged by high manufacturing costs and the requirement for advanced materials that can efficiently conduct ions at room temperature.

Quasi-solid-state batteries, on the other hand, aim to combine the best features of both liquid and solid electrolytes. They typically employ a gel or polymer electrolyte, which enhances flexibility and safety compared to liquid electrolytes, while still maintaining favorable ionic conductivity. This combination seeks to optimize the balance between flexibility, safety, and performance in flexible battery applications.<sup>30</sup> Despite these benefits, quasi-solid-state batteries must overcome issues related to mechanical stability and electrolyte compatibility with electrodes.

Each design offers unique advantages and presents distinct challenges. Solid-state batteries promise high energy densities and improved safety but are hindered by high production costs and material limitations. Quasi-solid-state batteries offer a balance between flexibility, safety, and performance but require further optimization to enhance their mechanical robustness and electrochemical efficiency. Continued research and development in these areas are essential to unlocking the full potential of flexible batteries for future technologies.

### 1.2.1.1 Flexible lithium-ion batteries

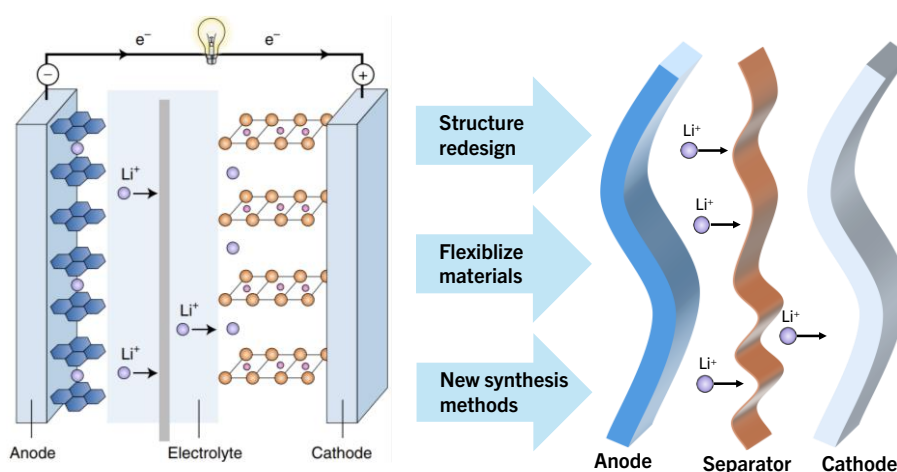


**Figure 1.3** Reaction mechanism of LIBs and schematic illustration of a flexible LIB. The figure is adapted from references.<sup>31</sup>

Flexible lithium-ion batteries are LIBs with moderate modifications to be adapted into flexible formats (Figure 1.3). These flexible LIBs retain the high energy density characteristic of traditional LIBs, with energy densities reaching or surpassing 300 Wh/kg. Desirable cycle life is also expected for flexible LIBs, considering applications of graphene and silicon nanowires to improve cycle life and maintain capacity over thousands of cycles.<sup>32</sup> These batteries usually incorporate flexible substrates and conductive materials which allow the battery to bend and conform to various shapes.

However, the intrinsic safety risks associated with LIBs also come along with flexible LIBs, making them unsuitable for applications in wearable devices and medical devices. Previous research has been reported on enhancements on electrolytes to relieve flexible LIBs from safety hazards. Mu et al. reported a phosphorus-fixed nonflammable gel polymer electrolyte (GPE) with a low content of flame retardant (7.5 wt.%) through in situ polymerization of tri(acryloyloxyethyl) phosphate and triethylene glycol dimethacrylate in electrolyte, with excellent fire safety demonstrated.<sup>33</sup>

Moreover, the integration of electrode materials with flexible substrates can complicate the manufacturing process, potentially necessitating significant modifications to existing industrial production techniques. High-performance materials such as graphene and silicon nanowires, while enhancing battery performance, are often costly, which can lead to increased overall expenses for flexible LIBs.

While LIBs dominate the market due to their high energy density and mature technology, their intrinsic safety risks and material limitations underscore the need to explore alternative battery chemistries. Other promising chemistries, such as lithium-sulfur, zinc-ion, sodium-ion, and aluminum-ion batteries, offer advantages in terms of safety, cost, and material abundance. However, these alternatives remain underexplored in the context of flexible applications.

### 1.2.1.2 Flexible lithium-sulfur batteries

The high theoretical capacity of Lithium-sulfur batteries (LSBs) makes them promising energy storage solutions for small wearable devices. LSBs offer a theoretical capacity of about 1675 mAh/g, which is significantly higher than that of LIBs.<sup>34</sup> Besides, sulfur is well known as an abundant and low-cost material, making LSBs more economically viable than LIBs.

However, LSBs tend to suffer from poor cycle stability due to the dissolution of polysulfides in the electrolyte. Polysulfides will further lead to the formation of lithium dendrites, which can pose severe safety risks such as short circuits and potential battery fires, which is unacceptable for wearable devices.

### 1.2.1.4 Flexible zinc-ion batteries

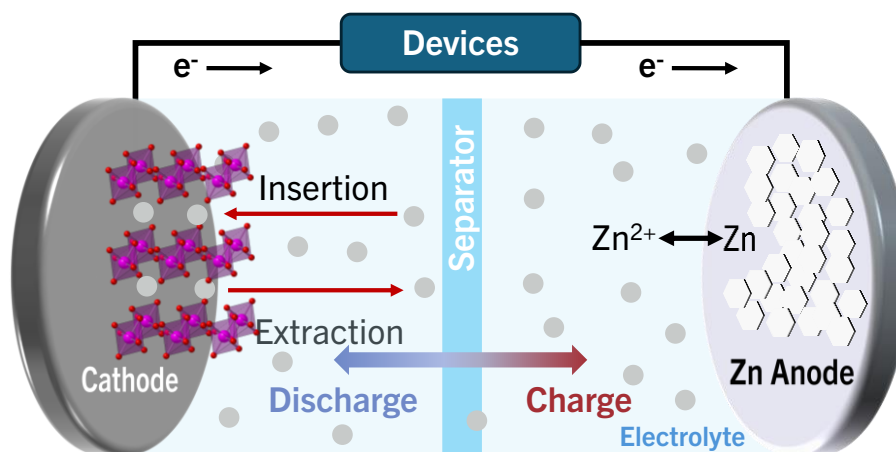


**Figure 1.4** Schematic illustration of the mechanism of zinc-ion batteries.

Zinc-ion batteries (ZIBs) are emerging as a viable alternative to LIBs due to their enhanced safety, cost-effectiveness, and environmental friendliness. By employing zinc as the primary active material, ZIBs offer several advantages, making them suitable for diverse applications, ranging from portable electronics to large-scale energy storage systems.

The easy availability of zinc reduces the material cost of batteries significantly compared to lithium. Aqueous electrolytes used in ZIBs are non-flammable, enhancing safety and reducing the risk of fires and explosions. Zinc is also less prone to dendrite formation compared to lithium, reducing the risk of short circuits and improving battery lifespan.<sup>35</sup> Moreover, zinc and its compounds are environmentally benign and easier to recycle.

ZIBs utilizing intercalative cathodes operate through the intercalation and deintercalation of zinc ions ( $\text{Zn}^{2+}$ ) between the anode and cathode during charge and discharge cycles (Figure 1.4).<sup>36</sup> Anode of ZIBs typically uses metallic zinc or zinc-based compounds. The cathode is usually composed of manganese oxides, vanadium oxides, or organic materials.

In summary, zinc-ion batteries (ZIBs) present a promising alternative to conventional lithium-ion batteries. This thesis delves into comprehensive research and development efforts aimed at improving their performance and commercial viability. A more detailed analysis of ZIBs is provided in sub-chapter 1.3.

## **1.2.2 Structural designs of flexible batteries**

### **1.2.2.1 Flexible solid-state batteries**

Solid-state electrolytes are capable of eliminating the risk of leakage and are less flammable compared to liquid electrolytes, enhancing battery safety. The potential adoption of flexible solid-state batteries (SSBs) is primarily driven by safety concerns associated with flexible electronics.<sup>37</sup> Flexible SSBs can also achieve high energy densities due to the use of thin-film technology and efficient ion transport. Additionally, they offer superior flexibility compared to their liquid counterparts. Solid-state electrolytes (SSEs) can be fabricated to be thin and flexible, enabling the entire battery to bend without the risk of electrolyte leakage.

Solid-state electrolytes (SSEs) can be categorized into three main types based on their composition: inorganic ceramic SSEs, polymer SSEs, and ceramic-polymer hybrid SSEs.<sup>38</sup> Among these, ceramic-based electrolytes, first discovered in the 1960s, marked a milestone in electrolyte technology. The fundamental mechanism of ionic conduction in ceramic-based SSEs lies in their unique material structure. These materials typically feature pathways for ion transport, such as crystal lattice defects, tunnels, or interconnected glass network structures. Ions directionally migrate through these pathways, facilitating efficient ionic conductivity. Ceramic-based SSEs exhibit superior ionic conductivity at high temperatures, due to enhanced ion mobility and increased concentration of mobile ions or vacancies at higher temperatures.

Hence, they can offer an expanded operating temperature range compared to traditional liquid electrolytes, making them suitable for diverse applications.

However, ceramic-based SSEs suffer from poor interfacial interaction, which not only increases impedance, resulting in polarization, but also adversely affects lifespan, rate capability, efficiency, and other electrochemical performances. SSEs are originally believed to be relieved from dendrite problems. However, recent research has proven that solid electrolytes could still be penetrated by deposited materials.<sup>39</sup> In recent research works, designs of ceramic-based composite electrolytes from “ceramic-in-polymer” (CIP) to “polymer-in-ceramic” (PIC) are widely investigated for their effectiveness in dendrite suppression but the interfacial defects remain a challenge for SSEs to be in practical applications.<sup>40</sup>

Compared to ceramic-based solid electrolytes and traditional liquid electrolytes, solid polymer electrolytes (SPEs) offer notable advantages, including better flexibility, enhanced plasticity, and improved safety, making SPEs particularly attractive for the development of flexible batteries. Additionally, the interfacial impedance between SPE and electrodes is reduced through their wetting property, facilitating efficient ion transport and improving overall battery performance.<sup>38</sup>

However, SPEs face several challenges. One critical issue is their mechanical strength. Dendrites can form and grow rapidly during cycling if the mechanical properties of SPE are insufficient.<sup>41</sup> The second major limitation of SPEs is their narrow electrochemical stability window. Most commonly investigated polymeric hosts for electrolytes, such as polyethylene oxide (PEO), are unable to withstand high voltages. This mismatch poses a significant challenge for their use in high-voltage applications and hinders their industrial scalability.<sup>42</sup>

Hybrid solid-state electrolytes (SSEs), which combine inorganic ceramic materials and polymer matrices, represent a cutting-edge approach to overcoming the limitations of single-component electrolytes.<sup>43</sup> These materials blend the mechanical strength, thermal stability, and high ionic conductivity of ceramics with the flexibility, processability, and improved electrode compatibility of polymers (Figure 1.5).

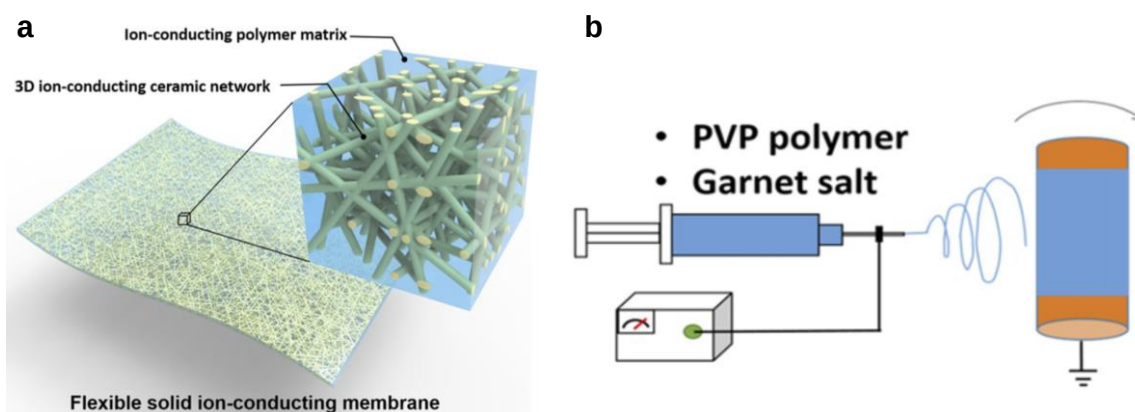


**Figure 1.5** (a) Schematic illustration of the hybrid solid-state composite electrolyte. (b) Setup of hybrid SSE nanofibers using garnet salt and PVP polymer.<sup>44</sup>

A key advantage of hybrid SSEs is their ability to mitigate interfacial challenges in ceramic-based systems. The polymer component enhances the interfacial interaction between the electrolyte and electrodes, significantly reducing interfacial resistance and improving ionic transport. Polymers can adapt to the electrode surface, providing better wetting properties and ensuring a seamless integration essential for efficient ion exchange. The inorganic ceramic phase, on the other hand, serves to improve the overall mechanical robustness of the hybrid electrolyte, reducing the risk of dendrite penetration. Additionally, ceramics expand the electrochemical stability window of the hybrid SSE, enabling their use in high-voltage applications. For example, metal-organic frameworks (MOFs), a class of inorganic-organic hybrid crystalline materials (also called coordination polymers), have been explored for their tunable ion pathways and ability to host functional groups that enhance ionic conductivity under various conditions.<sup>45</sup> However, the application of hybrid SSEs is impeded by the difficulty in finding matching ceramic/polymer material pairs. Another challenge is to fabricate ultrathin electrolyte membranes for small electronics devices when multiple materials are integrated, which also means higher electric resistance. Compared with single-material electrolytes, the cost of materials and fabrication for hybrid SSE is also higher.<sup>38</sup>

Generally, SSEs often have lower ionic conductivity compared to liquid electrolytes, which limits the battery's performance.<sup>46</sup> The fabrication process for flexible SSBs is also more complex and requires precise control over material properties and interfaces, bringing higher manufacturing difficulty and cost.

### 1.2.2.2 Flexible quasi-solid-state batteries

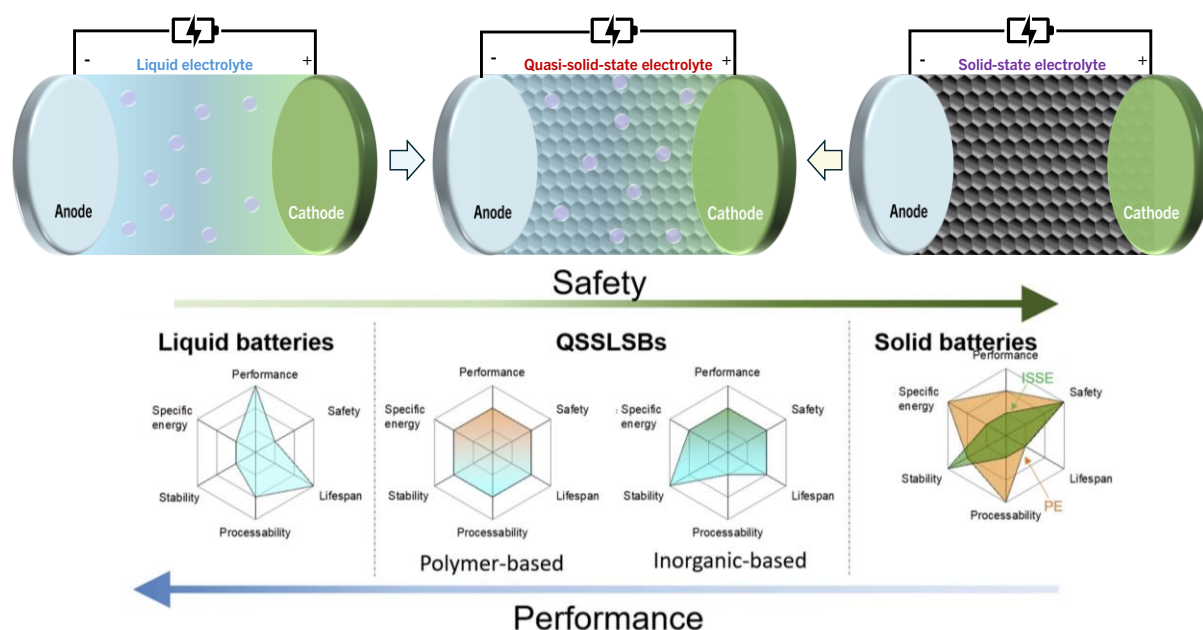


**Figure 1.6** Schematic illustration of quasi-solid-state electrolytes as a combination of both liquid and solid-state electrolytes, and comparisons of their advantages and drawbacks.<sup>47</sup>

Quasi-solid-state batteries combine features of both solid-state and liquid electrolyte batteries.<sup>48</sup> The electrolyte in quasi-solid-state batteries is typically a gel or a highly viscous liquid (Figure 1.6). This semi-solid state allows for better ion conductivity than a purely solid electrolyte while maintaining structural stability of the whole electrolyte to meet potential requirements on mechanical ductility.<sup>48</sup>

Quasi-solid-state batteries offer enhanced safety compared to traditional liquid electrolyte alternatives by mitigating the risks of electrolyte leakage and flammability associated with liquid electrolytes. They also exhibit higher energy densities due to the increased concentration of functional ions. Common materials for quasi-solid-state electrolytes include polymer matrices infused with liquid electrolytes or ionic liquids, which create a network that facilitates efficient ion transport.<sup>49</sup> The flexibility of polymers also makes them intrinsically suitable as flexible substrates and electrolytes for flexible batteries.

Cellulose-based hydrogel is considered an important contribution to low-cost and stable quasi-solid-state electrolytes.<sup>50</sup> Cellulose is well-known as a natural polymer that can be easily found in the cell walls of plants. The naturally formed 3D network structure inside cellulose can retain a tremendous amount of water. The high water content of cellulose-based hydrogel

significantly relieves flexible batteries from degradation caused by water evaporation.<sup>51</sup> The porous structure of hydrogel enhances efficient ion transport. The flexibility, mechanical durability, biocompatibility, and improved safety of cellulose hydrogel make it highly advantageous for applications in flexible wearable electronics. These attributes are crucial for advancing the broader commercialization of such batteries.

Paper, primarily composed of cellulose, is considered a low-cost raw material of cellulose-based quasi-solid-state electrolytes. Utilizing paper as the substrate for flexible quasi-solid-state batteries stems from researchers' efforts to develop low-cost, safe, and scalable flexible batteries. This approach aims to meet the demands for cost-effective and widely producible battery solutions. Paper-based batteries are more environmentally friendly, as paper is biodegradable and recyclable. The use of paper and simple fabrication techniques can reduce the overall cost of flexible batteries, making them attractive for massive applications in low-cost flexible devices. Moreover, paper is inherently flexible, allowing the battery to bend and fold easily.

Due to the low conductivity of paper, paper-based flexible batteries generally have lower energy densities compared to more advanced flexible batteries, limiting their application in energy-intensive devices. The mechanical stability of paper could also be broken after continuous bending, risking the safety of the entire flexible battery.

Ongoing research and development in materials science and fabrication techniques are critical to addressing these challenges and fully realizing the potential of flexible batteries across various applications. This thesis focuses on investigating flexible batteries, specifically advancing the electrode, electrolyte, substrate, and fabrication methods for flexible zinc-based batteries. By exploring innovative solutions for materials, structures, and production processes, this thesis aims to offer a comprehensive understanding of flexible zinc-ion battery technology and provide guidance on cost-effective methods for large-scale industrial production and commercialization.

### **1.2.3 Challenges of practical flexible batteries**

Despite the previous endeavors, the current achievable performance and lifespan of flexible batteries are still inferior to their rigid counterparts. The obstacles faced by flexible batteries can be summarized in the following contents.

Firstly, flexible batteries necessitate that all energy storage components including anode, cathode, separator, and electrolyte materials exhibit flexibility. These materials must not only be flexible but also capable of maintaining energy storage performance under significant deformation. Although extensive research has been conducted to identify suitable materials, a cost-effective and scalable solution has yet to be developed.

What's more, flexible devices are prone to structural changes, demanding high stability from the energy storage component. Safety concerns are particularly critical for applications such as medical and wearable devices. It is difficult to achieve high safety with flexible LIBs due to their thermal vulnerability. Achieving high safety in flexible lithium-ion batteries (LIBs) is challenging due to their susceptibility to thermal instability. Alternative technologies such as SIBs and ZIBs offer potentially more secure electrochemical reactions. However, these technologies require further investigation to match the energy density and efficiency of LIBs while ensuring comparable safety levels.

In the third aspect, flexible devices are typically designed to be lightweight and compact due to spatial constraints. Existing liquid-electrolyte-based batteries are often heavy and bulky, rendering them unsuitable for flexible applications. While solid-state batteries (SSBs) can be designed to be lightweight and compact, achieving flexibility with solid-state electrolytes remains challenging due to material limitations. Quasi-solid-state batteries present a promising alternative, with paper-based quasi-solid-state batteries showing significant potential. However, further investigation is needed to optimize these solutions for flexible applications.

## **1.3 Flexible zinc-ion batteries**

### **1.3.1 Opportunities and challenges of flexible zinc-ion batteries**

The limitations on flexible batteries have long been a significant barrier to the further development of this industry. Previous research has shown that zinc, one of the most abundant resources on Earth, is a promising anode material for flexible batteries.<sup>52</sup> Zinc is superior to Lithium in terms of annual global production (Zn 502000 tons vs Li 39000 tons), distribution (wide distribution of Zn vs uneven distribution of Li), and resource price (the low price of Zn vs high price of Li).<sup>53</sup> The low-cost nature of Zinc-based batteries further supports their potential to be widely applied in consumer products. Moreover, compared to LIBs, aqueous zinc-ion batteries (AZIBs) also hold the advantages of high theoretical volumetric capacity (5854 Ah L<sup>-1</sup>), excellent rechargeability, and inherently safe chemistry (Figure 1.7).<sup>54-58</sup> The

metallic zinc has a relatively high specific capacity of  $820 \text{ mAh g}^{-1}$ , which is much higher than those of intercalation-type electrode materials.<sup>59</sup>

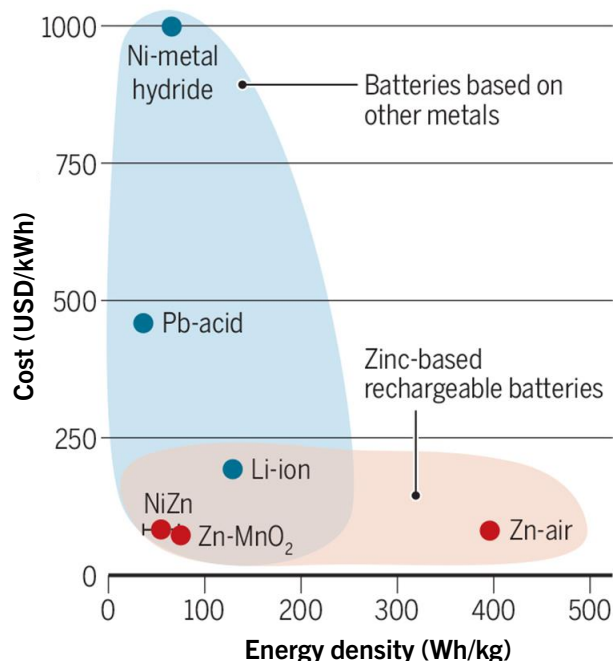


**Figure 1.7** Comparison of energy density (Wh/kg) and production cost (US dollar per kWh) of various battery technologies.<sup>60</sup>

Despite the above-mentioned superiorities, the energy density, power density, and lifespan of current Zn-based batteries are still inferior to their lithium-ion counterparts. Metallic zinc has a higher redox potential ( $-0.76 \text{ V vs. SHE}$ ) than that of lithium ( $-3.0 \text{ V vs. SHE}$ ), which will reduce the working potential according to the electrochemical mechanism. The thermodynamics of aqueous electrolytes also impose limitations on the performance potential of zinc-ion batteries (ZIBs) utilizing these electrolytes.

The requirements for flexibility and safety in aqueous Zn-based batteries impose strict limitations on the materials used for the anode, cathode, separator, and electrolyte. Under these constraints, current solutions for flexible Zn-based batteries remain ineffective.<sup>61</sup>

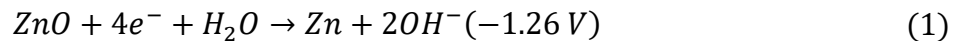
### 1.3.1.1 Zinc dendrites

Firstly, the stability of electrodes in zinc-based batteries remains a significant challenge. A primary issue is the formation of zinc dendrites during cycling. Dendritic growth on the electrode surface disrupts the uniformity of zinc deposition during charging and discharging cycles, leading to a progressive increase in internal resistance. This adversely affects the efficiency of ZIB. Safety concerns are triggered due to penetration of dendrites through the

separator which can result in internal short circuits, initiating thermal runaway due to Joule heating or direct contact between electrodes. Zinc dendrites also result in continuous consumption of active zinc and ZIB electrolyte, which reduces the Coulombic efficiency and weakens capacity retention. Over repeated cycles, dendrites will lead to severe degradation of battery performance, as outlined in previous research works.<sup>62,63</sup>

### 1.3.1.2 Zinc anode corrosion

Corrosion of the zinc anode in ZIBs arises primarily due to the high reactivity of zinc in aqueous electrolytes and the interplay of electrochemical and chemical reactions at the zinc-electrolyte interface.<sup>64</sup> The corrosion of zinc anodes in electrolytes can be categorized into chemical and electrochemical processes.<sup>52</sup> In alkaline electrolytes, chemical corrosion predominantly leads to passivation on the surface of the zinc anode. At a pH of 14, the standard redox potential for the Zn/ZnO equilibrium (-1.26 V vs. SHE) is more negative than the hydrogen evolution reaction (HER) potential (-0.83 V vs. SHE):



Therefore, chemical corrosion, specifically the reaction of Zn with water to produce ZnO and H<sub>2</sub>, exhibits a positive electromotive force, making it thermodynamically favorable. This process roughens the surface of the zinc anode, exacerbating parasitic reactions and creating uneven deposition sites. Furthermore, the ZnO by-product formed during this corrosion significantly increases the internal resistance of ZIBs, severely reduces the surface activity of anode through passivation, and ultimately contributes to capacity fading over repeated cycles.

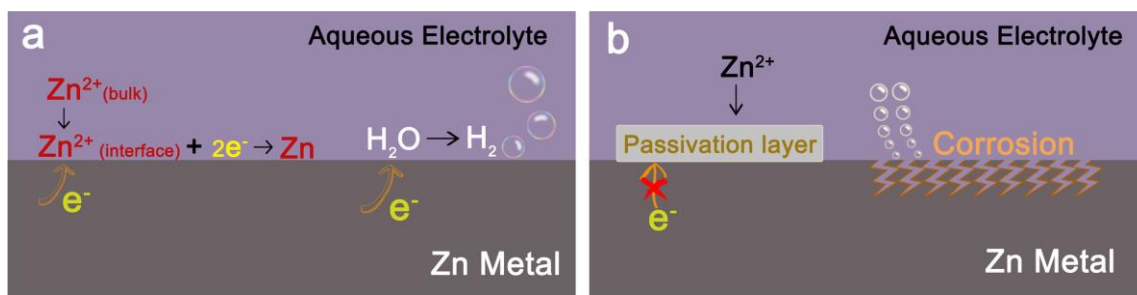


**Figure 1.8** Schematic diagrams illustrating interfacial reactions on the zinc anode in traditional aqueous electrolytes: (a) The zinc plating process accompanied by electrochemical hydrogen evolution due to water reduction at the anode surface, and (b) Surface passivation and corrosion arising from the thermodynamic instability of zinc in aqueous environments, resulting in the formation of by-products.<sup>65</sup>

In neutral or acidic electrolytes, electrochemical corrosion becomes the predominant mechanism driving surface passivation. Zinc reacts with water, especially at low potentials,

leading to the generation of hydrogen (Figure 1.8). This parasitic reaction results in the consumption of active zinc material reduced Coulombic efficiency, and gas accumulation, which can compromise the structural integrity of ZIB. Furthermore, metallic zinc is oxidized to  $\text{Zn}^{2+}$  during discharge processes, which subsequently interacts with anions in the electrolyte (e.g.,  $\text{OH}^-$  in KOH-based electrolytes or  $\text{SO}_4^{2-}$  in  $\text{ZnSO}_4$ -based electrolytes). This interaction leads to the formation of insoluble by-products, such as  $\text{ZnSO}_4 \cdot \text{Zn}(\text{OH})_{23} \cdot x\text{H}_2\text{O}$  in  $\text{ZnSO}_4$  electrolytes.<sup>52</sup>

The electrochemical corrosion of active zinc has severe consequences, including reduction in charge/discharge efficiency and capacity retention of ZIBs.<sup>66</sup> The insoluble by-products generated during this process adhere to the anode surface, covering active nucleation sites and forming rough protrusions. These irregularities create a nonuniform surface, which promotes uneven zinc deposition and the growth of zinc dendrites. Additionally, due to their poor electrical conductivity, these by-products significantly increase the internal impedance of the battery. This impedance impedes the transport of electrons and ions at the anode interface, leading to the passivation of the anode surface. As a result, the battery experiences further reductions in coulombic efficiency and long-term performance degradation.

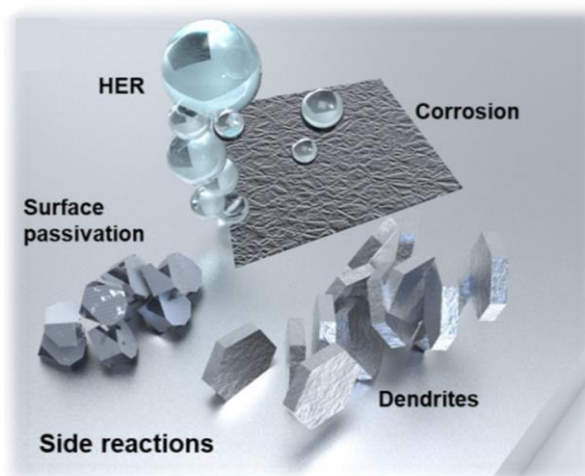


**Figure 1.9** Schematic illustration of side reactions of rechargeable ZIBs in mild acid/neural electrolytes. The figure is adapted from the reference.<sup>67</sup>

The request to limit zinc dendrite formation and other side reactions also brings challenges to electrolyte compatibility (Figure 1.9). Suitable electrolytes are required to not only be compatible with flexible substrates but also not induce dendrite formation. Traditional liquid

electrolytes easily leak, posing safety risks and reducing flexibility. Solid-state or gel electrolytes are potential solutions but come with their own set of challenges.

Electrode and electrolyte materials must not only maintain their electrochemical performance but also exhibit sufficient flexibility to withstand repeated bending and stretching. Continuous mechanical stress can lead to degradation of battery components, adversely affecting the battery's lifespan and performance.

Fourthly, a simple but efficient fabrication technique of flexible Zn-based batteries remains to be uncovered. Scalable manufacturing processes that can produce flexible batteries consistently and cost-effectively are a significant challenge. Flexible batteries should also be capable of seamlessly integration into flexible electronics and other devices without compromising performance.

Lastly, the cost of materials is a significant concern. Developing advanced materials that satisfy both the mechanical and electrochemical requirements of flexible zinc-based batteries can be prohibitively expensive, potentially hindering their viability for large-scale adoption.

### **1.3.2 Electrolytes of flexible zinc-ion batteries**

#### **1.3.2.1 Aqueous electrolytes**

Aqueous electrolyte uses water as the solvent to dissolve ionic compounds. In the context of flexible zinc-ion batteries, aqueous electrolytes play a significant role due to their high ionic conductivity, safety, and cost-effectiveness.  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$ , and  $\text{Zn(NO}_3)_2$  are among the most commonly used electrolytes. Aqueous electrolytes generally exhibit high ionic conductivity, facilitating efficient ion transport. These electrolytes are also non-flammable, reducing the risk of fire and explosions. Besides, water-based solutions are inexpensive and easy to prepare. Aqueous systems are environmentally benign, contributing to the sustainability of zinc-ion batteries.

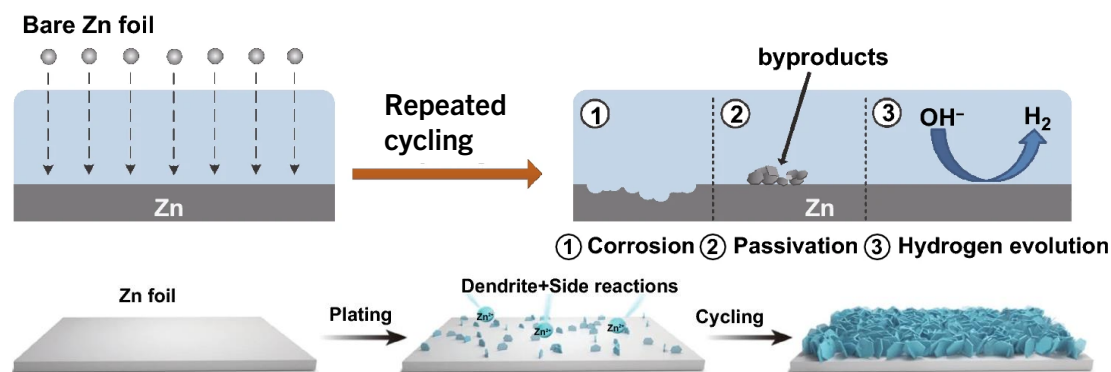


**Figure 1.10** Schematic diagram of the corrosion, passivation, and HER on bare Zn foil, with a detailed illustration of the influence of dendrite and side reactions on zinc foil.<sup>68</sup>

Despite the advantages, flexible aqueous zinc-ion batteries (FAZIBs) are limited by zinc dendrites and side reactions including anode corrosion, anode passivation, and Hydrogen Evolution Reaction (HER) (Figure 1.10). The growth of Zn dendrites increases the surface area of the Zn anode, thus bolstering surface-dependent reactions including corrosion and HER which result in continuous consumption of active anode material and fundamentally reduce the battery capacity.<sup>68</sup> At voltages below 1.23 V, water electrolysis can occur, leading to hydrogen gas evolution and efficiency loss.<sup>69</sup> The decomposition of water further limits the operation voltage range of aqueous ZIBs to about 1.8 V, which is lower than that of LIBs. Concurrently, the increase in  $\text{OH}^-$  concentration leads to formation of insoluble  $\text{Zn}(\text{OH})_2$ , causing surface passivation. This further reduces the conductivity of Zn anode and reduces the active nucleation sites of Zn, resulting in poor plating/stripping efficiency.

### 1.3.2.2 Gel/quasi-solid-state electrolytes for ZIBs

Gel electrolytes maintain high ionic conductivity, similar to liquid electrolytes, while also offering enhanced mechanical stability. They can be easily molded to accommodate the volumetric changes of electrodes during cycling, thereby providing superior mechanical flexibility and improved suitability for flexible electronics. The quasi-solid-state properties of gel electrolytes significantly mitigate the risk of electrolyte leakage, thereby enhancing the overall safety profile compared to their liquid counterparts. Polyvinyl alcohol (PVA)-based gel matrices, when doped with zinc salts, are frequently employed to synthesize gel electrolytes. These systems exhibit favorable ionic conductivity and mechanical stability. Alternatively, polyacrylamide (PAM) hydrogels are extensively utilized due to their superior mechanical robustness and high ionic mobility. The crosslinked network structure of PAM facilitates

efficient ion transport while maintaining dimensional stability under various operational conditions.

Gel electrolytes, while offering advantages in safety and form factor, present certain limitations, primarily reduced ionic conductivity relative to liquid electrolytes and susceptibility to polymer matrix degradation over time.<sup>70</sup> The diminished ionic conductivity is attributed to the increased viscosity and reduced free volume for ion migration within the polymer network. To address these challenges, cellulose-based electrolyte gels have emerged as a promising alternative for ZIBs. These materials leverage a three-dimensional network structure that facilitates the formation of high-mobility pathways for efficient ion and charge transport. The hierarchical porosity and interconnected channels within the cellulose matrix significantly enhance the effective diffusion coefficient of charge carriers, thereby mitigating the ionic conductivity limitations typically associated with conventional gel electrolytes.

### **1.3.2.3 Solid-State electrolytes for ZIBs**

Solid-state electrolytes, while exhibiting lower ionic conductivity relative to their liquid and gel counterparts, offer superior mechanical properties that enhance the overall electrochemical cell integrity and eliminate the risk of leakage.<sup>71</sup> The reduced ionic mobility in solid-state systems is primarily attributed to the lack of a fluid medium for ion transport and the presence of grain boundaries that impede ion migration. However, these electrolytes possess significantly higher Young's moduli and yield strengths, which contribute to maintaining structural stability under various operational conditions and effectively eliminate the risk of electrolyte leakage.

However, the implementation of solid-state electrolytes presents significant challenges, primarily related to electrode-electrolyte interfacial dynamics. The inherent rigidity of solid-state electrolytes impedes the formation of conformal interfaces with electrodes, resulting in elevated interfacial resistance. This phenomenon is exacerbated by the lack of wetting properties characteristic of liquid electrolytes, leading to reduced effective contact area and consequently diminished charge transfer kinetics. The increased interfacial impedance manifests as a substantial overpotential during cell operation, thereby compromising the overall energy efficiency of the electrochemical system.<sup>72</sup>

Furthermore, the fabrication processes for solid-state electrolytes often involve complex synthesis routes, including high-temperature sintering, hot pressing, or sol-gel methods. These processes are frequently characterized by stringent requirements for environmental control and

precise stoichiometry, contributing to elevated production costs. The intricate nature of these manufacturing techniques poses significant challenges for scalability, particularly in the context of flexible electronics applications where large-area, thin-film electrolytes are requisite. The incompatibility between the rigid nature of many solid-state electrolytes and the mechanical flexibility demanded by wearable or bendable devices further complicates their integration into flexible electronic systems.

#### **1.3.2.4 Key considerations for ZIB electrolyte development**

Firstly, high ionic conductivity is crucial for efficient operation of ZIBs. High ionic mobility minimizes internal ohmic resistance, thereby maximizing power density and overall electrochemical performance.

Secondly, the electrolyte should exhibit superior electrochemical stability within the operational voltage window of the ZIB. A robust electrochemical stability window mitigates electrolyte decomposition and parasitic redox reactions, which can lead to capacity fade and coulombic efficiency degradation.

Furthermore, the electrolyte should be chemically compatible with both the zinc anode and the cathode materials to prevent irreversible side reactions and enhance battery lifespan.

Electrolyte safety is also an important influencing factor considering the applications in wearable devices. Non-flammability, low toxicity, and resistance to leakage are critical for ensuring the safety of ZIBs.

Lastly, cost and scalability are crucial. The materials and manufacturing processes for the electrolyte should be cost-effective and scalable for mass production to make zinc-ion batteries commercially viable.

### **1.3.3 Electrodes of flexible zinc-ion batteries**

The judicious design and selection of electrode materials are critical determinants in the optimization of high-performance flexible energy storage systems. Two primary categories of electrodes for ZIBs have been the focus of extensive research and development efforts: intercalation-type and conversion-type electrodes. These classifications are based on the underlying mechanisms of charge storage and the nature of the electrochemical reactions occurring at the electrode-electrolyte interface.

### 1.3.3.1 Intercalation-type electrodes

Intercalation-type electrodes are the cornerstone of current LIBs technology, offering reliable performance and long cycle life. Intercalation-type electrodes, such as graphite, lithium cobalt oxide ( $\text{LiCoO}_2$ ), and lithium iron phosphate ( $\text{LiFePO}_4$ ), store energy through the intercalation and deintercalation of ions into and out of the host material's crystal lattice without significantly altering the structure of the electrodes (Figure 1.11). Intercalation-type electrodes lead to high cyclability since the stable host structure allows for many charge-discharge cycles without significant degradation. High Coulombic efficiency could also be achieved due to minimal side reactions.<sup>73</sup>

However, when using intercalation-type electrodes, the capacity is restricted by the number of intercalation sites available in the host material, resulting in relatively low capacity of ZIBs.<sup>74</sup> The diffusion of ions within the solid lattice can be slower compared to surface reactions, affecting high-rate performance.

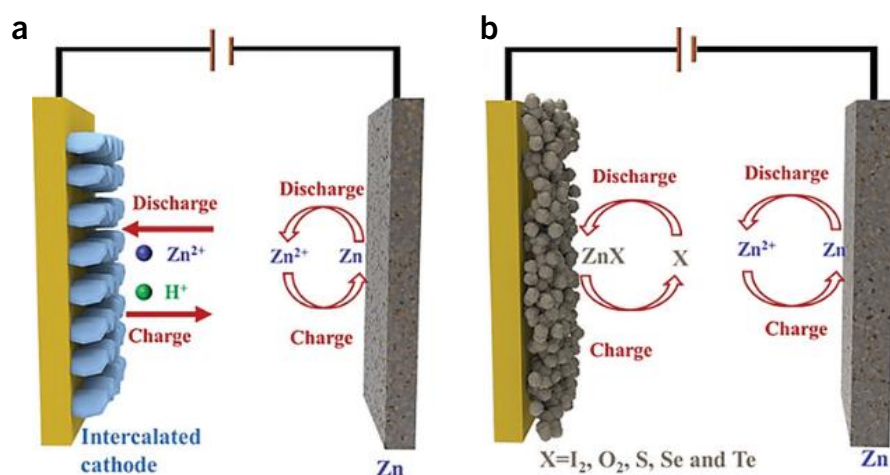


**Figure 1.11** Compare of mechanism of (a) intercalation-type electrodes and (b) conversion-type electrodes. The figure is adapted from references.<sup>75,76</sup>

### 1.3.3.2 Conversion-type electrodes

Conversion-type electrodes store energy through reversible redox reactions that involve the complete transformation of the electrode material into different phases upon ion insertion and extraction.<sup>74</sup> This process often leads to a substantial change in the structure and composition of the electrode (Figure 1.11).

The conversion mechanism allows for multiple electron transfers per formula unit, leading to significantly higher capacities compared to intercalation materials. A diverse array of compounds, including transition metal oxides, sulfides, and phosphides, can undergo conversion reactions, offering versatility in electrode design. This chemical diversity allows

for fine-tuning of redox potentials and reaction kinetics through compositional modifications. Despite the advantages, conversion-type electrodes suffer from the substantial change in electrode structure and composition. Large volumetric and structural changes during cycling can lead to mechanical degradation and loss of electrode integrity, even causing electrolyte leakage and battery safety hazards. The repeated formation and breaking of bonds can also result in capacity fade over cycles. Moreover, many conversion-type materials are inherently poor conductors, requiring conductive additives to improve performance.

Comparing conversion-type electrodes with their intercalation-type counterparts, conversion-type ones generally offer higher theoretical capacities and energy densities. While intercalation-type electrodes tend to have longer lifespans due to their stable host structures. Intercalation-type electrodes usually exhibit better rate capabilities due to the rapid intercalation/deintercalation reaction kinetics.

The optimal practical implementations of intercalation-type and conversion-type electrodes vary based on their respective performance characteristics. Intercalation-type electrodes exhibit potential for widespread commercial deployment in ZIBs across consumer electronics, electric vehicles, and grid-scale energy storage sectors, owing to their demonstrated reliability and mature technological foundation. Conversely, conversion-type electrodes are primarily emerging in applications where high gravimetric and volumetric energy density is paramount, such as in the realm of wearable electronics. While conversion-type electrodes show considerable promise for next-generation high-capacity energy storage systems, significant advancements in materials science and electrochemistry are requisite to surmount their inherent challenges, including capacity fading, poor cyclability, and voltage hysteresis.

### **1.3.5 Flexible zinc-air batteries**

Zinc-air batteries (ZAB) offer several advantages over traditional zinc-ion batteries, in terms of high energy density, low production cost, and environmental friendliness.<sup>77</sup> These attributes position zinc-air batteries (ZABs) as promising candidates for energy sources in flexible electronics. Consequently, the final section of this thesis is dedicated to investigating and experimenting with the potential of flexible ZABs. ZABs exhibit significantly higher energy densities compared to conventional zinc-based batteries. This is attributed to the fact that oxygen, which participates in the electrochemical reaction, is drawn from ambient air rather than being stored within the battery. The use of air cathodes reduces the weight and volume of the battery, allowing more space for the zinc anode, which in turn increases the overall energy

storage capacity. ZAB can achieve energy densities up to 300-400 Wh/kg,<sup>78</sup> whereas zinc-carbon batteries typically offer around 50-70 Wh/kg, and alkaline zinc-manganese dioxide batteries offer about 100-150 Wh/kg. ZABs can achieve nearly complete oxidation of zinc, providing higher capacities compared to the partial utilization seen in some other zinc-based batteries. The stable operating voltage of ZABs makes them ideal for applications where a steady power supply is necessary, such as in medical devices and portable electronics.

ZABs are relatively cost-effective due to the abundance and low cost of zinc and the utilization of atmospheric oxygen, which eliminates the need for expensive cathode materials. This makes them an economical choice for large-scale applications. ZABs are more environmentally friendly compared to many other battery types. Unlike lead-acid or nickel-cadmium batteries, ZABs do not contain heavy metals or highly toxic materials, reducing their environmental impact and making their disposal less hazardous. Zinc-air batteries have a long shelf life when not in use because the electrochemical reaction with oxygen does not occur until the battery is exposed to air. This makes them an active-in-demand energy source, suitable for emergency and backup applications where long-term storage without power degradation is essential.

These advantages make ZABs particularly appealing for various applications, including hearing aids, electric vehicles, and large-scale energy storage.

#### 1.3.5.1 Mechanism of zinc-air batteries

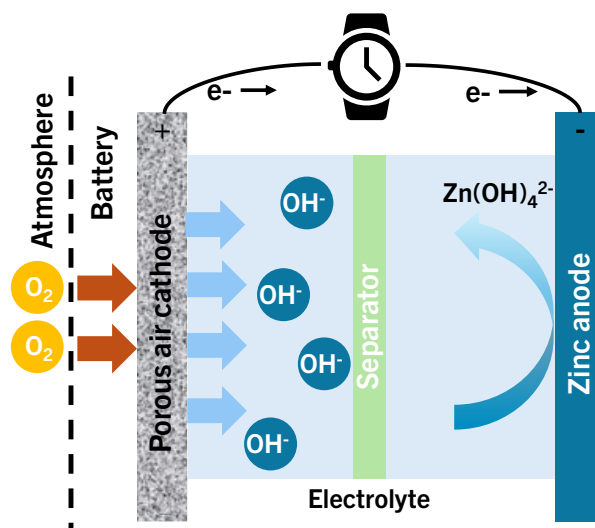
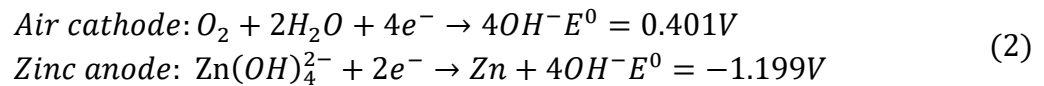


**Figure 1.12** Schematic illustration of the mechanism of Zinc-air batteries.

ZABs leverage the abundant and inexpensive zinc metal as the anode, while oxygen from the ambient air serves as the cathode reactant, making them fundamentally distinct from other battery technologies that rely on internally stored reactants (Figure 1.12).

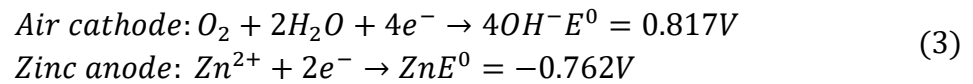
The basic principle of ZABs involves the electrochemical reaction between zinc and oxygen. When the battery is in use, oxygen is drawn from the air through a porous carbon-based cathode. This oxygen reacts with water and electrons from the external circuit to form hydroxide ions.<sup>79</sup> Hydroxide ions then migrate to the zinc anode, where they react with zinc to produce zincate and release electrons back to the circuit, generating electric power. Alkaline electrolytes including KOH and NH<sub>4</sub>Cl are commonly used in ZABs. The corresponding reaction equations could be summarized as follows:<sup>80</sup>



However, the prevalent use of liquid alkaline electrolytes contributes to Zn deterioration and Zn dendrites inside ZABs. Irreversible by-products may also be generated due to side reactions between alkaline electrolytes and atmospheric carbon dioxide, resulting in severe degradation of battery performance.<sup>77</sup>

### 1.3.5.2 Flexible neutral zinc-air batteries

Neutral electrolytes render opportunities to potentially relieve the detrimental effects associated with alkaline electrolytes since anode passivation and reaction with atmospheric CO<sub>2</sub> could be relieved in a neutral PH environment. The reaction equation for neutral ZAB could be summarized as follows:<sup>80</sup>



Neutral ZABs offer a compelling alternative to traditional zinc-based batteries due to their high energy density, cost-effectiveness, environmental friendliness, long shelf life, high theoretical capacity, and stable discharge voltage. These attributes make them particularly suitable for widespread use in small flexible electronic devices. The integration of an air cathode significantly reduces production costs. In our quest for low-cost, high-energy density, and safe flexible batteries, rechargeable neutral ZABs emerge as one of the most promising energy storage solutions.

## 1.3.4 Motivation and research scope

### 1.3.4.1 Motivation for adopting Zinc-ion mechanisms for flexible batteries

Based on the discussions in sub-chapters 1.1, 1.2, and 1.3, although lithium-ion battery chemistry and synthesis methods are well-developed, LIBs cannot simultaneously fulfill all the

requirements of an ideal energy storage device for flexible electronics. These requirements include high energy density, low production cost, high safety, and mechanical durability. ZIBs have been selected as the research focus of this thesis due to their promising characteristics in several critical areas, such as wearable devices and medical instruments, attributable to their high intrinsic safety and cost-effectiveness.

#### **1.3.4.2 Goal and objectives**

The main goal of this research is to advance the design and engineering of flexible ZIBs to bring them closer to practical applications and industrial-scale manufacturing. Flexible ZIBs hold immense potential as sustainable and safe energy storage solutions, particularly for next-generation wearable and portable electronic devices. However, several critical challenges must be addressed to make them commercially viable. These challenges include the shuttle effect caused by the dissolution and migration of active materials, zinc dendrite formation leading to short circuits and capacity decay, low energy density compared to lithium-ion batteries, the lack of affordable and robust flexible substrates, and the absence of scalable, cost-effective production methods suitable for industrial adoption.

Currently, previous works in this area focus on enhancing individual components of the battery, without addressing the interdependence of these components or the need for scalable integration strategies. In contrast, this thesis adopts a holistic approach to improving flexible ZIBs by systematically investigating and optimizing the key components: electrolytes, separators, and electrodes. Specifically, the objectives of this work are to explore advanced electrolyte formulations to mitigate the shuttle effect and inhibit dendrite growth, develop separators with enhanced ionic selectivity and mechanical flexibility, and design high-performance electrode materials with tailored microstructures to improve energy density.

Moreover, this thesis emphasizes the development of innovative structural designs that balance mechanical flexibility with electrochemical stability, addressing both requirements of durability and performance under mechanical deformation. Simple, rapid, and scalable fabrication methods are proposed to enable the efficient integration of these components, paving the way for industrially viable production processes. By tackling these interrelated challenges, this research aims to provide comprehensive solutions that enhance performance, reliability, and manufacturability of flexible ZIBs, thus contributing to their practical application and commercialization.

### 1.3.4.3 Scope of this research

The electrolyte and flexible substrates are first investigated. Electrolyte plays an important role in flexible batteries since traditional solution-type electrolytes won't be able to fit in flexible applications due to risk of liquid leakage. Paper-based flexible battery technology represents a burgeoning area in energy storage technology, merging the sustainability and flexibility of paper with the functionality of modern batteries. Paper is intrinsically suitable for flexible batteries due to their lightweight, foldable, and environmentally friendly characteristics. Zhang et al. developed a paper-based composite separator composed of electrolyte-affinitive cellulose fibers (CFs) and thermally stable aramid nanofibers (ANFs), achieving excellent mechanical stability and cycling stability.<sup>81</sup> Poulin et al. demonstrated a disposable paper battery using zinc as a biodegradable metal anode and graphite as a nontoxic cathode material and paper as a biodegradable substrate, highlighting the potential for single-use electronics with reduced environmental impact.<sup>82</sup> Xiong et al. created a paper-based supercapacitor introducing PVA and  $\text{ZnCl}_2$  into carbonized paper-based materials (APC-PVA@ $\text{ZnCl}_2$ ), achieving excellent temperature adaptability, plasticity, tensile strength, strong adhesion, and self-healing properties.<sup>83</sup> Despite the efforts, there is still a lack of investigation into low-cost paper batteries that have high safety and suitability for scalable production.

To solve the above-mentioned drawbacks, hydrogel reinforced cellulose paper (HCP) is designed as a highly compatible electrolyte and separator for flexible Zinc-based batteries in our research work. HCP-based Zn- $\text{MnO}_2$  batteries are prepared and investigated to provide an example of constructing low-cost flexible electrolytes and separators for ZIBs. This work focuses on using cellulose paper as the separator in aqueous zinc batteries to provide flexibility for the entire battery structure. We demonstrate the fabrication of large-area paper-based Zn- $\text{MnO}_2$  batteries that deliver high and stable voltage output.

Secondly, the electrodes are enhanced to overcome major bottlenecks including low energy density, poor rate performance, and formation of Zn dendrites. Intercalation-type electrodes lead to high cyclability and high Coulombic efficiency. However, they face limitations in capacity and rate capability due to structural constraints. In contrast, conversion-type electrodes, which store energy through reversible redox reactions, offer higher theoretical capacities and energy densities, making them more suitable for flexible batteries that require high energy and power densities. Nevertheless, conversion-type electrodes present challenges, including significant volume changes during cycling, relatively low cycling stability, and reduced

conductivity. Aimed at bringing in conversion-type electrodes for flexible batteries, in the third chapter, we explore enhancements in the structure of conversion-type materials to reduce electrode volume changes and increase cycling stability. An enhanced material EI-ZrP, based on ZrP, is investigated and proved to be a superior alternative for electrodes. EI-ZrP is further proved to be applied in Zn-I<sub>2</sub> flexible aqueous batteries to improve energy density and cycling stability. This uniquely designed conversion-type cathode material demonstrates its advantage in resulting in faster reaction kinetics and higher energy efficiency. The Zn-I<sub>2</sub> flexible aqueous battery utilizing EI-ZrP cathode demonstrates a high specific capacity of 205 mAh g<sup>-1</sup> at 1 C over 2500 cycles.

In the last part of this thesis, we initiated our investigation into applying ZABs as power sources for flexible electronics, for a further pursuit of low-cost and high-energy-density flexible zinc batteries. ZABs exhibit superior energy density and cost-effectiveness compared to other zinc-ion batteries (ZIBs), primarily due to the utilization of air cathodes. The major bottlenecks of flexible ZAB technology including low zinc utilization rate and poor lifespan. Our uniquely designed double-layer electrolyte gel for flexible ZABs addresses issues including anode passivation, generation of irreversible by-products, and high-cost electrolytes and catalysts. With our pioneering double-layer design, flexible ZABs show high potential in various industries, including medical devices, logistics, and wearables.

## Chapter 2 Flexible cellulose-paper-based Zn-MnO<sub>2</sub> battery

### 2.1 Introduction

Flexible electronics present challenges for traditional liquid-type electrolytes. Gel electrolytes, which offer ionic conductivity comparable to that of liquid electrolytes while providing enhanced mechanical stability, have emerged as a promising alternative for flexible batteries. Furthermore, the development of flexible batteries also raises concerns regarding scalable manufacturing methods and sustainability, particularly with respect to waste disposal and recyclability at the end of the battery's lifecycle. Cellulose paper, derived from abundant natural biomass on earth, presents an ideal separator material for developing flexible and environmentally sustainable batteries. The three-dimensional network structure of cellulose facilitates high water retention and enhances ion diffusion, contributing to improved battery performance. Because of its portability, renewability, and function tuneability, cellulose paper batteries could be widely applied in flexible devices. Meanwhile, the compatibility of paper to multiple flexible fabrication techniques including printing, deposition, and roll-to-roll processing allows facile fast embed of a wide variety of source materials,<sup>84,85</sup> further supporting the development the paper electronics.

The fundamental structure of paper-based flexible batteries involves integrating active battery materials onto or into a paper substrate, which serves as the primary structural support for the battery. Active materials, such as carbon nanotubes (CNTs), graphene, metal oxides, or conducting polymers, are deposited onto the paper substrate to function as electrodes. To maintain flexibility and prevent leakage, gel, quasi-solid-state, or solid-state electrolytes are typically used given the absence of a hard seal.

### 2.2 Challenges & Opportunities

Despite the advantages of paper-based flexible batteries, their performance is still hindered by the low conductivity and low mechanical stability of paper. Researchers have focused on the optimization of the performance of paper-based flexible batteries. Incorporating highly conductive materials such as graphene, CNT, or MXene to improve electron transport in paper batteries is investigated to provide enhanced conductivity.<sup>86</sup> A porous, conductive, and flexible MXene (Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>)/cellulose nanofiber (CNF)/Porous Carbon hybrid film is prepared by Chen et al. via a facile vacuum-filtration method. The enhanced cellulose-based material offers a

significantly high conductivity.<sup>87</sup> Flexible and conductive PEDOT:PSS/CNF nanopaper (PEDOT:PSS/CNP) were prepared from the PEDOT:PSS/CNF suspension by vacuum filtration and Dimethyl sulfoxide (DMSO) post-treatment by Du et al., providing a methodology to enhance cellulose with a conductive polymer.<sup>88</sup> The mechanical stability of the paper substrate is also improved through several innovations ensuring that the paper substrate and active materials can withstand bending, folding, and stretching without significant performance degradation.<sup>81,89</sup>

Paper-based Zn batteries have been a hot research topic due to their intrinsic safety and low cost. The current challenges faced by paper-based Zn batteries include their unsustainability towards continuous physical deformation and their inferior performance regarding capacity and energy density compared to commercial batteries.

Reported paper-based zinc-ion batteries are mainly classified into two categories. The first involves assembling active electrode materials directly on the surface of cellulose paper or fabricating freestanding active material films as paper-like electrodes.<sup>90-92</sup> The second category uses cellulose paper as the substrate, with batteries printed in-plane on one side, demonstrating an interdigitated configuration.<sup>93,94</sup> This method hinders the printability of paper, making the fabrication process complex. Printing electrode inks on both sides of the paper substrate is challenging due to its rough and permeable surface, which can lead to short circuits. Consequently, printed micro-batteries on paper typically achieve limited areal capacity and volumetric energy density, with values up to  $\approx 10 \text{ mWh cm}^{-3}$ . These limitations in energy storage components impede the integration and reliability of paper electronics.

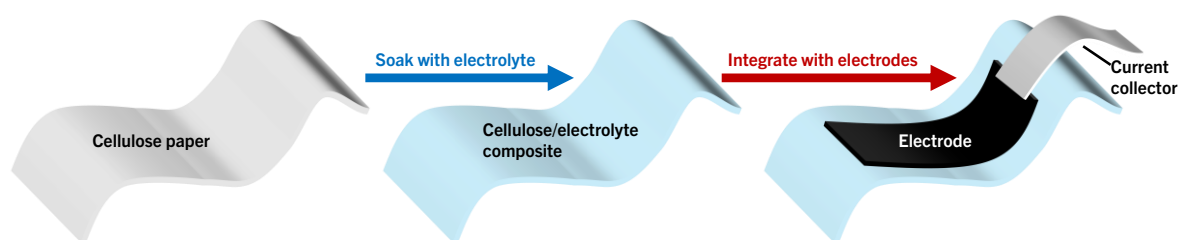
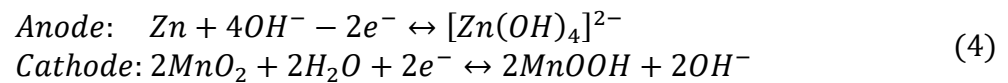


**Figure 2.1** Schematic illustration of the fabrication process of paper batteries from raw cellulose paper.

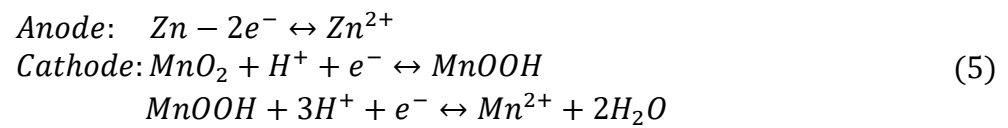
In this work, we developed a hydrogel-reinforced cellulose paper (HCP) for printable flexible zinc batteries. By integrating the unique properties of cellulose paper with hydrogel, the HCP composite achieves desirable mechanical strength and conductivity, making it suitable

as both the separator and electrolyte for quasi-solid-state ZIBs. The anode and cathode materials are printed on the front and back surfaces of the paper (Figure 2.1). This design deviates from traditional paper batteries by facilitating the easy integration of electrode materials with the HCP, thereby enabling the scalability of the battery to larger sizes.

Zn-Mn reaction mechanism is employed for the chemistry of the HCP-based paper battery, due to the high energy density, reliability, and relatively low cost of Zinc-Manganese Dioxide (Zn-MnO<sub>2</sub>) batteries. The anode of a Zn-MnO<sub>2</sub> battery is typically composed of metallic zinc. During discharge, zinc atoms oxidize into zinc ions (Zn<sup>2+</sup>) and release electrons. MnO<sub>2</sub> serves as the cathode material, considered an efficient material for capturing and storing electrons during discharge. MnO<sub>2</sub> undergoes reduction reactions and accepts electrons, forming manganese ions (Mn<sup>2+</sup>). The electrolyte in rechargeable Zn-MnO<sub>2</sub> batteries is usually an alkaline solution, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), the reactions are expressed as follows:<sup>95</sup>



In neutral or mildly acidic electrolytes:<sup>95</sup>



## 2.3 Comparative advantages

In this work, the designed paper-based flexible Zn-MnO<sub>2</sub> battery is capable of delivering a capacity of over 300 mAh with a large areal size up to 8 × 8 cm<sup>2</sup> while maintaining a small thickness of 5 mm. By connecting five cells in parallel, the combined battery could achieve a high capacity of 1.3 Ah, which is comparable to that of commercial batteries. The areal capacity of the paper battery is measured to be 4.6 mAh cm<sup>-2</sup>, which is comparable with commercial LIBs. The volumetric energy density is measured to be 112 mWh cm<sup>-3</sup>. The bending tests further support the high flexibility of paper-based Zn-MnO<sub>2</sub> batteries, indicating promising applications in various industries. Moreover, the HCP based membrane gives the paper battery high biodegradability.

## 2.4 Synthesis of materials



**Figure 2.2** Digital images of the fabrication process of HCP paper battery.

In this study, we developed hydrogel-reinforced cellulose paper (HCP) by synthesizing the hydrogel directly within the cellulose fibers (Figure 2.2). Initially, cellulose filter paper was immersed in a  $2 \text{ mol L}^{-1}$  acrylamide solution, which contained  $4 \times 10^{-4} \text{ mol L}^{-1}$  N,N'-methylenebis(acrylamide) as a crosslinking agent and  $4 \times 10^{-4} \text{ mol L}^{-1}$  potassium persulfate as an initiator. The wetted cellulose paper was then sandwiched between two pieces of polyethylene-covered glass and heated at  $60^\circ\text{C}$  under nitrogen protection for 6 hours. The resulting HCP was vacuum dried, and any excess hydrogel on the surface was removed by polishing with sandpaper.

For the construction of the Mn-Zn battery, zinc foil was used as the anode. The cathode ink was formulated by mixing commercial  $\text{MnO}_2$  powder, carbon black, and PVDF in a 1:0.2:0.2 weight ratio. This ink was then screen printed onto the dry HCP and dried under vacuum at  $40^\circ\text{C}$ . The effective mass loading of  $\text{MnO}_2$  ranged from 1 to  $26 \text{ mg cm}^{-2}$ . A hybrid electrolyte composed of 2 M  $\text{ZnSO}_4$  and 0.5 M  $\text{MnSO}_4$  was employed, and gold foil served as the current collector for the cathodes.

## 2.5 Results and discussion

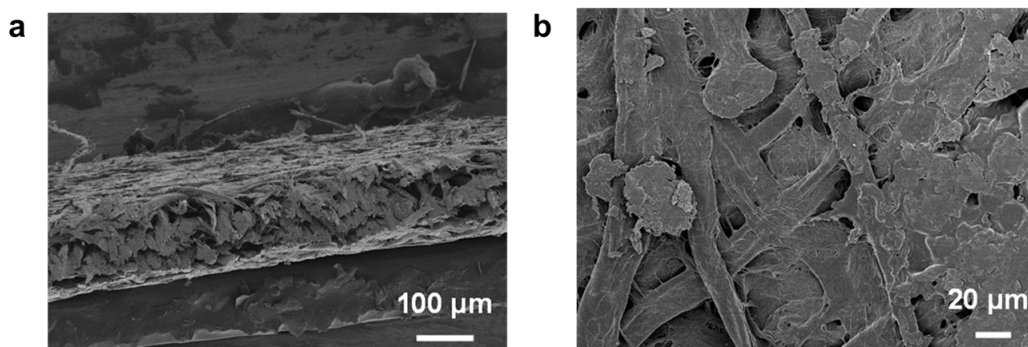


**Figure 2.3** SEM Images of HCP: (a) cross section and (b) top surface.

Recorded SEM images show abundant gaps between cellulose fibers in the paper (Figure 2.3), which are subsequently filled by hydrogel after polymerization. The abundance of gaps, standing for 3D network structure inside HCP, also contributes to the fast transport of ions in HCP.

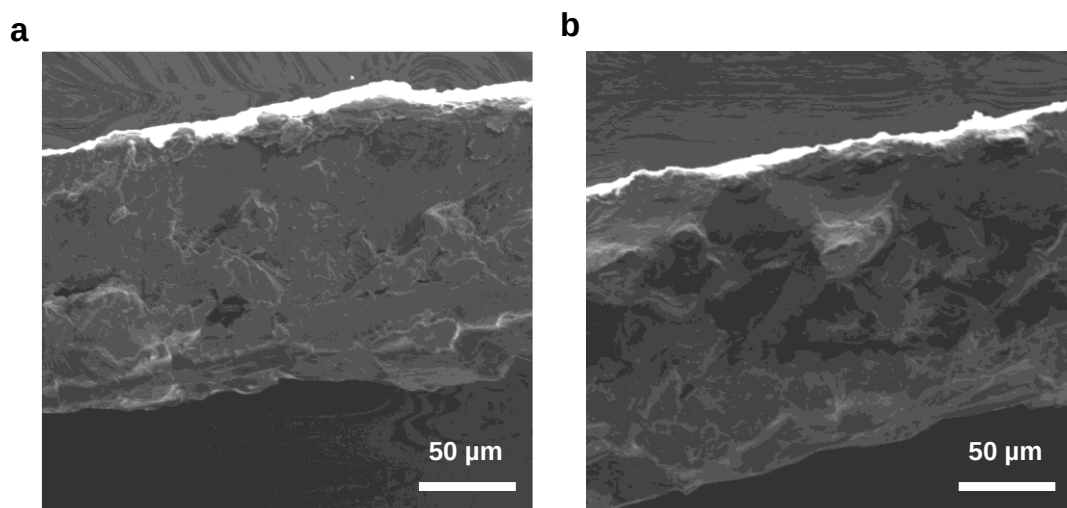


**Figure 2.4.** SEM images illustrating the cross-section of HCP (a) before and (b) after 100 cycles of repeated bending under an angle of 90°.

Cross-sectional SEM images have been included to illustrate the deformation of the HCP before and after 100 cycles of repeated bending at a 90° angle, as shown in Figure 2.4. In Figure 2.4a, the cellulose matrix and hydrogel electrolyte exhibit a smooth and uniform interface prior to bending, with no visible gaps or breaks. After 100 bending cycles at 90°, the cross-sectional image (Figure 2.4b) reveals that the cellulose matrix and hydrogel electrolyte maintain their interfacial integrity, with no significant separation or delamination observed.

While some small gaps have formed within the interface due to bending, these do not compromise the functionality of the HCP. The ionic pathways remain intact, ensuring efficient ion transport. Additionally, the hydrogel electrolyte continues to adhere tightly to the cellulose matrix, preserving the overall performance and stability of the structure.

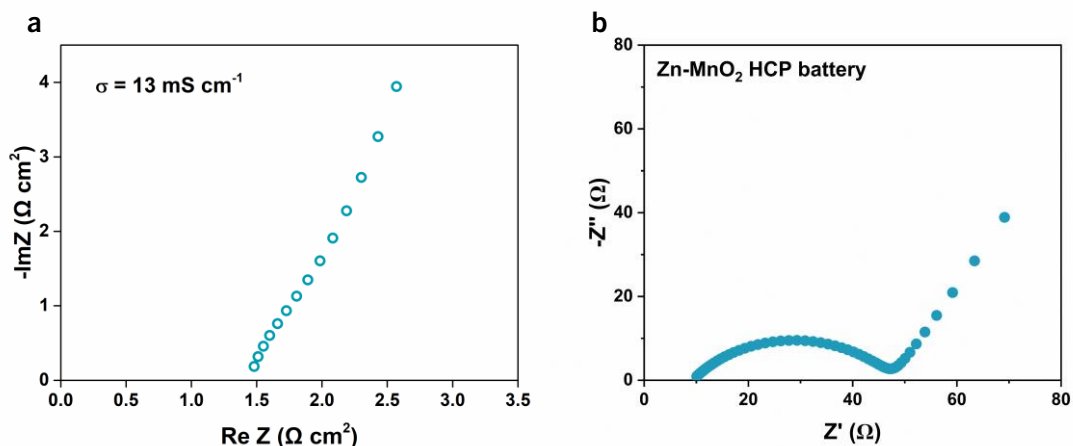


**Figure 2.5** Impedance measurement results of HCP and HCP-based Zn-MnO<sub>2</sub> battery. (a) The impedance of HCP, which was swollen in 2 mol L<sup>-1</sup> ZnSO<sub>4</sub> electrolyte. (b) The Electrochemical Impedance Spectroscopy measurement results of Zn-MnO<sub>2</sub> HCP battery.

The resistance of the HCP electrolyte layer is analyzed through impedance spectra (Figure 2.5a). Following soaking in 2 M ZnSO<sub>4</sub> solution, the HCP exhibits a conductivity of 13 mS cm<sup>-1</sup>, which is higher than that of pure PAM hydrogel with 1-2 M ZnSO<sub>4</sub> electrolyte ( $\approx 0.12$ -5.56 mS cm<sup>-1</sup>).<sup>96,97</sup> The ion transport in HCP separator-based Zn-MnO<sub>2</sub> battery also benefits from the high conductivity of HCP, which is supported by the low battery impedance revealed from EIS measurements (Figure 2.5b).

The cyclic voltammetry (CV) curves of the HCP-based Zn-MnO<sub>2</sub> battery at various scan rates (0.2, 0.4, 0.6, 0.8, and 1.0 mV/s) (Figure 2.6) show minimal changes in potential with increasing scan rates, indicating efficient redox chemistry. This efficiency is attributed to the extensive ion pathways facilitated by the 3D network structure of the cellulose in the HCP-based paper battery.

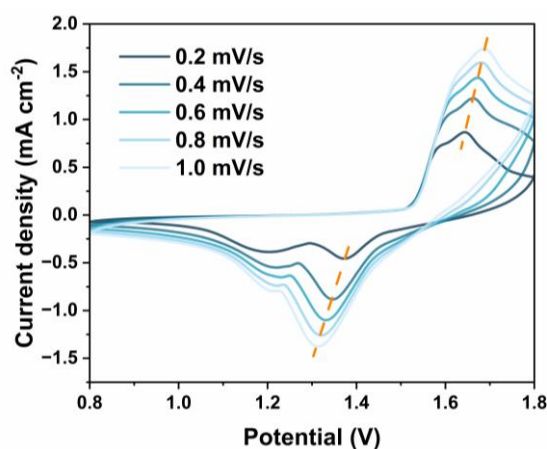


**Figure 2.6** Cyclic voltammetry curves of the Zn-MnO<sub>2</sub> HCP battery with scan rates of 0.2, 0.4, 0.6, 0.8, and 1.0 mV/s.

The paper batteries also display high Coulombic efficiency and specific capacity in long-term cycling experiments (Figure 2.7a). Cycling at  $1.0 \text{ mA cm}^{-2}$  current, the Zn-MnO<sub>2</sub> paper battery maintains a relatively stable specific capacity of approximately  $125 \text{ mAh g}^{-1}$ . A Coulombic efficiency close to 100% was retained for more than 1900 cycles, indicating desirable cycling stability. From the charge and discharge curves (Figure 2.7b), a low polarization is revealed. When the current density is fixed at  $1 \text{ mA cm}^{-2}$ , the retained specific capacity shows a negligible decline over increasing cycle numbers, with the capacity at cycle 1500 remaining comparable to that at cycle 50. This cycling stability further underscores the effectiveness of the HCP separator.

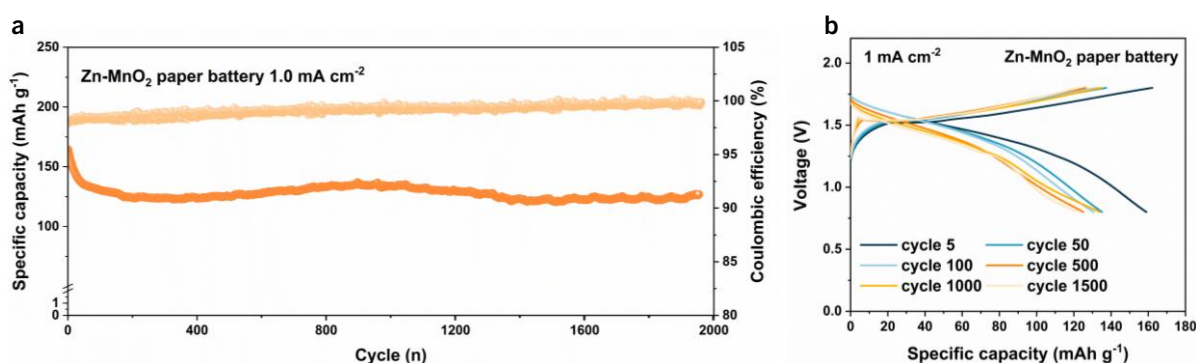


**Figure 2.7** Long-term cycling performance of Zn-MnO<sub>2</sub> HCP battery. (a) Specific capacity and coulombic efficiency of Zn-MnO<sub>2</sub> HCP battery in long-term cycling experiment under a current density of  $1.0 \text{ mA cm}^{-2}$ . (b) The charge-discharge profiles under different cycles including cycles 5, 50, 100, 500, 1000, and 1500 at a fixed current density of  $1.0 \text{ mA cm}^{-2}$ .

The Zn-MnO<sub>2</sub> HCP-based flexible paper battery is evaluated against state-of-the-art research on paper-based zinc batteries. Compared to other designs, the HCP-based battery presented in this study demonstrates an extended lifespan, exceeding 1900 cycles. Its energy density is also comparable to, or in some cases exceeds, other flexible Zn-MnO<sub>2</sub> battery designs. When compared to the paper-based zinc-air battery proposed in Nature article<sup>98</sup>, the HCP-based Zn-MnO<sub>2</sub> flexible battery offers a much longer lifespan (1900 cycles vs. 70 cycles), even though with a lower energy density. This highlights the potential of the HCP design for applications requiring high durability. Moreover, the HCP concept is adaptable and inspires its potential application in zinc-air batteries, as further discussed in Chapter 3.

**Table 2.1** Comparison of state-of-the-art zinc paper battery performances.

| Batteries | Energy density | Cycle number | Paper type | Fabrication method | Ref. |
|-----------|----------------|--------------|------------|--------------------|------|
|-----------|----------------|--------------|------------|--------------------|------|

|                                                                     |                               |      |                              |                       |              |
|---------------------------------------------------------------------|-------------------------------|------|------------------------------|-----------------------|--------------|
| Planar Zn-MnO <sub>2</sub> battery                                  | 184.24<br>mAh g <sup>-1</sup> | 500  | Bond<br>paper                | Inkjet<br>printing    | 99           |
| Zn-MnO <sub>2</sub> in-plane<br>micro-batteries                     | 81<br>mAh g <sup>-1</sup>     | 2000 | Filter<br>paper              | Transform<br>printing | 100          |
| Zn-MnO <sub>2</sub> bar coated<br>flexible battery                  | 80<br>mAh g <sup>-1</sup>     | NA   | Filter<br>paper              | Bar<br>coating        | 101          |
| Water-activated Zinc<br>paper battery                               | 0.125<br>mAh cm <sup>-2</sup> | NA   | Filter<br>paper              | Stencil<br>printing   | 82           |
| NH <sub>4</sub> V <sub>4</sub> O <sub>10</sub> -Zn paper<br>battery | 123.2<br>mAh g <sup>-1</sup>  | 200  | Weighing<br>paper            | Coating               | 102          |
| Zn-V <sub>2</sub> O <sub>5</sub> paper battery                      | 309<br>mAh g <sup>-1</sup>    | 1000 | Weighing<br>paper            | Insertion             | 103          |
| Paper-based zinc-air<br>battery                                     | 614<br>mAh g <sup>-1</sup>    | 70   | Filter<br>paper              | Coating               | 98           |
| Zn-MnO <sub>2</sub> HCP flexible<br>battery                         | 125<br>mAh g <sup>-1</sup>    | 1900 | cellulose<br>filter<br>paper | Coating               | This<br>work |

The practicality of HCP-supported Zn-MnO<sub>2</sub> battery is validated through charge and discharge tests under different bending angles (Figure 2.8a). Under different bending angles including 0°, 30°, 45°, 60°, and 90°, the battery demonstrates no significant changes in specific capacity, confirming that the HCP battery is not adversely affected by physical deformation. The high flexibility and good capacity retention against bending of HCP-based Zn-MnO<sub>2</sub> battery underscore its potential for practical applications in flexible electronics.

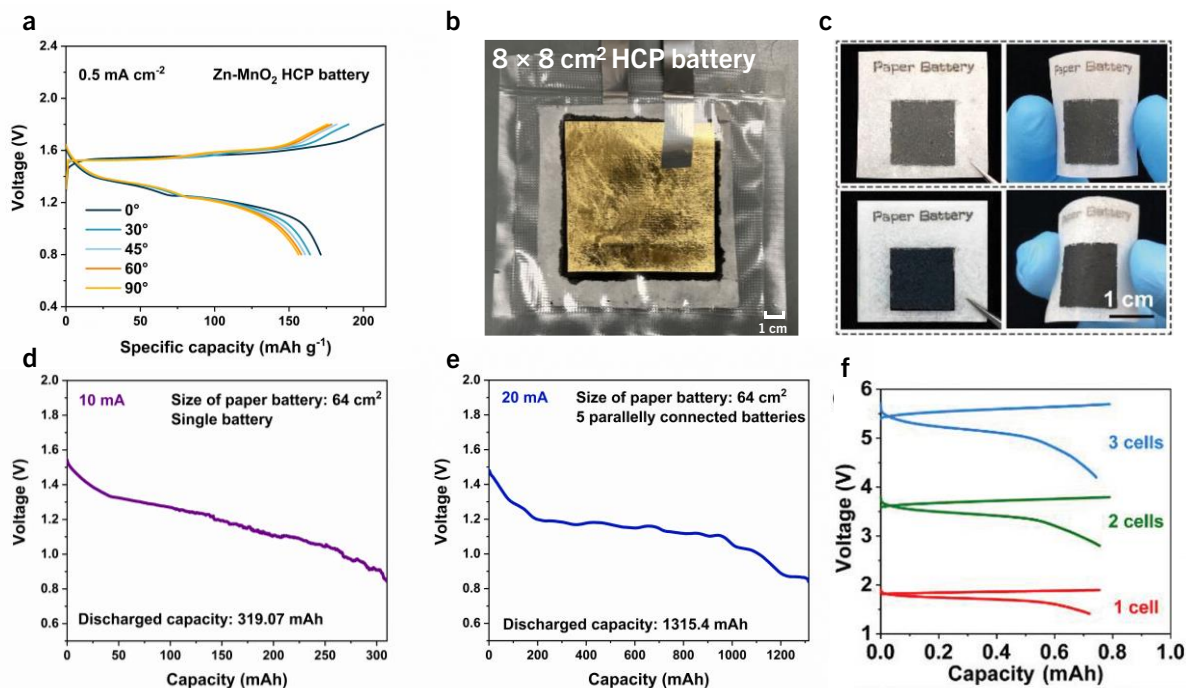


**Figure 2.8** (a) Galvanostatic charge-discharge profiles of Zn-MnO<sub>2</sub> HCP battery under varying bending angles including 0°, 30°, 45°, 60°, and 90°, at a current density of 0.5 mA cm<sup>-2</sup>. (b) Digital images of our size-expanded HCP battery, with a large areal size up to 8 × 8 cm<sup>2</sup>. Our HCP battery can have a much larger size than (c) previously reported state-of-the-art paper battery, whose size is limited to around 2 cm<sup>2</sup>,<sup>104</sup> affirming higher practicality. Discharging profiles of Zn-MnO<sub>2</sub> HCP battery with a size of 64 cm<sup>2</sup> under current densities of (d) 10 mA and (e) 20 mA, compared to a (f) previously reported paper battery<sup>104</sup>.

The size of HCP-based Zn-MnO<sub>2</sub> battery could be significantly scaled up to suit practical applications. Zn-MnO<sub>2</sub> battery with a large aerial size of 8 × 8 cm<sup>2</sup> is fabricated using an enlarged HCP separator (Figure 2.8b). High electrode mass loading was employed on the HCP separator to achieve higher capacity. The synthesized large-area HCP battery exhibited exceptional discharge capacity. For a single Zn-MnO<sub>2</sub> HCP battery, measured discharged capacity is 319.1 mAh at a high discharge current of 10 mA (Figure 2.8d). For a 5-cell battery connected in parallel, the discharge capacity measured at a higher current of 20 mA is 1315.4 mAh (Figure 2.8e), showcasing excellent discharge capability which is comparable to commercial coin cells. The demonstrated discharge capability of Zn-MnO<sub>2</sub> large-area HCP battery is much higher than a previously reported state-of-the-art paper battery, whose discharged capacity is below 1 mAh at a lower discharge current of 5 mA (Figure 2.8c and 2.8f).

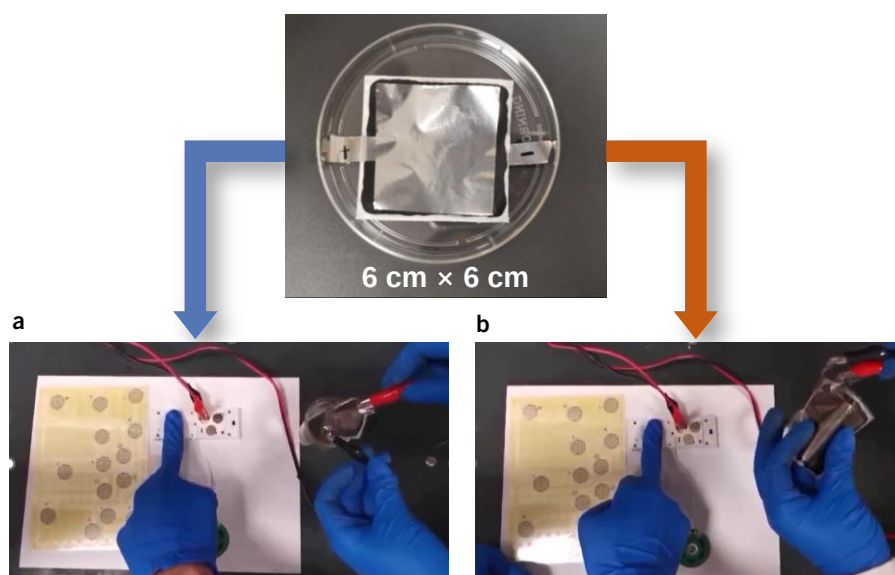


**Figure 2.9** A demo application of using a Zn-MnO<sub>2</sub> HCP battery to drive an audiobook (a) while rolling the battery and (b) under bending conditions.

The practical demonstration of the Zn-MnO<sub>2</sub> paper battery using HCP is through continuous powering of an audio book. As presented in Figure 2.9, the HCP battery is capable of providing

stable power output under either rolling or bending status, demonstrating excellent flexibility. The Zn-MnO<sub>2</sub> battery is measured to be able to continuously power the audiobook for 5 minutes, revealing a large discharge capacity. This demonstration provides strong evidence for the broad applicability of the HCP separator in flexible electronics.

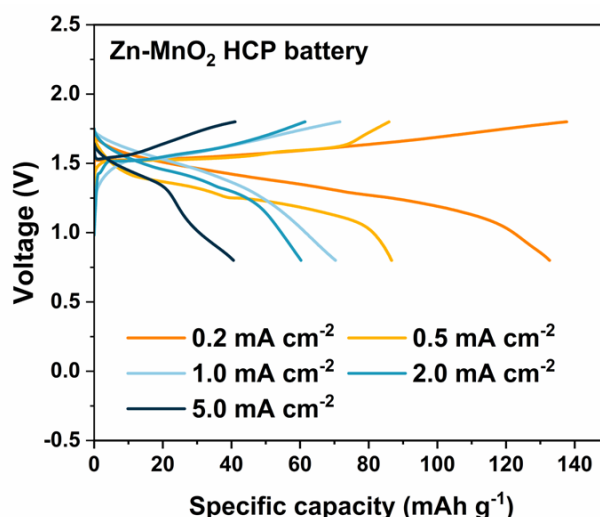


**Figure 2.10** The charge-discharge profiles of the Zn-MnO<sub>2</sub> HCP battery under varying current densities including 0.2, 0.5, 1.0, 2.0, and 5.0 mA cm<sup>-2</sup>.

Despite the above-mentioned notable electrochemical performances demonstrated by the HCP-based Zn-MnO<sub>2</sub> battery, from the charge and discharge curves (Figure 2.9), relatively weak capacity retention along with increasing current density could be observed. When the current density is raised twenty-fivefold (from 0.2 to 5.0 mA cm<sup>-2</sup>), the specific capacity of Zn-MnO<sub>2</sub> battery drops to  $\approx 40$  mAh g<sup>-1</sup>, retaining  $\approx 30\%$  of the initial capacity measured at a current density of 0.2 mA cm<sup>-2</sup>.

The weak capacity retention with large current densities could be ascribed to the inefficiency of reaction mechanism on cathode. The reaction type on cathode of Zn-MnO<sub>2</sub> batteries is intercalative, where deposition of MnO<sub>2</sub> and dissolution of Mn<sup>2+</sup> take part in the transportation of electrons. Such a reaction mechanism will easily cause lattice distortion and structural collapse, which further causes energy inefficiency along with large charge and discharge currents. In state-of-the-art research works, conversion-type electrodes have been proved to own the advantages of high reversibility, satisfying voltage output, and suitability for monovalent/multivalent ions. The conversion-type reaction mechanism is a promising choice for rechargeable, high-energy-density devices, aligning well with the requirements for energy

storage in flexible electronics. In the subsequent chapter, we explore the application of conversion-type cathodes to enhance the performance of paper-based aqueous zinc batteries.

## **2.6 Conclusion**

Hydrogel cellulose paper, owing to its good flexibility and conductivity, proves to be an effective separator material for flexible ZIBs. Additionally, the cost-effective nature of cellulose paper supports its potential for widespread commercial applications. Zn-MnO<sub>2</sub> batteries utilizing HCP demonstrated high redox efficiency, superior long lifespan, desirable discharging capability under large currents, and substantial capacity. The flexible Zn-MnO<sub>2</sub> battery also reveals stable electrochemical performance across varying bending angles, validating the efficacy of HCP as a separator for flexible batteries. However, the suboptimal capacity retention of flexible Zn-MnO<sub>2</sub> batteries is attributed to the limitations of intercalative electrodes, which will be further explored and optimized in the subsequent chapters.

## Chapter 3 Immobilizing polyiodides with expanded $\text{Zn}^{2+}$ channels for flexible zinc-iodine battery

### 3.1 Challenges & Opportunities

The rapidly growing market for integrated electronics creates an urgent demand for portable energy storage devices with low-cost, high energy density, and remarkable flexibility.<sup>105-107</sup> Rechargeable aqueous Zn-based battery has gained wide attention owing to the abundant resources of Zn metal, and high safety.<sup>108-111</sup>

Among various types of aqueous Zn-ion batteries, iodine cathode delivers high theoretical specific capacity ( $211 \text{ mAh g}^{-1}$  based on  $\text{I}_0/\text{I}^-$  conversion), suitable reaction potential (1.38 V vs.  $\text{Zn}/\text{Zn}^{2+}$ ), good reversibility, and faster redox kinetics compared with common metal oxides materials with ion intercalation/de-intercalation mechanisms.<sup>112</sup> Nevertheless, the practical application of AZIBs is mainly hindered by the intrinsic shuttle effect of soluble polyiodides ( $\text{I}_3^-$ ,  $\text{I}_5^-$ , etc.) in aqueous electrolytes.<sup>113-117</sup> In addition, the poor conductivity of both  $\text{I}_2$  and  $\text{ZnI}_2$  may lead to cathode surface passivation and low iodine utilization.<sup>118,119</sup> Above issues have a detrimental effect on the cycling life of AZIBs.

Till now, numerous strategies have been proposed to solve these limitations and improve the performance of AZIB. Typically, to immobilize the iodine species in cathode, porous carbon materials with various guest ions doping or functional group modification are widely employed. For example, Liu et al. prepared a flexible nitrogen and phosphorus co-doped porous carbon matrix with single iron ions embedded to form a stronger bond between carbon material and iodine.<sup>120</sup> Oxygen-containing functional groups were also induced on carbon nanotubes to enhance the hydrophilicity and further regulate the deposition of  $\text{ZnI}_2$ .<sup>121</sup> Besides, materials with high ionic conductivity and high polarity are also considered compatible iodine hosts. Li et al. fabricated the 211 type Nb-based MXene  $\text{Nb}_2\text{CTx}$  for iodine storage, where the  $\text{I}_2$  can be anchored between the layered crystalline of MXene to alleviate the shuttling.<sup>122</sup> Similarly, Prussian blue (PB) can also be doped by  $\text{I}^-$  on PB to serve as an iodine host for shuttle effect prohibition.<sup>123,124</sup> Zn anode protection can also raise the long lifespan of iodine cathode. For instance, sulfonate groups enriched membrane is applied for iodide repulsion and homogeneous Zn deposition.<sup>125,126</sup> To our knowledge, carbon-based materials deliver limited polarity for soluble intermediates immobilization, and the common-used polar compounds

oxides and sulfides show poor ionic/electric conductivity. For those studies related to the crystalline interlayer iodine storage behavior, the facet distances are narrow for long-chain molecular insertion (less than 1 nm).<sup>127</sup>

Therefore, it is reasonable to design an iodine host with intercalated layer structures that can provide sufficient active sites for iodine redox, and polyiodides capture, and enable smooth hydrated zinc ion transport simultaneously.

## 3.2 Comparative advantages

Herein, with the assistance of n-butylamine insertion, the interlayer spacing of layer-structured  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\alpha$ -ZrP) can be expanded from 7.5 Å to 18.3 Å (expanded-interlayer ZrP, denoted as EI-ZrP), which is feasible for the hydrated Zn ions (8.6 Å) transport and can provide abundant active sites for polyiodides confinement.<sup>128-131</sup> Moreover, the expanded layered structure of EI-ZrP is proved to facilitate electron transport for lowering the activation barrier of solid  $\text{I}_2$  and  $\text{ZnI}_2$  reactions. As expected, the assembled ZIBs with EI-ZrP additive in iodine cathode demonstrate a high specific capacity of 205 mAh g<sup>-1</sup> at 1 C over 2500 cycles. Additionally, a specific capacity of 140 mAh g<sup>-1</sup> over 10000 cycles at 20 C can also be maintained. By combining hydrogel cellulose paper (HCP) as the separator, a paper battery with EI-ZrP in the cathode material is fabricated. For practical application, compatibility of the Zn-I<sub>2</sub> paper battery with flexible circuits and devices will allow it to be utilized as a power source for a flexible system (herein, a pressure sensor). This cathode additive design for polyiodide confinement and iodine redox kinetics enhancement, and its construction on the paper platform, may pave the way for the development of durable flexible electronics.

## 3.3 Synthesis of materials

### 3.3.1 Preparation of expanded ZrP (EI-ZrP)

The manufacturing process of the material with high flexibility is illustrated in Figure 1a schematically. In the first step, 0.5 grams of layer-structured  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ , ( $\alpha$ -ZrP) was mixed with 50 milliliters of deionized water. Then, 1 milliliter of n-butylamine (99%, Aladdin) was mixed to increase the interlayer spacing of ZrP. The suspension was exposed to ultrasonic waves for 30 minutes and later stirred for 48 hours at room temperature. The resulting powder

was then collected by centrifugation. After being washed with deionized water, the material was put in a vacuum oven at 60 °C for 12 hours to be dried, which finally led to EI-ZrP.

### 3.3.2 Preparation of EI-ZrP /I<sub>2</sub> electrode

Preparation of EI-ZrP /I<sub>2</sub> electrode includes the following steps. First, a composite of SuperP/I<sub>2</sub> was prepared by mixing different weights of I<sub>2</sub> powder with SuperP and then sealed into a glass bottle at 120 °C for 6 hours. The thermogravimetric analysis was used to measure iodine loading (Figure 3.2b). Next, an EI-ZrP /I<sub>2</sub> electrode was prepared by combining SuperP/I<sub>2</sub> composites, EI-ZrP, SuperP and polyvinylidene fluoride binder with N-Methylpyrrolidone (NMP; AR grade, Aladdin) solvent in 7:1:1:1 (mass ratio). This mixture was then stirred vigorously to obtain a homogeneous slurry, which was dispersed onto a titanium foil, and then dried at 40 °C for 4 hours in a vacuum oven to obtain a mass loading measured approximately 1.0 mg cm<sup>-2</sup>. The same method was utilized to fabricate  $\alpha$ -ZrP/I<sub>2</sub> and SuperP/I<sub>2</sub> electrodes as two comparative samples.

### 3.3.3 Preparation of Hydrogel-reinforced cellulose paper (HCP)

HCP functions as the separator in the proposed battery. Cellulose filter paper (Whatman) was first submerged in 2 mol L<sup>-1</sup> acrylamide solution with a crosslinking agent ( $4 \times 10^{-4}$  mol L<sup>-1</sup> n,n'-methylenebis(acrylamide)) and an initiator ( $4 \times 10^{-4}$  mol L<sup>-1</sup> potassium persulfate). Two pieces of polyethylene-covered glass were then used to sandwich the wet cellulose paper before being heated at 60 °C with nitrogen protection for 6 hours. After vacuum drying, excess hydrogel on the surface was removed by polishing with sandpapers to obtain the hydrogel-cellulose paper (HCP).

### 3.3.4 Characterizations

Morphological analyses were performed on a scanning electron microscope (SEM, JEOL FESEM 7600F) with an energy-dispersive X-ray spectroscopy (EDS) detector. X-ray diffraction (XRD) was operated on a Bruker XRD analyzer (D8 ADVANCE). The X-ray photoelectron spectra (XPS) were collected by a Thermo Fisher machine (ESCALAB 250X). The content of iodine in carbon/iodine was analyzed by thermal gravimetric analysis measured under N<sub>2</sub> flow at a heating rate of 10 °C min<sup>-1</sup>. The absorption spectra of ZnI<sub>x</sub> in aqueous

solutions were carried out by an ultraviolet-visible spectrophotometer (UV-vis, UV-2550, Shimadzu). Surface area measurement is carried out with Micromeritics 3Flex BET.

### 3.3.5 Electrochemical Characterizations

The full ZIBs were assembled in coin cells (CR-2032) with glass fiber as separator and in punch cells with HCP as separator. Titanium foil and zinc foil were used as current collector and anode, separately. For the ZnIx symmetric cells test, electrolyte was prepared by adding 0.05 M ZnI<sub>2</sub>, 0.05 M I<sub>2</sub>, and 2 M ZnSO<sub>4</sub> in DI water. The ethanol dispersions of  $\alpha$ -ZrP and EI-ZrP were separately dopped on carbon papers ( $\sim 1 \text{ mg cm}^{-2}$ ) followed by vacuum drying. During the symmetric batteries test, usage of electrolyte was controlled to be around 30  $\mu\text{L}$  per cell. Batteries were tested within a voltage window from 0.6~1.6 V vs. Zn/Zn<sup>2+</sup>. The battery cycling stability was operated on LAND battery testing system (CT3002AU, 5 V 2 mA & 20 mA, Wuhan, China) and NEWARE battery cycler (CT-4008-5V 10mA-164, Shenzhen, China). A CHI 760E electrochemical workstation was used to perform cyclic voltammetry and a CHI 760D was used to assess electrochemical impedance spectroscopy (EIS) whose frequency ranges from 100 kHz to 10 MHz. Applied alternating current amplitude was 5 mV. The ionic conductivity of electrolytes was tested via EIS measurement. EI-ZrP films were aged by electrolyte and sandwiched between two stainless steel spacers to measure EIS. A Neware battery test system was utilized for galvanostatic charge-discharge. A Land battery test system is utilized for potentiostatic deposition tests. The carbon/ $\alpha$ -ZrP/EI-ZrP electrode is tested in 0.05 M ZnI<sub>2</sub> and 1 M ZnSO<sub>4</sub> electrolyte under 1.25V for 3000 seconds. The battery cycling stability was performed on a sare battery cycler (CT-4008-5V10mA-164, Shenzhen, China).

### 3.3.6 Calculation methods

The DFT calculations<sup>132,133</sup> were performed with Projector Augmented Wave (PAW) method<sup>134</sup> by using Vienna Ab-initio Simulation Package (VASP).<sup>135</sup> The Perdew, Burke, and Ernzerhof (PBE)<sup>136,137</sup> functional, including van der Waals corrections (DFT-D3 method)<sup>138</sup>, was employed to describe the exchange-correlation energy. The electron wave functions were cutoff with a kinetic energy of 520 eV. The Brillouin zone was sampled using the Monkhorst–Pack scheme.<sup>139</sup> The adsorption energies ( $E_{\text{ads}}$ ) were calculated as follows:

$$E_{\text{ads}} = \frac{E_{\text{slab-ads}} - E_{\text{slab}} - E_{\text{ads}}}{n} \quad (5)$$

where  $E_{\text{slab-ads}}$  is the total energy of species absorbed surface,  $E_{\text{slab}}$  is the energy of SEI surface,  $E_{\text{ads}}$  is the energy of Li ions, and  $n$  is the atomic number of absorbed species, respectively.

### 3.4 Results and discussion

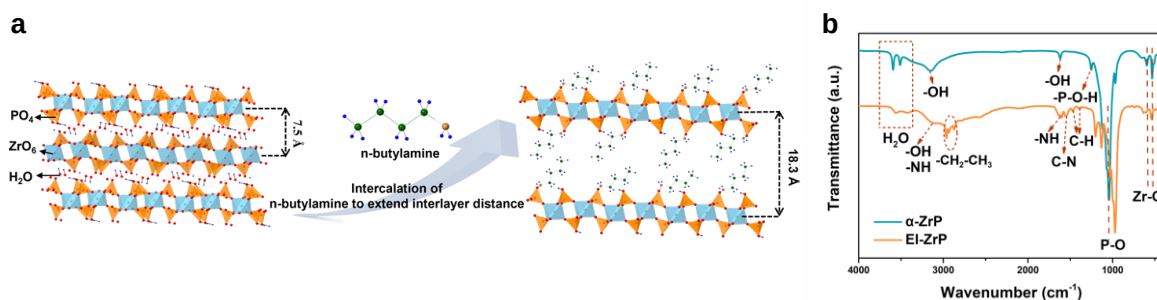


**Figure 3.1** Characterizations of  $\alpha$ -ZrP/EI-ZrP materials. (a) The schematic illustration of EI-ZrP. (b) The FT-IR spectra of  $\alpha$ -ZrP and EI-ZrP.

As schematically exhibited by Figure 3.1a, N-butylamine is employed as pillars to be intercalated into pre-prepared  $\alpha$ -ZrP material to further expand the interlayer spacing. After ultrasonication treatment, stirring, and washing processes, the layer-expanded EI-ZrP is obtained. The FT-IR spectrum provides strong evidence that n-butylamine has been successfully intercalated into the  $\alpha$ -ZrP. The characteristic absorptions of n-butylamine are observed (Figure 3.1b), including the dips around  $1500\text{ cm}^{-1}$  (C-N) and  $2900\text{ cm}^{-1}$  (-CH<sub>3</sub> and -CH<sub>2</sub>).

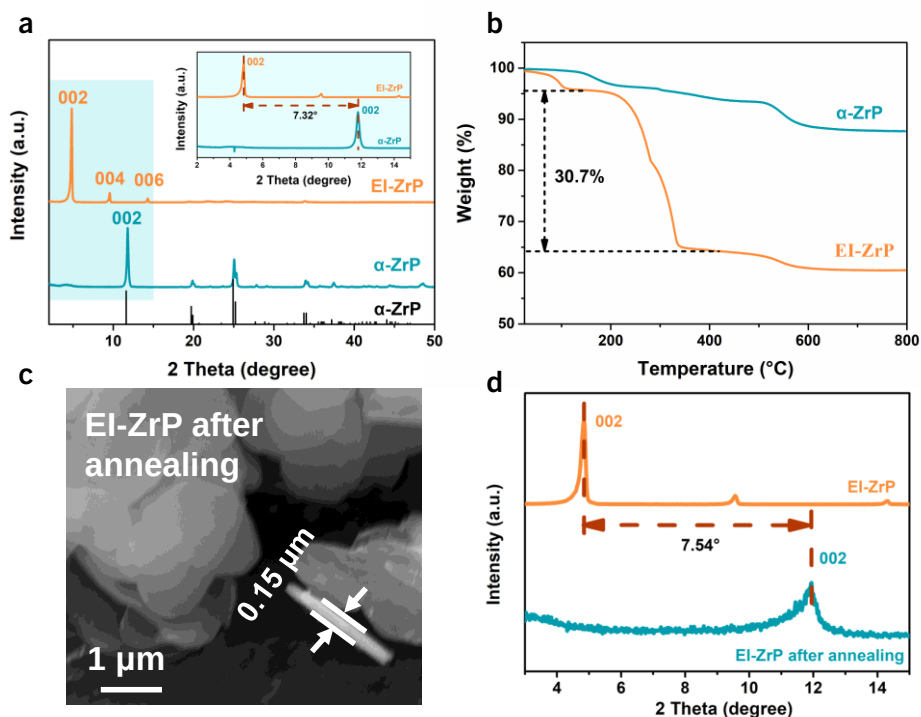


**Figure 3.2** (a) The XRD of  $\alpha$ -ZrP and EI-ZrP. (b) Thermogravimetric curves of  $\alpha$ -ZrP and EI-ZrP. (c) SEM image of EI-ZrP after annealing. (d) XRD patterns of EI-ZrP before and after annealing.

By comparing XRD patterns of ZrP before and after layer expansion (Figure 3.2a), the diffraction peaks of EI-ZrP shift to lower angles due to the n-butylamine intercalation. The (002) interplanar spacing is about 7.5 Å for  $\alpha$ -ZrP and 18.3 Å for EI-ZrP. The left shift of the 002 plane signal (7.32°) supports the intercalation process. The thermogravimetric analysis (TGA) was conducted to estimate the quantity of n-butylamine after intercalation (Figure 3.2b). Compared with  $\alpha$ -ZrP, a significant weight loss (30.7 wt%) can be observed around 250 °C for EI-ZrP, which can be assigned to the thermal decomposition of n-butylamine in air.<sup>128</sup> Compared with  $\alpha$ -ZrP, a significant weight loss (30.7 wt%) can be observed around 250 °C for EI-ZrP, which can be assigned to the thermal decomposition of n-butylamine in air. The intramolecular dehydration of protonated phosphate groups from  $\text{Zr}(\text{HPO}_4)_2$  leads to a weight loss of around 530 °C when amorphous  $\text{ZrP}_2\text{O}_7$  forms.  $\text{ZrP}_2\text{O}_7$  is stable until 1000 °C when  $\text{ZrP}_2\text{O}_7$  has a phase transition from an amorphous one to an orthorhombic phase.<sup>140</sup>

To completely remove n-butylamine, EI-ZrP was annealed at 260 °C for 2 hours. SEM and XRD measurements (Figure 3.2c, d) show that the thickness of EI-ZrP is about 0.15 μm after the annealing (removal of n-butylamine), the same as that of  $\alpha$ -ZrP. In addition, the interlayer space of EI-ZrP reduces to 5.9 Å, which is close to and even smaller than that of  $\alpha$ -ZrP (7.5 Å).

Hence, it can be inferred that the large interlayer space originates from n-butylamine which serves as the skeleton.

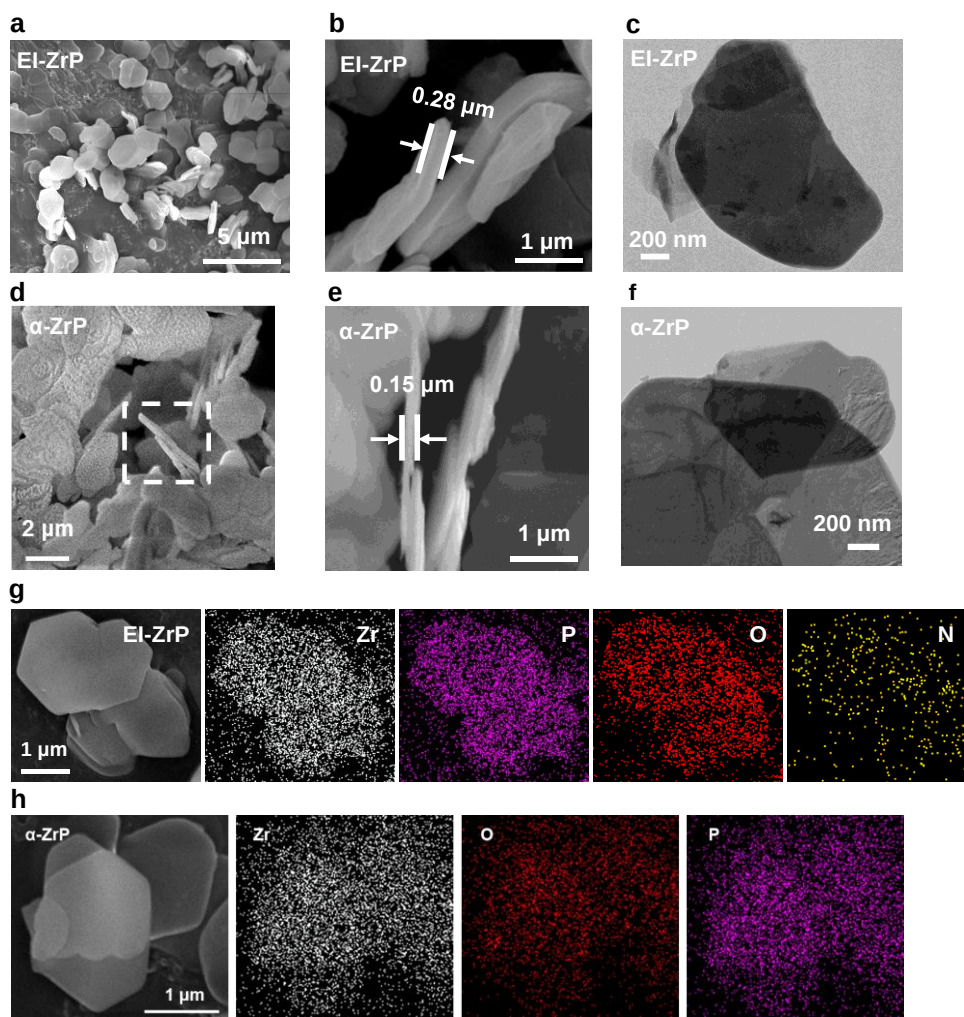


**Figure 3.3** Characterizations of  $\alpha$ -ZrP/EI-ZrP materials. (a) (b) The SEM and (c) TEM images of EI-ZrP. (d) (e) The SEM and (f) TEM images of  $\alpha$ -ZrP. (g) The high-resolution SEM images of EI-ZrP and corresponding elemental mappings. (h) The high-resolution SEM images of  $\alpha$ -ZrP and corresponding elemental mappings.

Layered structures of  $\alpha$ -ZrP and EI-ZrP are compared (Figure 3.3 a,b,d,e). Both materials consist of hexagonal nanoplates with smooth surfaces. The main difference is that EI-ZrP nanoplates are thicker than  $\alpha$ -ZrP ones, but the overall shape is retained, indicating that the intercalation of n-butylamine into  $\alpha$ -ZrP does not cause structural collapse. The larger interlayer spacing of EI-ZrP (18.3 Å) than that of  $\alpha$ -ZrP (7.5 Å) will enable EI-ZrP to absorb polyiodides more efficiently than  $\alpha$ -ZrP, and also for the absorption of solvated zinc ion (zinc hexahydrate) with a diameter of around 8.60 Å.<sup>129,141</sup> The TEM and high-resolution SEM examinations reveal the uniform distribution of Zr, P, O, and N components on the surface of

EI-ZrP (Figure 3.3 c,f-h), implying that the interlayer expansion does not change the distribution of different components.

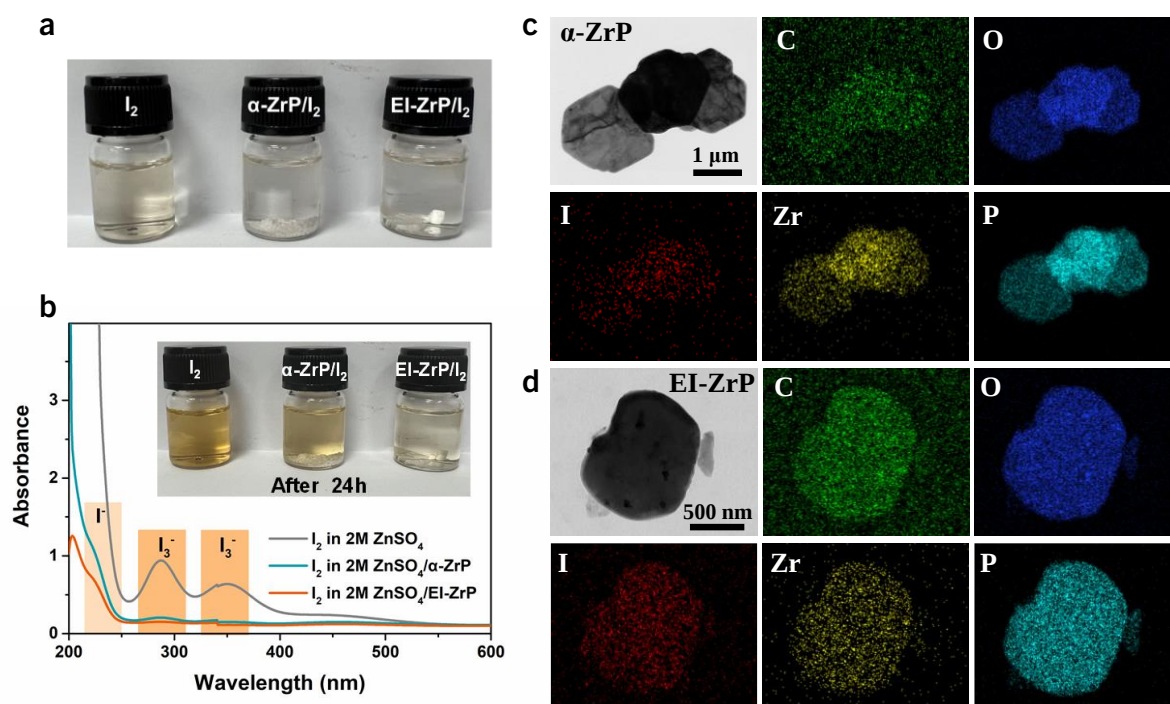


**Figure 3.4** (a) Digital photos of solutions composed of  $I_2$ ,  $\alpha\text{-ZrP}/I_2$  and  $\text{EI-ZrP}/I_2$  and 2 M  $\text{ZnSO}_4$  electrolyte before absorption. (b) The images of solutions composed of  $I_2$ ,  $\alpha\text{-ZrP}/I_2$  and  $\text{EI-ZrP}/I_2$  and 2 M  $\text{ZnSO}_4$  electrolyte after absorption, and the result of ultraviolet-visible spectroscopy tests of three solutions. EDX mapping images of (c)  $\alpha\text{-ZrP}$  and (d)  $\text{EI-ZrP}$  after immersing in the  $I_2/2\text{ M ZnSO}_4$  electrolyte.

The superior sustainability of EI-ZrP as a host material for iodine is investigated further by preparing solutions composed of  $I_2$ ,  $\alpha\text{-ZrP}/I_2$  and  $\text{EI-ZrP}/I_2$  in 2 M  $\text{ZnSO}_4$  electrolyte, respectively (Figure 3.4a). The same amount of iodine (0.7 mg) was added to 2 M  $\text{ZnSO}_4$  electrolyte for each bottle. Subsequently, 0.1 mg  $\alpha\text{-ZrP}$  and EI-ZrP were added to the second and third bottles, respectively. The three bottles were placed in ambient conditions for 24 hours to observe the change in color. Change in color of electrolytes reveals the dissociation of iodine in electrolyte after 24 hours (Figure 3.4b inset). Among all three solutions, the solution with  $\text{EI-ZrP}/I_2$  shows the slightest color change, indicating that most polyiodides were absorbed effectively. The samples undergo ultraviolet-visible (UV-vis) spectroscopy tests after 24 h (Figure 3.4b). Those peaks ascribed to  $I_3^-$  are from the dissolution of iodine with  $I^-$  forming soluble  $I_3^-$ . Compared to the samples with  $I_2$  and  $\alpha\text{-ZrP}/I_2$ , a weaker signal of  $I^-$  appeared in EI-ZrP/ $I_2$  solution. Furthermore,  $I_3^-$  is barely detected, implying that EI-ZrP with a preferable interlayer distance effectively confines polyiodides and thus suppresses the dissolution of

polyiodides. In addition, EI-ZrP has better absorption of iodine and polyiodides as indicated by more uniform and denser distribution of iodine in EI-ZrP after immersing in the  $I_2/2\text{ M ZnSO}_4$  electrolyte compared to  $\alpha$ -ZrP and EI-ZrP (see EDX mapping images in Figure 3.4 c and d). This confinement effect is expected to suppress the shuttle effect of AZIB.

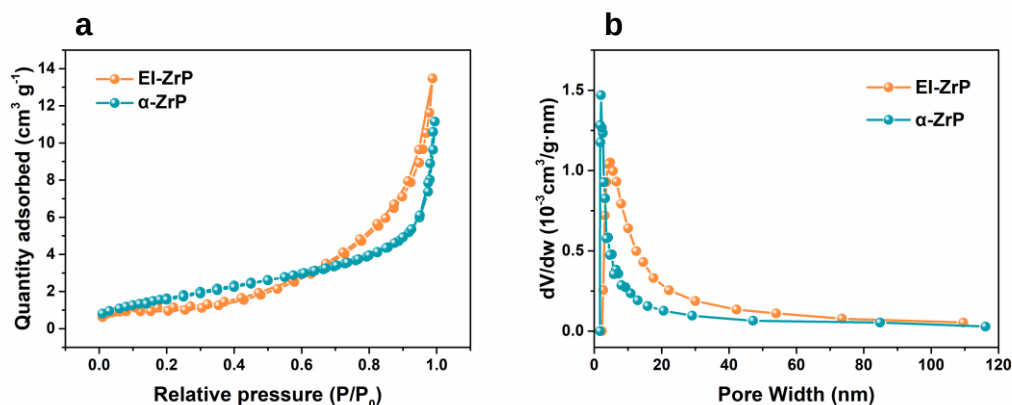


**Figure 3.5** (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) pore size distribution curves of  $\alpha$ -ZrP and EI-ZrP.

The  $\text{N}_2$  adsorption-desorption isotherms of  $\alpha$ -ZrP and EI-ZrP are investigated to measure specific surface area and pore structure (Figure 3.5). Presence of a hysteresis ring ( $P/P_0 > 0.2$ ) indicates the formation of porous structures. The average pore size ranges from 3 to 4.5 nm, suggesting microporous structures inside EI-ZrP. The increasing adsorbed volume with increasing relative pressure can be observed. EI-ZrP has a larger surface area and pore size than  $\alpha$ -ZrP.

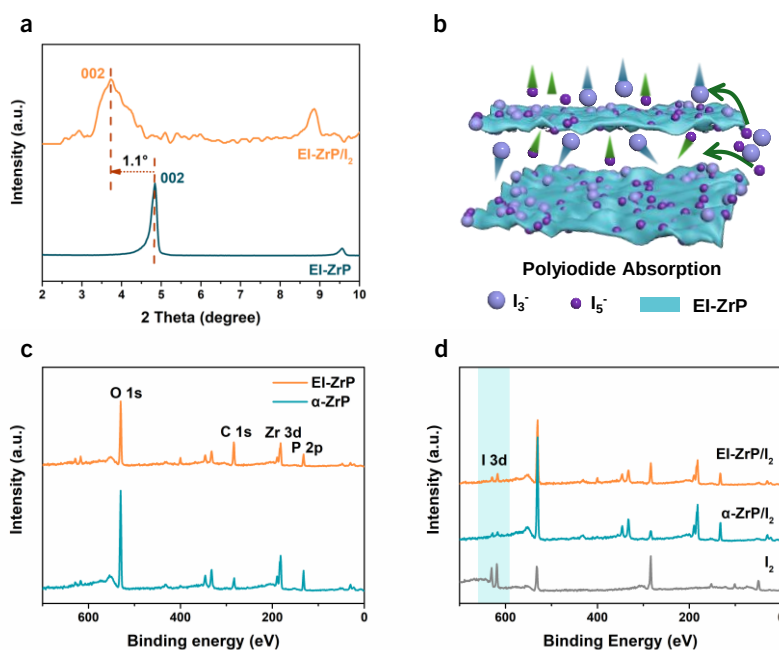


**Figure 3.6** (a) The XRD results of EI-ZrP and EI-ZrP/I<sub>2</sub>. (b) Schematic diagram of EI-ZrP interlayer adsorption of polyiodide. XPS survey spectra of (c)  $\alpha$ -ZrP and EI-ZrP, and (d) I<sub>2</sub>,  $\alpha$ -ZrP/I<sub>2</sub> and EI-ZrP/I<sub>2</sub>.

XRD peak analysis of EI-ZrP before and after I<sub>2</sub> absorption (Figure 3.6a) shows that the interlayer spacing of EI-ZrP expands from 18.3 to 24.6 Å. The difference is comparable to the size of polyiodide ions (5.8-11.7 Å).<sup>142</sup> The expansion of the lattice is attributed to absorption of polyiodide into interlayer spacing of EI-ZrP. Hence, the EI-ZrP can absorb polyiodide through both surface and interlayer (Figure 3.6b), which is to be discussed below.

**Table 3.1** Elements content derived from XPS survey spectra.

| Atom ratio / % | C     | P     | Zr    |
|----------------|-------|-------|-------|
| $\alpha$ -ZrP  | 42.99 | 38.20 | 18.81 |
| EI-ZrP         | 70.97 | 19.06 | 9.97  |

XPS spectra are analyzed to further investigate the absorption of iodine into  $\alpha$ -ZrP and EI-ZrP. A stronger peak for C can be observed for EI-ZrP than that of  $\alpha$ -ZrP (Figure 3.6c, Table 3.1), which is ascribed to intercalation of organic compounds. The higher density of I<sub>3</sub>d observed in the XPS survey spectra of EI-ZrP/I<sub>2</sub> than  $\alpha$ -ZrP supports that EI-ZrP is better at absorption of iodine (Figure 3.6d).

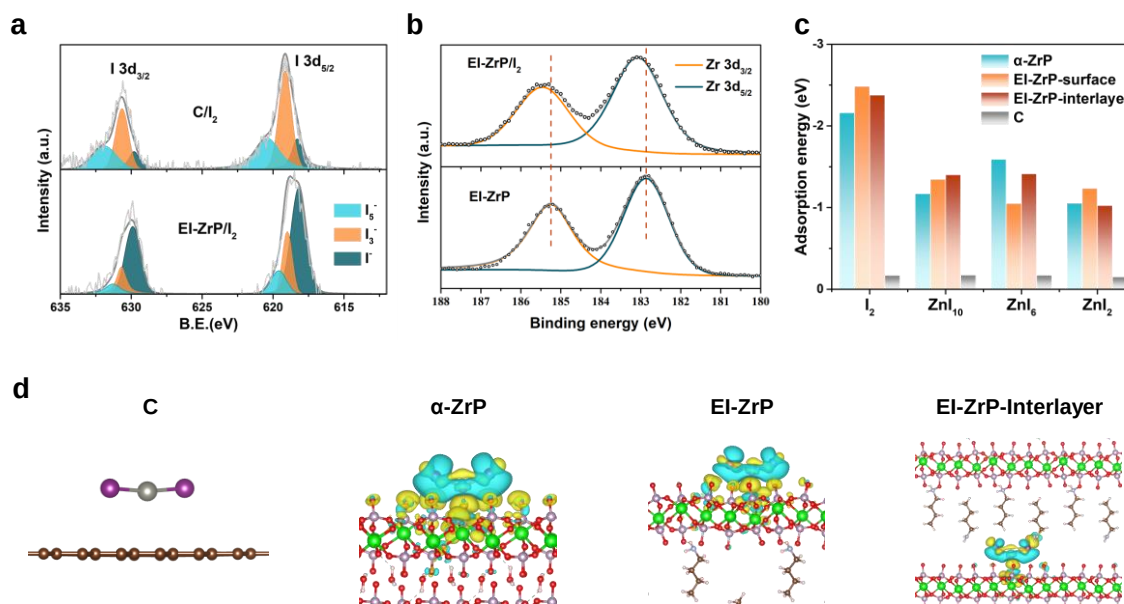


**Figure 3.7** (a) The XPS curves of C/I<sub>2</sub> and EI-ZrP/I<sub>2</sub>, with peaks divided. (b) The XPS curves of EI-ZrP and EI-ZrP/I<sub>2</sub>. (c) The bonding energies and (d) charge density difference of the optimized configurations of host materials (C,  $\alpha$ -ZrP, EI-ZrP) with iodine species (I<sub>2</sub>, ZnI<sub>10</sub>, ZnI<sub>6</sub> and ZnI<sub>2</sub>).

In Figure 3.7a, the two distinct peaks at 618.3 and 629.8 eV are assigned to  $I^-$  in C/ $I_2$ , while the two peaks at 618.2 and 629.9 eV are assigned to  $I^-$  in EI-ZrP/ $I_2$ . Two pairs of coupling peaks around 618.9/630.6 and 619.6/631.3 eV are assigned to  $I_3^-$  and  $I_5^-$  for EI-ZrP.<sup>143-145</sup> The peaks of  $I^-$  in EI-ZrP/ $I_2$  are larger than those in C/ $I_2$ , indicating  $I^-$  tends to form on EI-ZrP. The smaller peaks of  $I_3^-$  and  $I_5^-$  in EI-ZrP/ $I_2$  also suggest better confinement of polyiodides in EI-ZrP/ $I_2$  than in C/ $I_2$ . Furthermore, compared to pure EI-ZrP, the binding energy for Zr3d of EI-ZrP/ $I_2$  shifts towards a higher position, indicating a strong interaction between phosphate and iodine which influences the electron density of Zr (Figure 3.7b).

To shed more light on the origins of confinement of iodine species in EI-ZrP, density functional theory (DFT) calculations are conducted. The bonding energies of host materials (C,  $\alpha$ -ZrP, EI-ZrP) with iodine species ( $I_2$ ,  $ZnI_{10}$ ,  $ZnI_6$  and  $ZnI_2$ ) are employed to evaluate the polyiodide confinement. In Figure 3.7c, the bonding energies of polyiodides on the surface of carbon material are significantly smaller than that on surfaces of both  $\alpha$ -ZrP and EI-ZrP, exhibiting unsatisfying polyiodide adsorption. In addition, the large interlayer distance of EI-ZrP can enable interlayer polyiodide confinement, leading to better polyiodide confinement.

The isosurfaces of local charge density difference are further utilized to reveal the mechanism of polyiodide confinement. In Figure 3.7d, the isosurfaces show quite different charge redistributions around the polyiodide. The minuscule charge redistributions on C indicate that the carbon material adsorbs polyiodide mainly through vdW interactions. On the contrary, large charge redistributions can be found in all these ZrP-based materials, indicating the chemisorption nature of polyiodide confinement in both  $\alpha$ -ZrP and EI-ZrP. Overall, the enhanced polyiodide adsorption performance of EI-ZrP stems from the high surface polarity enabled strong chemisorption, as well as the special interlayer adsorption mechanism.

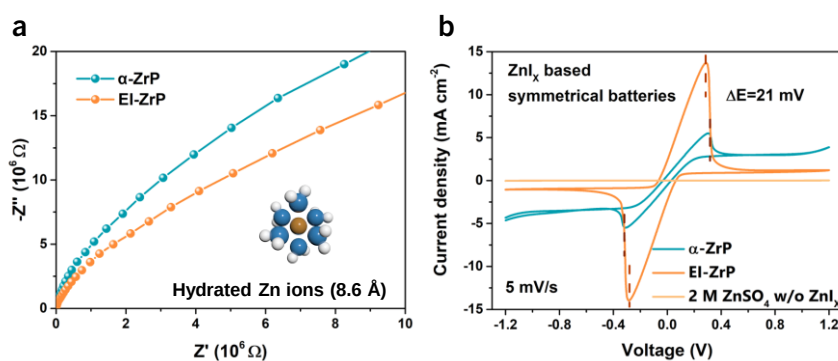


**Figure 3.8** (a) Nyquist plots of  $\alpha$ -ZrP and EI-ZrP interface, and the illustration of hydrated zinc ion. (b) Relation between  $Z_{real}$  and  $\omega^{-0.5}$  in the low frequency range for SuperP,  $\alpha$ -ZrP, and EI-ZrP.

In addition, the superiority of EI-ZrP due to enlarged interlayer space is verified by comparing the electrocatalytic activities of various cathode additives. First,  $\text{Zn}^{2+}$  conductivity ( $\sigma_{\text{Zn}^{2+}}$ ) was measured through EIS spectra using stainless steel as blocking electrodes (Figure 3.8a).<sup>128,146</sup> A larger value of  $\sigma_{\text{Zn}^{2+}}$  of EI-ZrP ( $3.5 \text{ mS cm}^{-1}$ ) compared with that of  $\alpha$ -ZrP ( $0.4 \text{ mS cm}^{-1}$ ) supports efficient charge transport through the expanded interlayer space. Second, the increased interlayer spacing in EI-ZrP also facilitates the diffusion of  $\text{Zn}^{2+}$ .

**Table 3.2** Summary of  $D_{\text{Zn}^{2+}}$  at oxidation and reduction peaks of  $\alpha$ -ZrP and EI-ZrP cathodes.

| Cathode       | $D_{\text{Zn}^{2+}}$ at oxidation | $D_{\text{Zn}^{2+}}$ at reduction |
|---------------|-----------------------------------|-----------------------------------|
| $\alpha$ -ZrP | $5.65 \times 10^{-9}$             | $1.69 \times 10^{-8}$             |
| EI-ZrP        | $7.77 \times 10^{-9}$             | $2.28 \times 10^{-8}$             |

Unit:  $\text{cm}^2 \text{ s}^{-1}$

Based on the Warburg impedance in low frequency region (Figure 3.8a), the smaller slope between  $Z_{\text{real}}$  and  $\omega^{-0.5}$  of EI-ZrP compared with  $\alpha$ -ZrP implies larger diffusion coefficient of the former than the latter. The Randles-Sevcik equation is adopted to calculate the diffusion coefficient of  $\text{Zn}^{2+}$  in both  $\alpha$ -ZrP/ $\text{I}_2$  and EI-ZrP/ $\text{I}_2$  cathodes:

$$i_p = 2.69 \times 10^5 n^{3/2} A C \sqrt{Dv} \quad (6)$$

where  $i_p$  is the peak current (unit in amps),  $A$  is the electrode area ( $\text{cm}^2$ ),  $C$  is the zinc ion concentration in the electrolyte ( $\text{mol cm}^{-3}$ ),  $n$  is the number of electrons in the redox reaction (1 for  $\text{I}^0/\text{I}^-$ ), and  $v$  is the scan rate ( $\text{V s}^{-1}$ ). According to estimation from the Randles-Sevcik equation (see Table 3.2 and notes),<sup>147</sup> the diffusion coefficient of  $\text{Zn}^{2+}$  in EI-ZrP/ $\text{I}_2$  cathodes is roughly 1.3 times that of  $\alpha$ -ZrP/ $\text{I}_2$  under both the oxidation and reduction processes. The increased ionic conductivity and diffusion coefficient verify the advantageous effect of the large interlayer space in boosting the Zn ion transfer.<sup>120</sup> Additionally, cyclic voltammetry (CV) curves of symmetric batteries with  $\alpha$ -ZrP and EI-ZrP cathodes (in the same  $\text{ZnI}_x$  based electrolyte) at  $5 \text{ mV/s}$  scan rate<sup>148</sup> indicate that the current for EI-ZrP/ $\text{I}_2$  cathode is nearly doubled that of  $\alpha$ -ZrP/ $\text{I}_2$  cathode (Figure 3.8b). The smaller potential difference between the pair of redox peaks also reveals lower polarization and better reversibility of EI-ZrP/ $\text{I}_2$  cathode.

The Arrhenius equation:

$$\frac{1}{R_{\text{ct}}} = A e^{\frac{-E_a}{RT}} \quad (7)$$

is employed to calculate the activation energy for the reaction ( $E_a$ ).<sup>149-151</sup>  $R_{ct}$  is the charge-transfer resistance,  $A$  is the pre-exponential factor or frequency factor,  $R$  is the universal gas constant,  $T$  is the absolute temperature at which the reaction takes place (in units of Kelvin).

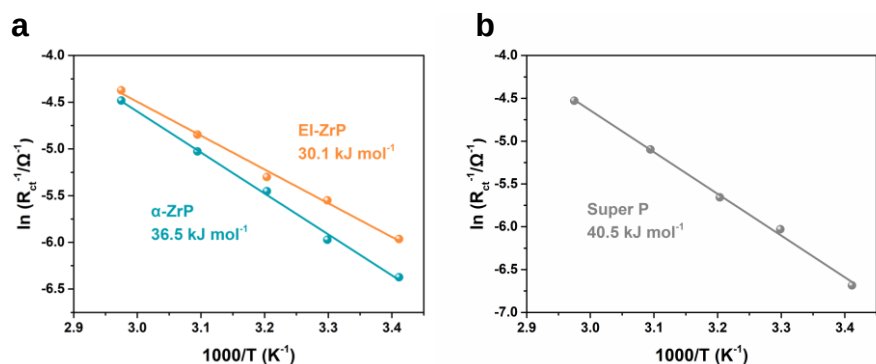


**Figure 3.9** The charge transfer resistances for varying temperatures of (a)  $\alpha$ -ZrP/EI-ZrP ZIB and (b) Super P ZIB.

The charge transfer resistances are measured at varying temperatures (Figure 3.9). The estimated  $E_a$  are 30.1 kJ mol<sup>-1</sup> for EI-ZrP, 36.5 kJ mol<sup>-1</sup> for  $\alpha$ -ZrP and 40.5 kJ mol<sup>-1</sup> for conductive carbon (SuperP). The lowest activation energy of EI-ZrP enhances the dynamic process of electrocatalytic redox reactions of iodine.

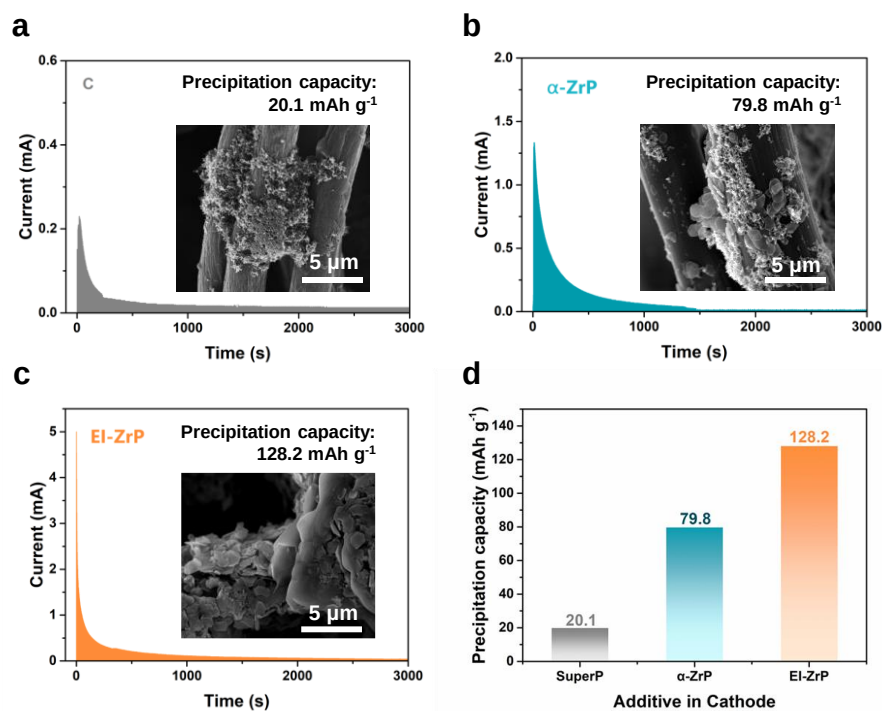


**Figure 3.10** The potentiostatic deposition curves of 0.05 M ZnI<sub>2</sub> in 1 M ZnSO<sub>4</sub> solution on (d) C (e)  $\alpha$ -ZrP (f) EI-ZrP electrodes, with the morphology of I<sub>2</sub> deposit displayed on the inset images, respectively. (d) Precipitation capacity of I<sub>2</sub> on three cathodes with different additives.

During charging process, the complete oxidation of iodide results in the formation of iodine on surface of electrodes, which is a heterogeneous nucleation process. Potentiostatic deposition experiments are conducted to investigate the growth of  $I_2$  on C/ $\alpha$ -ZrP/EI-ZrP electrodes (Figures 3.10 a-c). The peak current density of EI-ZrP (5.0 mA) is higher than C (0.2 mA) and  $\alpha$ -ZrP (1.3 mA). Moreover, based on the concentration of iodide in the electrolyte and the integral of current, the EI-ZrP electrode exhibits the highest  $I_2$  precipitation capacity of 128.2 mAh g<sup>-1</sup>, while C and  $\alpha$ -ZrP cathodes only demonstrate 20.1 and 79.8 mAh g<sup>-1</sup>, respectively (Figure 3.10d). The highest iodine deposition capacity of EI-ZrP cathode indicates that iodine nucleation kinetics are improved by EI-ZrP.

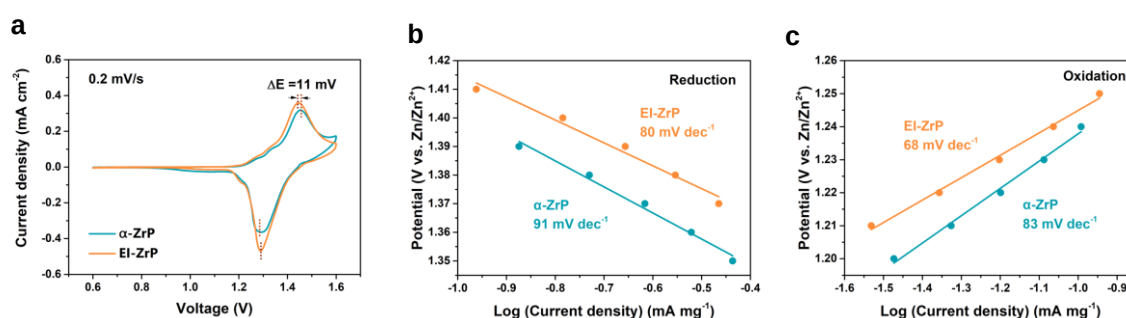


**Figure 3.11** (a) CV curves of AZIBs with  $\alpha$ -ZrP/ $I_2$  and EI-ZrP/ $I_2$ . Tafel slope of the initial (b) discharging stage and (c) charging stage.

CV curves of the AZIBs with  $\alpha$ -ZrP/EI-ZrP are analyzed to demonstrate the improvement of EI-ZrP on iodine redox reactions. The lower polarization and better reversibility of the EI-ZrP/ $I_2$  electrode compared to  $\alpha$ -ZrP/ $I_2$  are supported by the smaller potential difference between redox peaks (Figure 3.11a). Tafel slope, which is deduced from the CV curves, is applied to characterize the specific reaction kinetics during discharging (Figure 3.11b) and charging (Figure 3.11c) processes for AZIBs with  $\alpha$ -ZrP and EI-ZrP. The EI-ZrP electrode has a smaller Tafel slope of about 80 and 68 mV · dec<sup>-1</sup> in the reduction and oxidation processes, compared to that of the  $\alpha$ -ZrP/ $I_2$  electrode (91 and 83 mV · dec<sup>-1</sup>). The lower  $\eta$  values indicate a higher electrocatalytic activity and faster kinetics of the EI-ZrP/ $I_2$  electrode.

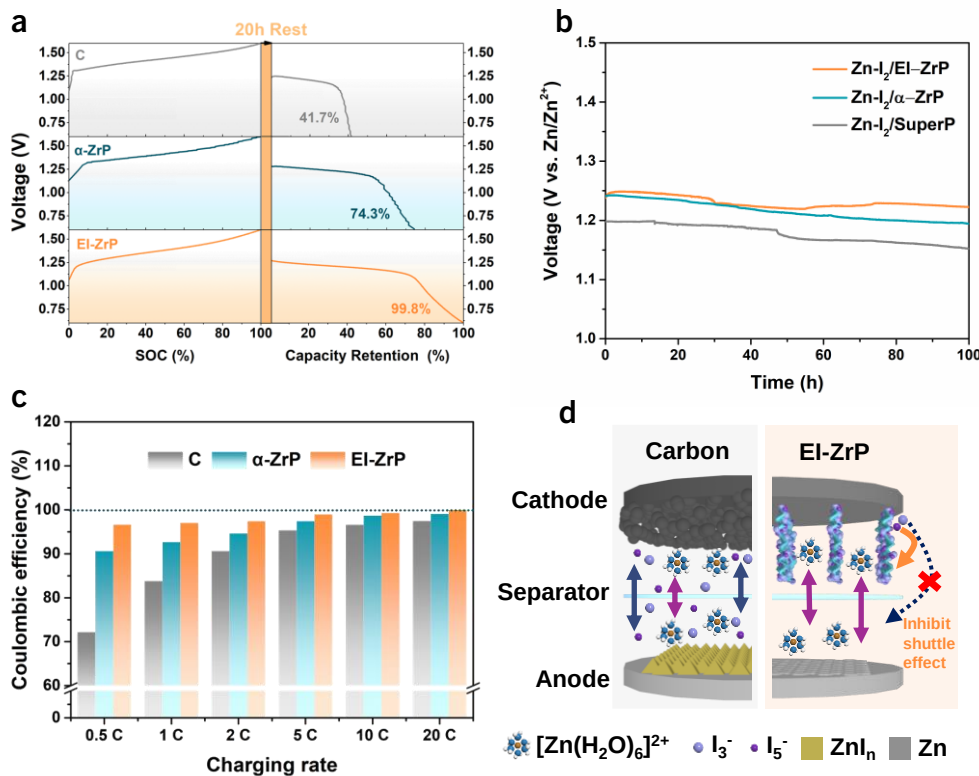


**Figure 3.12** (a) Capacity retention of AZIB with different cathodes after 20 h rest. (b) The self-discharging profiles of cells with SuperP/ $\alpha$ -ZrP/EI-ZrP cathodes. After fabrication, the batteries are monitored for the open-circuit voltage for 100 hours. (c) Comparison of coulombic efficiency of cells with C/ $\alpha$ -ZrP/EI-ZrP additives at different charging and discharging rates. (d) Schematic diagram of confinement effect of polyiodides with EI-ZrP in AZIB.

To analyze the confinement effect of EI-ZrP, self-discharge experiments are conducted. The cells are rested for 20 hours before being discharged. AZIB with EI-ZrP/I<sub>2</sub> cathode shows over 99% capacity retention while the other two only retain 41.7% and 74.3% of the original capacity (Figure 3.12a). Comparison of the self-discharging profiles of the three cells also proves the efficiency of the EI-ZrP in inhibiting the shuttle effect (Figure 3.12b).

Under different charging and discharging rates (0.5 C - 20 C), AZIB with EI-ZrP/I<sub>2</sub> cathode shows superior coulombic efficiency, which further supports that EI-ZrP plays an important role in immobilizing polyiodide (Figure 3.12c). The difference in reaction mechanism between C/I<sub>2</sub> and EI-ZrP/I<sub>2</sub> is illustrated (Figure 3.12d). When using carbon material as cathode, polyiodides tend to travel to the anode, leading to the formation of ZnI<sub>2</sub>. Therefore, the quantity of active materials will decrease accompanied by capacity decay. Compared to carbon material, both surface and interlayer of EI-ZrP can prevent the movement of polyiodides, thus effectively inhibiting shuttle effect.

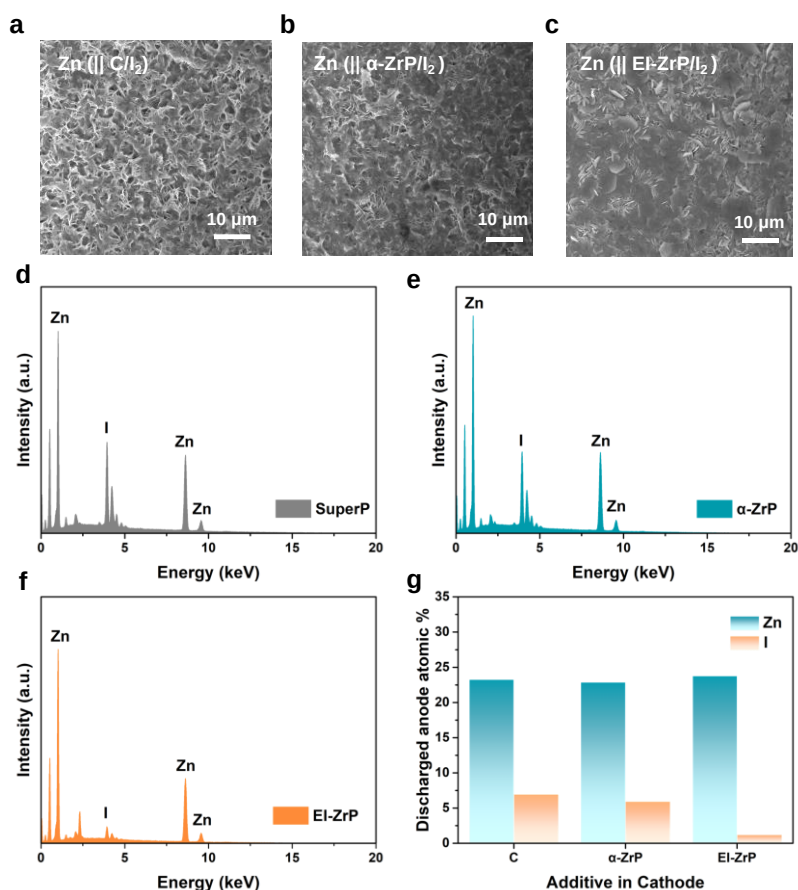


**Figure 3.13** SEM images of zinc anode pairing with (a) C/I<sub>2</sub> (b) α-ZrP/I<sub>2</sub> (c) EI-ZrP/I<sub>2</sub> cathodes after 50 cycles of charging and discharging. EDS spectra of zinc anode pairing with (d) C/I<sub>2</sub> (e) α-ZrP/I<sub>2</sub> (f) EI-ZrP/I<sub>2</sub> cathodes after 50 cycles of charging and discharging. (g) Different atomic percentages of Zn and I on the surface of Zn anodes after 50 cycles from EDS mapping. Percentages of other main components (carbon and oxygen from the substrate) are not shown here for clarity.

The surface morphologies of zinc anode are investigated by scanning electron microscope (SEM) images after 50 cycles of charging and discharging when paired with three cathodes containing different additives C, α-ZrP or EI-ZrP (Figure 3.13 a-c). Elemental analysis shows that (Figure 3.13 d-f) the EI-ZrP/I<sub>2</sub> cathode results in the lowest concentration of iodine on the anode surface compared to the other cathodes, indicating the strongest confinement of EI-ZrP on polyiodides (Figure 3.13g).

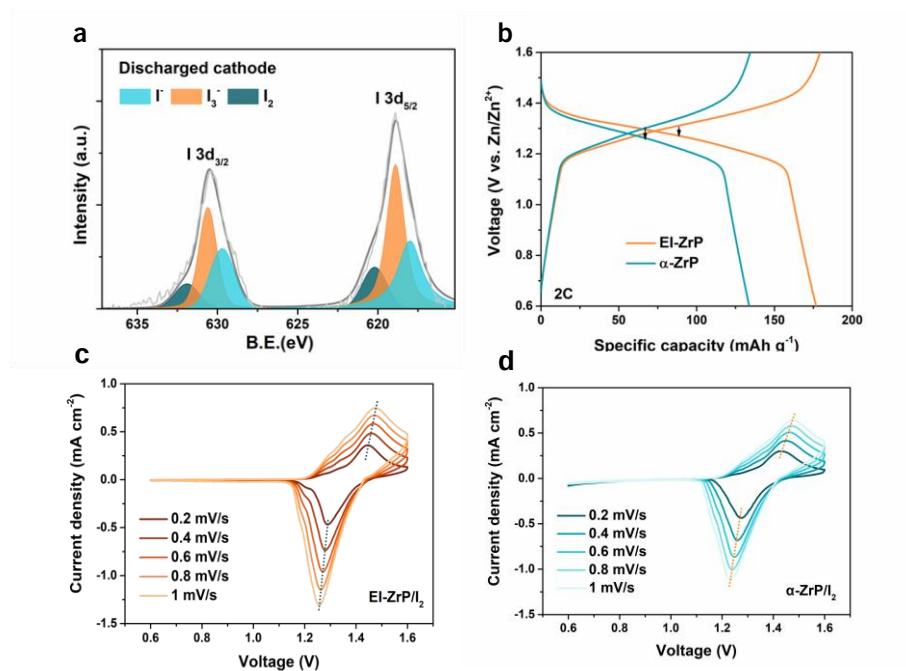


**Figure 3.14** (a) XPS curves of cathode material after discharging. (b) The charge-discharge profiles of the ZIBs with  $\alpha$ -ZrP/EI-ZrP. Electrochemical performance of AZIBs with various cathode additives. (c) CV curves of the AZIB with the EI-ZrP/ $I_2$  cathode at different scan rates. (d) CV curves of ZIB with  $\alpha$ -ZrP/ $I_2$  at various scan rates.

After discharging, the EI-ZrP/ $I_2$  cathode material underwent XPS measurement (Figure 3.14a). The formation of  $I^-$  suggests the 2-electron redox reaction in AZIB, i.e.,  $2I^- \leftrightarrow I_2 + 2e^-$ . To further investigate the superiority, coin-type cells are constructed. Different cathodes are assembled with C,  $\alpha$ -ZrP or EI-ZrP as additives. The smaller electrochemical polarization of the battery with EI-ZrP/ $I_2$  electrode indicates favorable redox kinetics and larger specific capacity during charging/discharging process (Figure 3.14b). The CV curves (Figure 3.14c) of the AZIB with EI-ZrP/ $I_2$  electrode at different scan rates (0.2, 0.4, 0.6, 0.8, and 1.0 mV/s) prove that the potential changes with increasing scan rates are small, thus demonstrating efficient redox chemistry. Additionally, CV curves of  $\alpha$ -ZrP/ $I_2$  electrode at various scan rates (Figure 3.14d) exhibit a larger shift in potential with increasing scan rate compared to those of EI-ZrP/ $I_2$  electrode, thus suggesting the higher redox reversibility of EI-ZrP/ $I_2$  cathode.

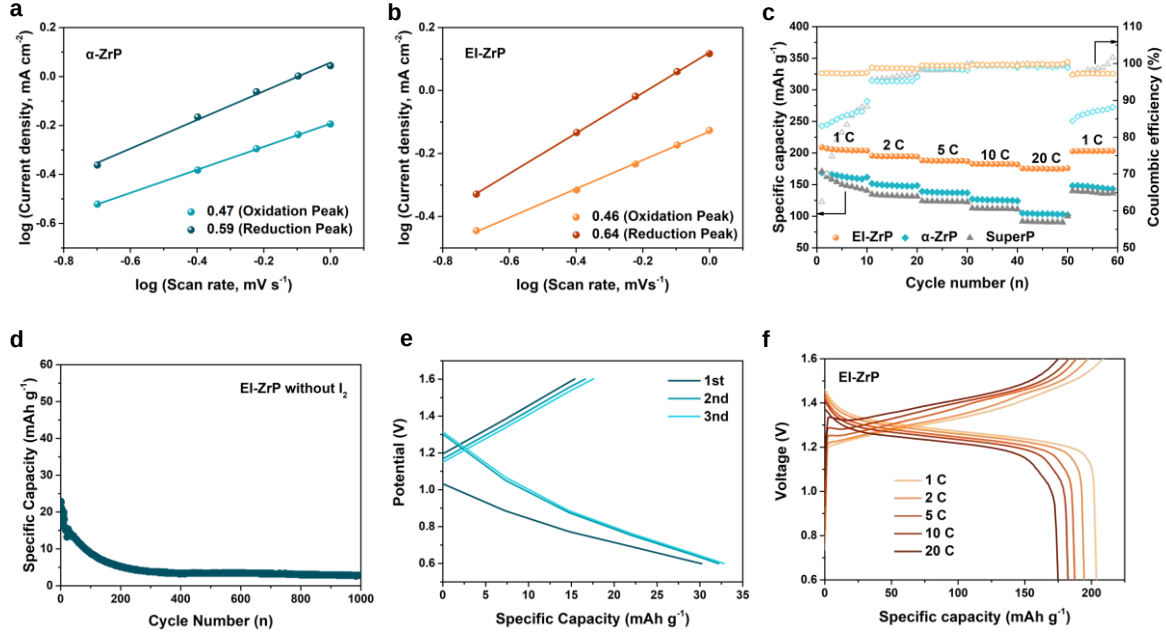


**Figure 3.15** Log  $i$  versus log  $v$  plots of the cathodic and anodic current response at the peaks shown in CV curves of (a) Figure 3.11b and (b) Figure 3.11c with  $b$  values marked. (c) Rate performance comparison of AZIBs with three cathodes. (d) Cycling performance & (e) GCD curves of EI-ZrP electrode without  $I_2$  at 10 C. (f) Galvanostatic charge-discharge (GCD) curves of AZIBs with EI-ZrP.

Furthermore, the electrode reaction kinetics is analyzed based on the relationship between current and scan rate (Figure 3.15a, 3.15b),<sup>152,153</sup> which suggests the diffusion-dominant battery behavior in all electrodes but the capacitive contribution for EI-ZrP/ $I_2$  is larger than that for  $\alpha$ -ZrP/ $I_2$ .

The electrode reaction process is analyzed based on the relationship between current ( $i$ ) and scan rate ( $v$ ) following the equation:

$$i = av^b \quad (8)$$

where  $i$  is the peak current,  $v$  is the potential sweep rate,  $a$  and  $b$  are adjustable parameters used to fit in the measured data points. The  $b$ -values are determined from the slopes of the log  $i$  - log  $v$  plots. A high redox efficiency and capacitive contribution will benefit the rate performance. Indeed, for both large and small discharge currents, the specific capacities achieved by AZIB with EI-ZrP/ $I_2$  are consistently higher than those with SuperP/ $I_2$ ,  $\alpha$ -ZrP/ $I_2$  electrodes (Figure 3.15c). When the current returns to 1 C, the AZIB with EI-ZrP/ $I_2$  cathode retains a specific capacity of 203.1 mAh g<sup>-1</sup>, which is close to the initial value of 203.8 mAh g<sup>-1</sup>, exhibiting good reversibility. The capacity originates from redox reaction with  $I_2$ , as our control experiment shows that the battery with pure EI-ZrP cathode (without  $I_2$ ) has a

negligibly small capacity of 3 mAh g<sup>-1</sup> (Figure 3.15d, 3.15e) without the redox reaction. Consistent with its high-rate performance, AZIB with EI-ZrP/I<sub>2</sub> also maintains a stable voltage plateau when operating with various rates from 1 C to 20 C (Figure 3.15f).

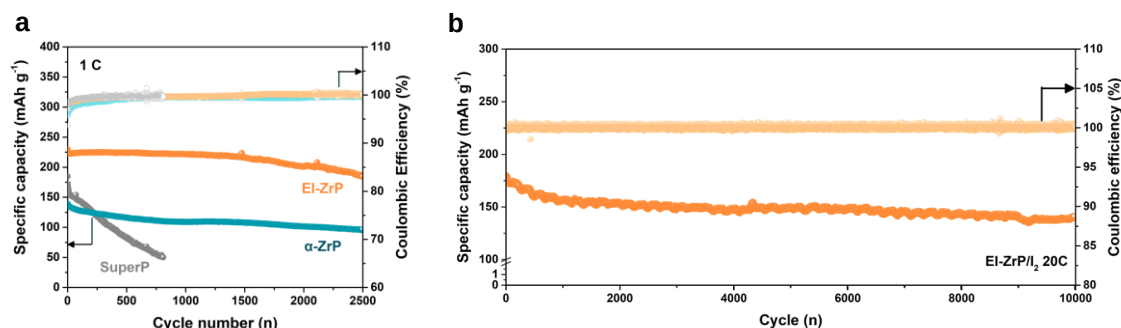


**Figure 3.16** (a) Specific capacity and coulombic efficiency of AZIBs with three cathodes at 1 C (1 C = 211 mAh g<sup>-1</sup>). (b) Specific capacity and coulombic efficiency of AZIB with EI-ZrP at 20 C.

The charging and discharging cycle performance of AZIBs are compared at 1 C (Figure 3.16a). Specific capacity around 205 mAh g<sup>-1</sup> at 1 C and almost 100% coulombic efficiency can be achieved with EI-ZrP/I<sub>2</sub> cathode, which is a significant improvement compared to the other two. At a higher current rate (20 C), the AZIB with EI-ZrP/I<sub>2</sub> cathode delivers a capacity of around 140 mAh g<sup>-1</sup> and stable coulombic efficiencies up to 10000 cycles (with a 0.02 % decay rate per cycle), indicating good cycling stability of the EI-ZrP/I<sub>2</sub> cathode (Figure 3.16b). AZIBs using EI-ZrP/I<sub>2</sub> cathode exhibited relatively better electrochemical performances with a moderate I<sub>2</sub> mass loading compared to previously reported works (Table 3.3).

**Table 3.3** Comparison of Zn-I<sub>2</sub> battery performance.

| Methods                                          | Specific capacity (mAh g <sup>-1</sup> ) | Cycle number | Current density | I <sub>2</sub> Mass loading (mg cm <sup>-2</sup> ) | I <sub>2</sub> Mass Ratio | Ref. |
|--------------------------------------------------|------------------------------------------|--------------|-----------------|----------------------------------------------------|---------------------------|------|
| Zn-I <sub>2</sub> /microporous carbon            | 143                                      | 3000         | 2C              | 0.75                                               | 40%                       | 154  |
| Zn-I <sub>2</sub> /PNC-1000                      | 200                                      | 10000        | 5 C             | 3.0                                                | 58%                       | 148  |
| Zn-I <sub>2</sub> /PBA                           | 165.6                                    | 1500         | 10C             | 1.8-2.0                                            | 80%                       | 123  |
| Zn-I <sub>2</sub> /B-Fe-NC                       | 170                                      | 10000        | 10C             | 1.0                                                | 70%                       | 155  |
| Zn-Ti <sub>3</sub> C <sub>2</sub> I <sub>2</sub> | 125                                      | 2800         | 14 C            | 1.0-1.5                                            | 70%                       | 156  |

|                                      |        |       |      |         |       |     |
|--------------------------------------|--------|-------|------|---------|-------|-----|
| Zn-I <sub>2</sub> /PB                | 206    | 1500  | 19 C | 0.5-2.0 | 80%   | 157 |
| Zn-I <sub>2</sub> (Zeolite Membrane) | 48.9   | 30000 | 19 C | 2.0-3.0 | 90%   | 158 |
| Zn-I <sub>2</sub> /GC-PAN            | 105.1  | 2000  | 20 C | 1.5-2.0 | 80%   | 159 |
| Zn-I <sub>2</sub> (VS additive)      | 164.22 | 40000 | 20 C | 2.5-2.8 | 33.3% | 127 |
| Zn-I <sub>2</sub> /ZrP               | 180    | 10000 | 20C  | 1.0     | 70%   |     |

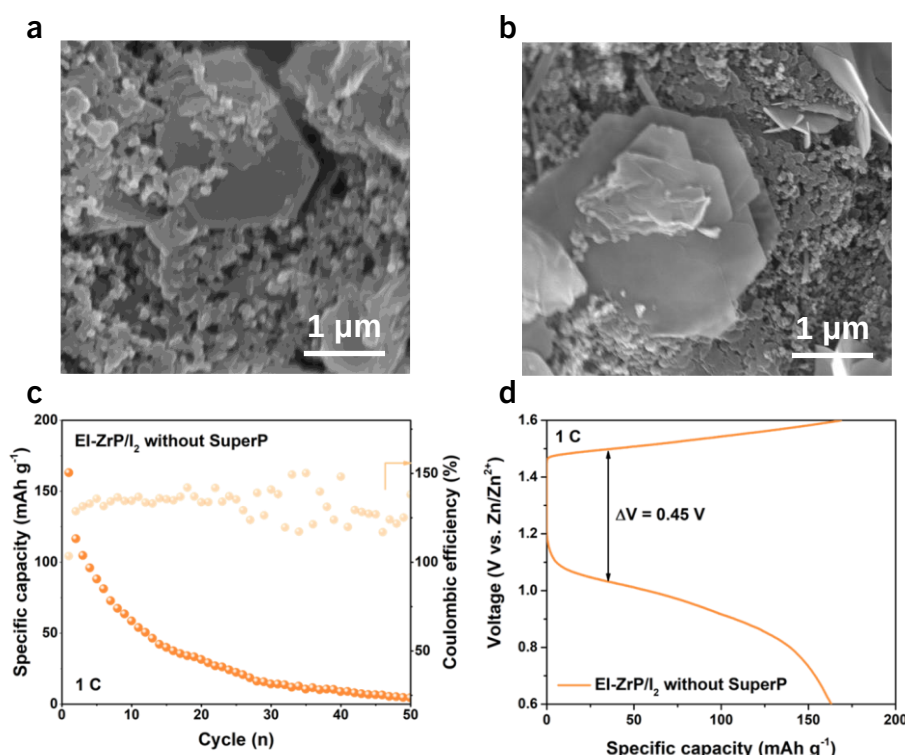


**Figure 3.17** SEM images of cathode material (a) before and (b) after cyclability test. (c) Specific capacity and coulombic efficiency and (d) Galvanostatic charge-discharge (GCD) curves of AZIBs with EI-ZrP/I<sub>2</sub> cathode but without SuperP at 1 C.

According to SEM observation of the cathode materials after long-term test (Figure 3.17a, b), the hexagonal nanoplate of EI-ZrP with smooth surfaces remains, implying that the EI-ZrP morphology has not changed during cycling. Furthermore, we assembled batteries using EI-ZrP as the cathode host without SuperP. The capacity is lower than that with EI-ZrP and SuperP and drops to nearly zero within 50 cycles (Figure 3.17c). Additionally, this battery gives a much larger electrochemical polarization (0.45 V) than that with the combination of EI-ZrP and SuperP (Figure 3.17d). The drawback of EI-ZrP is its poor conductivity, which needs to be compensated for by carbon material. Moreover, heating at 120 °C for 6 hours is a practical approach to evenly disperse iodine. However, when the SuperP is replaced by EI-ZrP, the high-

temperature treatment (120 °C for 6 hours) results in partial loss of the n-butylamine skeleton, causing structural collapse and shrinkage of the interlayer space. This will aggravate its function of polyiodide immobilization and transport of hydrated zinc ions. In conclusion, the carbon material (herein, SuperP) as the host is necessary to ensure high performance of the EI-ZrP based cathode.

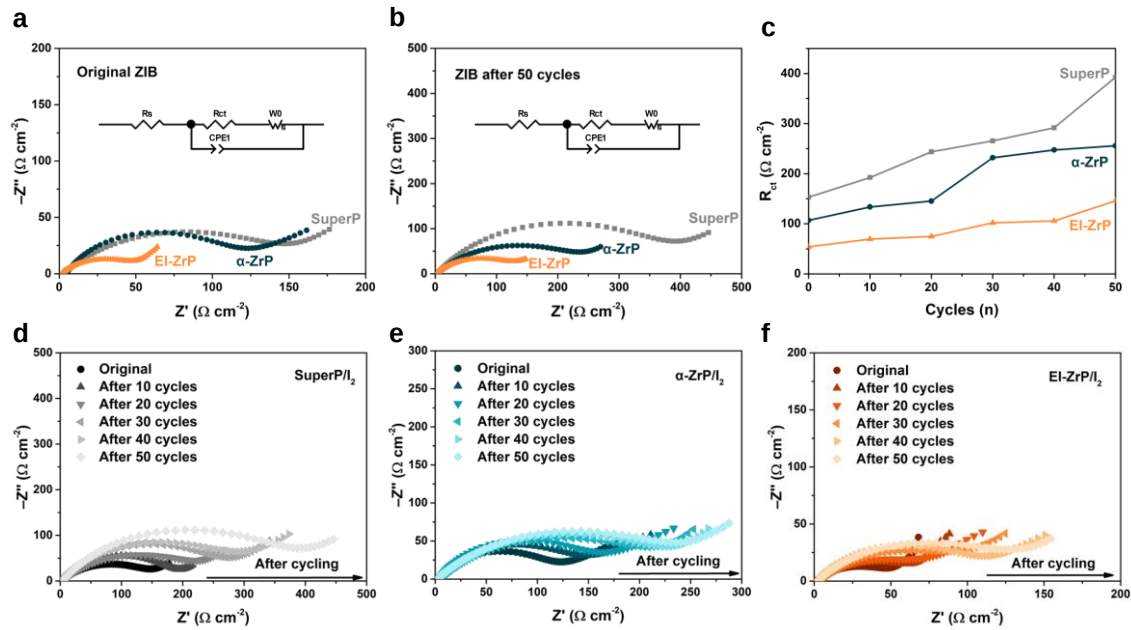


**Figure 3.18** (a, b) Nyquist plots before and after 50 cycles. (c) Comparison of  $R_{ct}$  after different cycles. The Nyquist plots of (d) C/I<sub>2</sub> (e)  $\alpha$ -ZrP/I<sub>2</sub> (f) EI-ZrP/I<sub>2</sub> after 0/10/20/30/40/50 cycles.

**Table 3.4** The fitting results of the EIS of Figure 3.18 d-f.

| Fitting result |        |                |             |
|----------------|--------|----------------|-------------|
|                | Cycles | $R_{ct}$ (ohm) | $R_s$ (ohm) |
| SuperP         | 0      | 152.9          | 2.708       |
|                | 10     | 192.4          | 2.362       |
|                | 20     | 243.8          | 2.174       |
|                | 30     | 265.5          | 3.994       |
|                | 40     | 291.6          | 3.187       |
|                | 50     | 392.6          | 3.972       |
| $\alpha$ -ZrP  | 0      | 106.8          | 4.573       |
|                | 10     | 133.6          | 4.391       |
|                | 20     | 145.2          | 3.849       |
|                | 30     | 231.9          | 2.805       |

|               |    |       |       |
|---------------|----|-------|-------|
|               | 40 | 247.5 | 2.527 |
|               | 50 | 255.8 | 2.34  |
| <b>EI-ZrP</b> | 0  | 53.97 | 1.324 |
|               | 10 | 69.4  | 2.800 |
|               | 20 | 74.84 | 2.177 |
|               | 30 | 101.9 | 2.583 |
|               | 40 | 105.6 | 2.579 |
|               | 50 | 145.8 | 2.894 |

The Nyquist plots of the EI-ZrP/I<sub>2</sub> electrode are further investigated after various cycles and compared with those of C/I<sub>2</sub> and  $\alpha$ -ZrP/I<sub>2</sub> (Figure 3.18, and Table 3.4). The Nyquist plots exhibit a similar shape. The charge transfer resistance (R<sub>ct</sub>) presents a semicircular arc in high-frequency domain and a straight line in low-frequency domain, which is related to ion diffusion. Among the three materials, EI-ZrP exhibits smaller R<sub>ct</sub> compared to C/ $\alpha$ -ZrP, which benefits the redox kinetics. The increase in the resistance of the battery with EI-ZrP for different cycles is also the smallest among the three electrode additives, which supports enhanced stability by EI-ZrP/I<sub>2</sub> (Figure 3.18c).

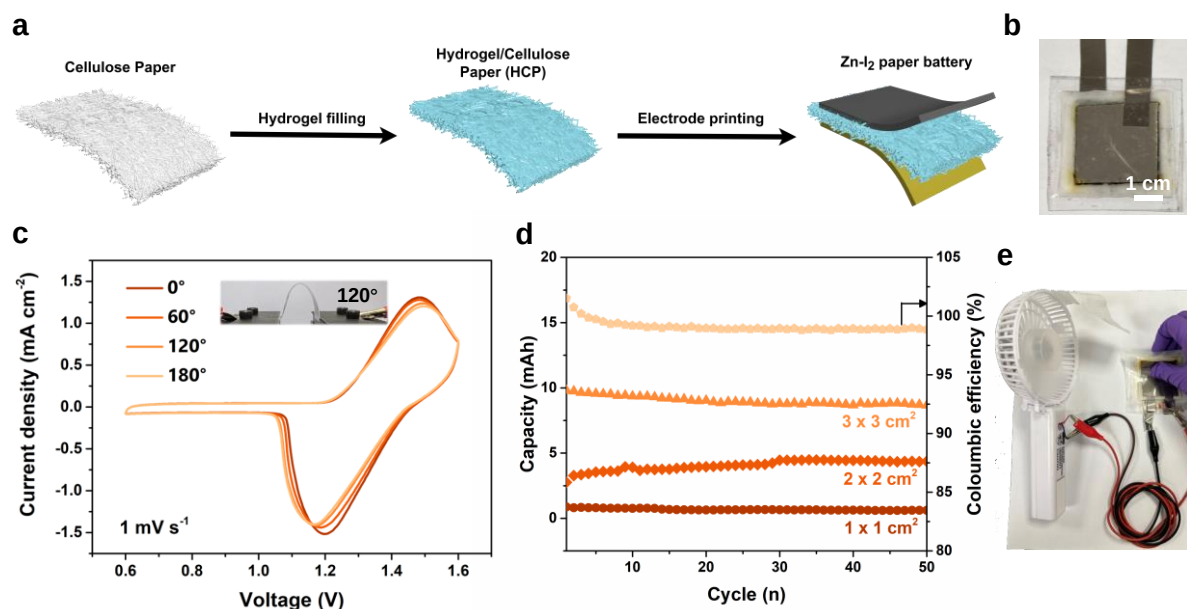


**Figure 3.19** Demonstration of flexible Zn-I<sub>2</sub> paper batteries with EI-ZrP cathodes. (a) Fabrication process of flexible battery based on cellulose paper. (b) Digital photo of a 3×3 cm<sup>2</sup> paper battery. Demonstration of flexible Zn-I<sub>2</sub> paper batteries with EI-ZrP cathodes. (c) CV curves under different bending angles and the digital photo of the paper battery under 120° bending (inset). (d) Capacities of flexible paper batteries with three sizes and the coulombic efficiency of the 3×3 cm<sup>2</sup> battery. (e) Demonstration of the power output of the 3×3 cm<sup>2</sup> flexible battery and its flexibility by driving a 4.5 W cooling fan under bending.

Flexible sensors with low energy consumption have been widely investigated in recent years.<sup>160-165</sup> A suitable energy supply is the bottleneck for general usage. A flexible paper battery, which employs EI-ZrP as the cathode additive, is assembled to demonstrate its potential for practical applications. The preparation process involves coating a slurry of EI-ZrP/I<sub>2</sub> onto titanium foil to achieve a cathode mass loading of approximately 4.6 mg I<sub>2</sub> cm<sup>-2</sup>. Zinc foil is used as the anode, while hydrogel cellulose paper (HCP) serves as the separator (Figure 3.19a, b). The HCP separator is composed of cellulose paper and hydrogel, which is synthesized using a previously reported procedure.<sup>104,147</sup> The assembly was then placed in 2 M ZnSO<sub>4</sub> electrolyte and packed with plastic film. The N/P ratio of the paper battery is measured to be around 1.2. The bending tests show that CV curves for the battery under different bending angles (0°, 60°, 120°, 180°) are barely affected, thus demonstrating mechanical reliability of the flexible paper battery (Figure 3.19c). Three paper batteries are fabricated with sizes of 1×1, 2×2, and 3×3 cm<sup>2</sup> to demonstrate stable energy output in desired sizes. The capacities of three paper batteries show a linear correlation with the sizes (Figure 3.19d). A 3×3 cm<sup>2</sup> paper battery can deliver sufficient power to drive a 4.5 W cooling fan (Figure 3.19e). It is noted that coulombic efficiency of the 3×3 cm<sup>2</sup> paper battery is way below unity. Possible reason is that the hydrogel-enhanced paper separator introduces high resistance, which even becomes worse after long runs due to imperfect contact with the electrodes. Further enhancement of the capacity and power requires careful optimization of the HCP separator.

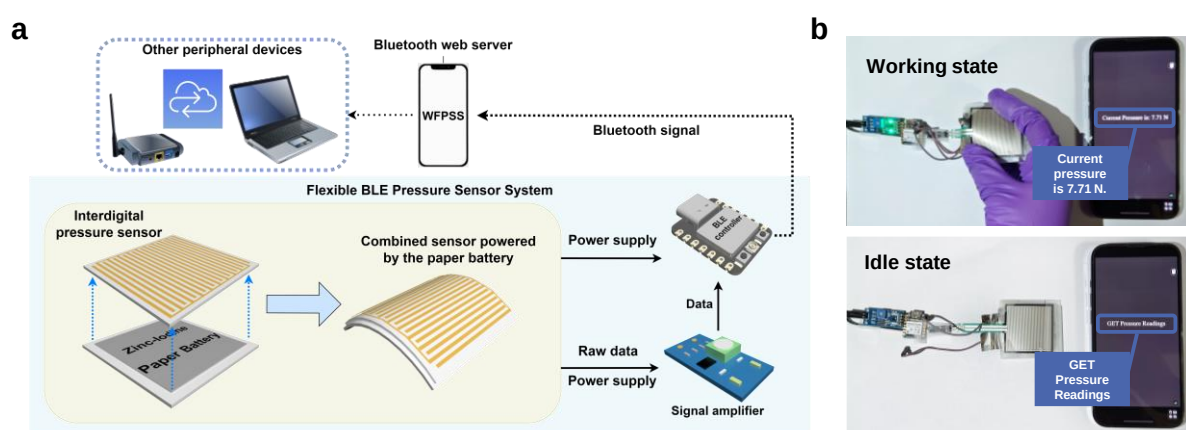


**Figure 3.20** Demonstration of flexible Zn-I<sub>2</sub> paper batteries with EI-ZrP cathodes. (a) Diagram of the wireless flexible pressure sensor system (WFPSS) and peripheral devices. (b) Demonstration of the flexible sensor system in working state and idle state under bending.

The flexible paper battery is further investigated for its ability to power a flexible pressure sensor, a Bluetooth Low Energy (BLE) platform and supporting circuits (Figure 3.20a). The WFPSS has great potential in the medical sensor industry for its safety, lightness, and low cost.

To power the system, three flexible paper-based batteries with EI-ZrP as the cathode additive are connected in series to push the output voltage level to around 3.6 V, which is required to power a micro controller unit (MCU) with a connected pressure sensor and circuits. The flexible battery is integrated with a pressure sensor, resulting in a combined device that maintains small thickness, low weight, and high flexibility. An nRF52840 BLE MCU is used to capture sensor data.<sup>166</sup> A built-in web server programmed on a smartphone platform is applied to receive data transmitted from the BLE MCU and display the change in pressure readings on a designed web page dynamically, for real-time monitoring. The flexible battery can support the whole wireless sensor system for continuous usage for over 30 min (Figure 3.20b).

### 3.5 Conclusion

In summary, this study proposed a ZIB with EI-ZrP/I<sub>2</sub> cathode. The interlayer expanded material not only offers abundant channels for efficient zinc ion transport but also exhibits a confinement effect on polyiodide to inhibit the shuttle effect. XRD results and microscope images demonstrate that the EI-ZrP/I<sub>2</sub> cathode material has a larger interlayer distance that can confine polyiodides and improve the effect of depressing the shuttle effect. The enhanced absorption of polyiodides is also supported by UV-vis spectroscopy tests and absorption energy calculations. The XPS results and DFT calculation of the EI-ZrP cathode provide solid support for its ability to facilitate the electron transfer between iodine and the cathode material, enhancing the redox kinetics. The expanded interlayer distance also leads to a larger diffusion coefficient (D) of Zn<sup>2+</sup>, thus supporting efficient ion transport. The proposed ZIB with an EI-ZrP /I<sub>2</sub> cathode exhibits great reversibility and desirable cycling performance. The paper-based ZIB with the EI-ZrP /I<sub>2</sub> cathode proves its capability of supporting a flexible BLE pressure sensor system, demonstrating the potential of the proposed flexible battery in portable electronics applications.

## Chapter 4 Flexible aqueous zinc-air battery with asymmetric kosmotropism-stabilized double-layer hydrogel

### 4.1 Challenges & Opportunities

The rapid advancement of wearable technology has underscored the pressing need for flexible batteries capable of providing high energy and power density.<sup>167</sup> Inherent safety risks and poor flexibility associated with commercial lithium-ion batteries cast doubts about their suitability for wearables.<sup>168,169</sup>

Zinc air batteries (ZABs) have attracted substantial interest for their promising energy density ( $1350 \text{ Wh kg}^{-1}$ ), safety,<sup>170</sup> and low production cost.<sup>171,172</sup> The currently achievable lifespan of ZAB in industrial scenarios is merely around 150 cycles, with a typical cycling energy efficiency of less than 60%.<sup>173</sup> The undesirable battery performance of ZAB is largely attributed to the prevalent use of liquid alkaline electrolytes,<sup>80</sup> which contribute to Zn deterioration and dendrites through water-induced parasitic reactions.<sup>77</sup> Irreversible by-products may also be generated due to side reactions between alkaline electrolytes and atmospheric carbon dioxide, resulting in electrolyte consumption and eventual pore clogging within cathode.<sup>174</sup> In particular, continuous electrolyte solution consumption is severe in alkaline ZABs.<sup>175</sup> Water is involved in the oxygen reduction reaction (ORR) on cathode<sup>176</sup> and evaporates over time, which increases the concentration of  $\text{Zn(OH)}_4^{2-}$  anions and accelerates anode degradation. Previous endeavors for alkaline ZABs have primarily focused on development of efficient catalysts for air cathode<sup>80,177-181</sup> and extending ZAB lifespan through anode structure design<sup>182</sup> or the use of additives in electrolytes.<sup>174,183-185</sup> However, these efforts have yielded very limited enhancement in battery performance.

Neutral electrolytes render opportunities to potentially relieve the detrimental effects associated with alkaline electrolytes.<sup>80</sup> Several important works have been reported on improving the stability and efficiency of neutral ZABs by engineering neutral electrolytes.<sup>176,181,186-188</sup> The Wang group reported a Zn-O<sub>2</sub>/zinc peroxide (ZnO<sub>2</sub>) chemistry which operates via a  $2\text{e}^-/\text{O}_2$  process in zinc trifluoromethanesulfonate ( $\text{Zn(OTf)}_2$ ) electrolyte.<sup>176</sup> Despite the high performance, the cost of  $\text{Zn(OTf)}_2$  compared to  $\text{ZnCl}_2$  and zinc acetate (13 times more expensive than  $\text{ZnCl}_2$  on *Sigma-Aldrich*) is a concern. Winter and colleagues reported a neutral ZAB based on reversible formation/decomposition of zinc hydroxyacetate dihydrate.<sup>187</sup> This electrolyte is relatively more cost effective, but the liquid

nature of zinc acetate electrolyte may pose a heightened risk of electrolyte leakage and liquid evaporation.

## 4.2 Comparative advantages

Recently, ionic compounds have been integrated into cellulose hydrogel networks, offering immense enhancement in capacity and energy/power density of zinc-ion capacitors.<sup>189,190</sup> Inspired by these breakthroughs, herein we have designed a kosmotropism-stabilized double-layer gel as quasi-solid neutral electrolyte for ZAB. This double-layer gel comprises a layer of  $\text{ZnCl}_2/\text{CaCl}_2$  cellulose hydrogel serving as the primary pathway for Zn ions, and an additional  $\text{ZnSO}_4$  polyacrylamide ( $\text{ZnSO}_4$  PAAM) hydrogel aimed at shielding Zn anode from passivation. Our ZAB featured with this dual-function gel electrolyte eliminates the use of separator (e.g., glass fiber), diminishes evaporation of liquid electrolytes, and renders device flexibility. The high battery performance is manifested by its extended durability (>800 hours), prolonged calendar life (stable discharging performance after resting for 336 hours), and high zinc utilization (89.3%). The feasibility of our low-cost neutral ZAB for practical applications is further substantiated through powering of a flexible, cost-effective, and lightweight GPS tracking device. In our trials, the ZAB-powered GPS devices work continuously for over 40 min. Our research underscores that ZABs with DLKgel exhibit superior performance, rendering them ideal for powering electronic devices as sustained and reliable flexible power sources.

## 4.2 Synthesis of materials

### 4.2.1 Preparation of $\text{ZnSO}_4$ Polyacrylamide (PAAM) hydrogel on Zn anode

$\text{ZnSO}_4$  PAAM hydrogel serves as a protective layer affixed to Zn anode within the DLKgel system, designed to shield the Zn anode from passivation caused by  $\text{ZnCl}_2$ . To fabricate this protective layer, a solution of  $\text{ZnSO}_4$  ( $2 \text{ mol L}^{-1}$ ) was blended with acrylamide solution ( $2 \text{ mol L}^{-1}$ ), incorporating a crosslinking agent ( $8 \times 10^{-4} \text{ mol L}^{-1}$  n,n'-methylenebis(acrylamide)) and an initiator ( $8 \times 10^{-4} \text{ mol L}^{-1}$  potassium persulfate). This composite mixture was then poured into a mold wrapped in plastic and affixed to a Zn foil substrate. Subsequent in-situ polymerization ensued by heating the amalgamation to  $60^\circ\text{C}$  under nitrogen protection for 6 hours, culminating in the fabrication of the ZAB Zn anode featuring the protective  $\text{ZnSO}_4$  layer.

#### **4.2.2 Preparation of Zinc chloride (ZnCl<sub>2</sub>) cellulose hydrogel**

ZnCl<sub>2</sub> cellulose gel is utilized to synthesize the double-layer distinct kosmotropism based gel (DLKgel) as the layer applied to air cathode. The synthesis process begins with the combination of 4.9 grams of ZnCl<sub>2</sub> with 1 mL of distilled water, heated to 65°C until a clear solution is achieved. While maintaining this temperature, 0.2 grams of cellulose filter paper (Whatman) and 0.1 grams of calcium chloride (CaCl<sub>2</sub>) are added to the solution and stirred until completely dissolved, resulting in a viscous mixture. Subsequently, the viscous solution is subjected to sonication to eliminate any bubbles, followed by the addition of 1 mL of distilled water to expedite gelation and generate the desired hydrogel.

#### **4.2.3 Preparation of potassium hydroxide (KOH) electrolyte**

The electrolyte was prepared by dissolving KOH in deionized water. The concentration of the KOH electrolyte for the zinc-air cells was 6 m (m, mol kg<sup>-1</sup>).

#### **4.2.4 Preparation of air cathode**

In the process of preparing the air cathode, a paste was created by thoroughly mixing 0.9 g of carbon black and 0.1 g of polytetrafluoroethylene (PTFE) binder (a dispersion of 60 wt% in H<sub>2</sub>O), along with approximately 3 ml of isopropanol, in a mortar. This paste was then uniformly applied onto a piece of carbon cloth, acting as a gas diffusion layer. After the coating procedure, the air cathode was left to rest at room temperature for 24 hours to facilitate the evaporation of isopropanol.

#### **4.2.5 Preparation of ZAB with DLKgel**

The manufacturing process of the ZAB utilizing DLKgel is demonstrated schematically in Figure 4.1b. Initially, ZnSO<sub>4</sub> PAAM hydrogel was applied onto the Zn anode via in-situ polymerization. Following this, the prepared ZnCl<sub>2</sub> cellulose gel was layered onto the ZnSO<sub>4</sub> PAAM layer, creating the double-layer structure characteristic of DLKgel. Lastly, the air cathode was coated onto the ZnCl<sub>2</sub> cellulose hydrogel layer, resulting in the production of ZAB with DLKgel electrolyte. This entire fabrication process is both straightforward and expeditious, making it highly suitable for large-scale industrial production.

#### 4.2.6 Characterizations

Morphological analyses were performed on a scanning electron microscope (SEM, JEOL FESEM 7600F) with an energy-dispersive X-ray spectroscopy (EDS) detector. X-ray diffraction (XRD) was operated on a Bruker XRD analyzer (D8 ADVANCE). Fourier Transform Infrared (FTIR) was conducted on an FTIR Spectrometer (PerkinElmer L1280034).

#### 4.2.7 Electrochemical Characterizations

ZABs were fabricated employing Zn foil as anode, air cathode, and either ZnCl<sub>2</sub> cellulose gel, ZnSO<sub>4</sub> PAAM gel or DLKgel as the electrolyte in a sandwiched configuration, with titanium foil serving as the current collector. Batteries underwent testing under fixed current densities (0.1, 0.5, 1 mA cm<sup>-2</sup>) and a fixed capacity (1 mAh cm<sup>-2</sup>) mode. Cycling stability was evaluated using LAND battery testing system (CT3002AU, 5 V 2 mA & 20 mA, Wuhan, China). A CHI 760D was utilized to assess electrochemical impedance spectroscopy (EIS), covering a frequency range from 100 kHz to 10 MHz, with an applied alternating current amplitude of 5 mV. The ionic conductivity of electrolytes was tested via EIS measurement, wherein the electrolytes including DLKgel, ZnCl<sub>2</sub> cellulose gel, and ZnSO<sub>4</sub> PAAM were sandwiched between two stainless steel spacers. Galvanostatic charge-discharge tests were conducted using the LAND battery testing system.

### 4.3 Results and discussion

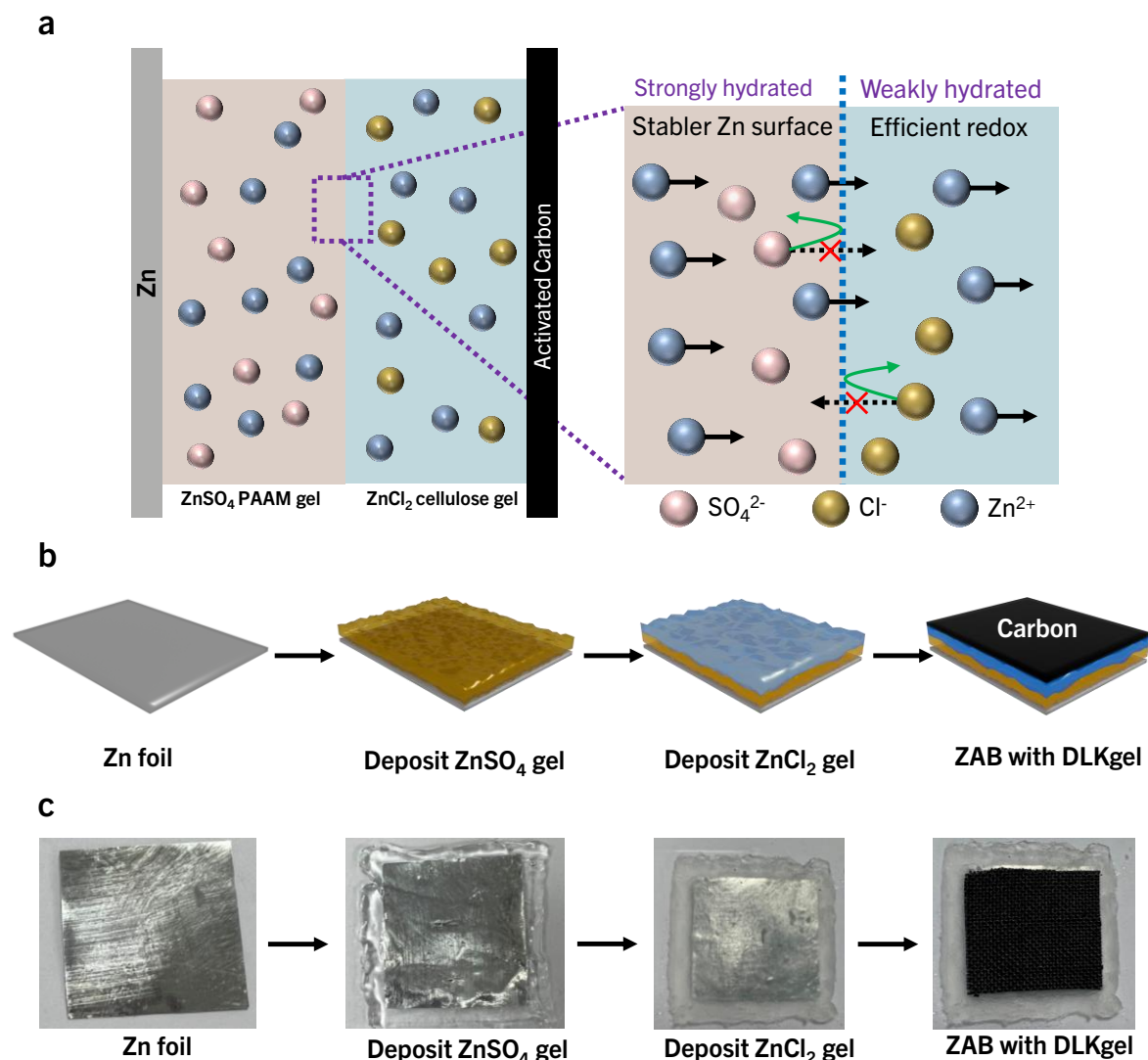


**Figure 4.1** Design of aqueous ZAB with double-layer DLKgel. (a) (Left) Structure of double-layer gel electrolyte, with  $\text{ZnSO}_4$  PAAM gel facing the Zn anode side while the  $\text{ZnCl}_2$  cellulose gel facing the activated carbon cathode side. (Right) DLKgel adopts the advantages of both gels and limits their drawbacks, enabling stabler Zn surface and achieving efficient redox through phase separation. (b) Schematic of synthesis process and (d) digital images of real fabrication process from Zn foil to ZAB with DLKgel.

As illustrated in Figure 4.1a, our battery comprises two neutral electrolytes ( $\text{ZnCl}_2$  and  $\text{ZnSO}_4$ ), forming a distinct double-layer kosmotropism based gel (DLKgel) that leverages the divergent kosmotropic properties of these anions to segregate the gel into two discrete layers. This innovation is rooted.<sup>191,192</sup> The design effectively mitigates potential adverse reactions that may arise from inadvertent exposure of the two electrolytes to electrodes. In contrast to conventional alkaline electrolyte or pure  $\text{ZnSO}_4$  electrolyte configurations, the non-alkaline  $\text{ZnCl}_2$  cellulose hydrogel electrolyte near the air cathode can enhance the zinc utilization by

minimizing the formation of irreversible by-products, for example, potassium carbonate  $[K_2CO_3]$  in  $KOH$ <sup>173</sup> and zinc sulfate hydroxide  $[Zn_4(OH)_6SO_4 \cdot 0.5H_2O]$  (ZHS) in  $ZnSO_4$ <sup>176</sup>, thereby improving redox efficiency, maintaining cycling stability, and extending lifespan of ZABs.

Additionally, the moderate-concentration  $ZnCl_2$  maintains a high ionic conductivity, thus avoiding the issues associated with high-concentration aqueous electrolytes.<sup>193-195</sup> The function of  $ZnSO_4$  PAAM layer in our DLKgel acts as a protective barrier to prevent direct interaction between  $ZnCl_2$  gel and Zn anode.  $ZnSO_4$  is preferred because of the stable anionic structure of  $SO_4^{2-}$  and its good compatibility with Zn anodes by in situ polymerization will contribute to a stable Zn surface.<sup>196,197</sup> It is crucial as the utilization of moderate-concentration  $ZnCl_2$  often results in severe passivation on the Zn electrode,<sup>198-200</sup> which reduces active reaction sites on Zn anode and hampers electrode conductivity.<sup>80,199,201</sup>

The fabrication process of DLKgel using  $ZnCl_2$  cellulose hydrogel and  $ZnSO_4$  PAAM hydrogel is straightforward and conducted at ambient conditions (schematic in Figure 4.1b, digital images showed in Figure 4.1c, detailed in sub-chapter 4.2).  $ZnSO_4$  PAAM hydrogel was applied onto Zn foil anode through in situ polymerization.<sup>104,177,202</sup> Subsequently,  $ZnCl_2$  cellulose hydrogel was put on top of  $ZnSO_4$  PAAM layer to form the double-layer structure of DLKgel. Air cathode was coated onto  $ZnCl_2$  layer as the last step of the production. The DLKgel also serves as a separator, rendering an advantage to the conventional ZABs that require a membrane separator.

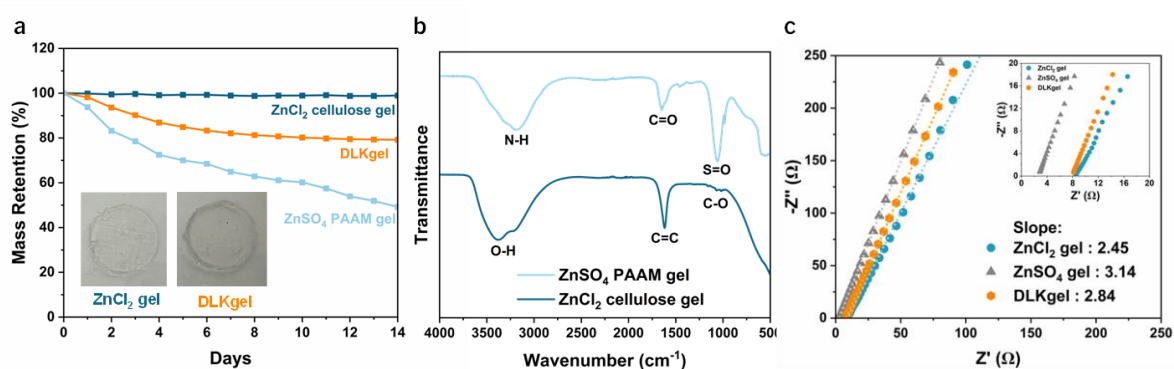


**Figure 4.2** (a) Comparison of mass retention in two weeks and photos of DLKgel,  $ZnSO_4$  PAAM and  $ZnCl_2$  cellulose gels. (b) Fourier transform infrared spectroscopy (FT-IR) results of  $ZnSO_4$  PAAM gel and  $ZnCl_2$  cellulose gel. (c) Impedance fitting results of  $ZnCl_2$  gel,  $ZnSO_4$  gel, and DLKgel. Inset is a zoomed view in the range of 0-50 Ω.

The DLKgel demonstrates superior water retention capabilities compared to conventional neutral electrolytes, owing to the strong water absorption properties of  $ZnCl_2$  hydrogel.<sup>203</sup> The

masses of DLKgel, ZnCl<sub>2</sub> cellulose gel (referred as ZnCl<sub>2</sub> in the following content), and ZnSO<sub>4</sub> PAAM gel (referred as ZnSO<sub>4</sub> in the following content) were assessed before and after a two-week resting period at 20 °C (Figure 4.2a). ZnCl<sub>2</sub> gel maintains 98.9% weight after the resting period due to its high water-absorption capacity. DLKgel experienced a modest mass loss, retaining 79.2% of its original weight after the resting period. In contrast, ZnSO<sub>4</sub> gel lost over 50.8% of its mass after two weeks of resting, underscoring the effective inhibition of water evaporation with the double-layer design.

The FT-IR spectra of ZnCl<sub>2</sub> gel and ZnSO<sub>4</sub> gel identified strong peaks representing existence of functional groups corresponding to cellulose and PAAM (Figure 4.2b). The impedance fitted plot of DLKgel falls between those of ZnCl<sub>2</sub> gel and ZnSO<sub>4</sub> gel (Figure 4.2c). The slope of fitted line for DLKgel is 2.84, greater than that of ZnCl<sub>2</sub> gel (2.45) and smaller than ZnSO<sub>4</sub> gel (3.14), indicating that the diffusion impedance of DLKgel originates from both of its constituent materials. A moderate solution resistance of DLKgel could also be observed from the inset of Figure 4.2c. The ionic conductivity of ZnSO<sub>4</sub> gel, ZnCl<sub>2</sub> gel, DLKgel are 11.1, 3.7, 3.9 mS cm<sup>-1</sup>, respectively. These impedance properties ensure that conductivity of DLKgel is not severely sacrificed by double-layer structure.

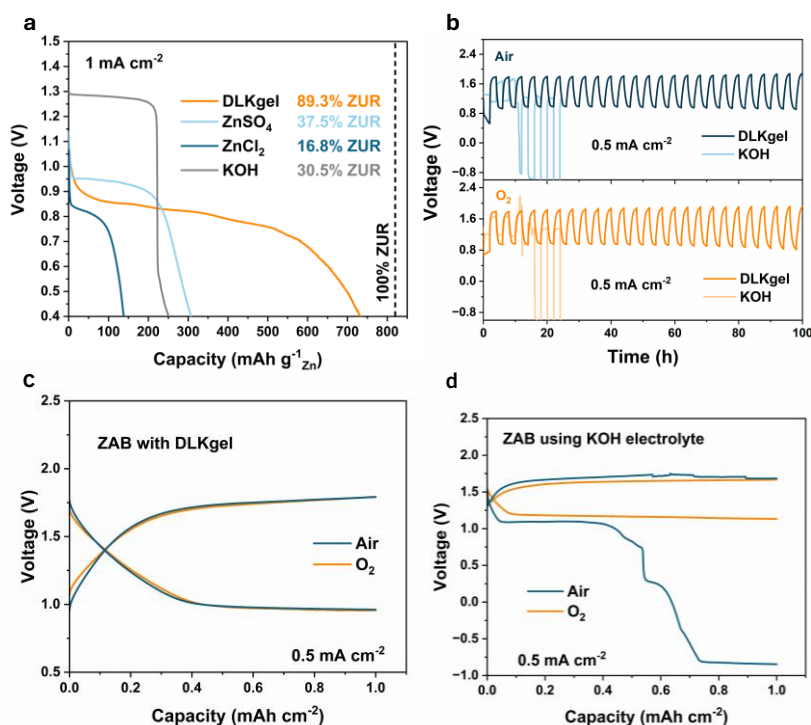


**Figure 4.3** (a) Galvanostatic discharge profiles of ZABs in liquid KOH, ZnSO<sub>4</sub> gel, ZnCl<sub>2</sub> gel, and DLKgel electrolytes at 1 mA cm<sup>-2</sup> (cutoff voltage: 0.4 V). The zinc utilization rates (ZURs) are calculated from the capacity axis. (b) Galvanostatic charge/discharge profiles of ZABs in liquid KOH and DLKgel electrolytes at 0.5 mA cm<sup>-2</sup> under air and O<sub>2</sub> atmosphere. Galvanostatic voltage profiles of ZAB using (c) DLKgel and (d) KOH at a current density of 0.5 mA cm<sup>-2</sup> under air and O<sub>2</sub> atmosphere.

To demonstrate the superiority of DLKgel in increasing Zn utilization rate of ZABs, ZAB with DLKgel electrolyte has been prepared for comparison against ZABs employing commonly used electrolytes including liquid KOH, ZnSO<sub>4</sub> gel and ZnCl<sub>2</sub> gel electrolytes. One-cycle discharging experiments are conducted on the ZABs with four different electrolytes, and their galvanostatic discharge profiles are compared. Notably, ZAB employing DLKgel exhibits an extended discharging capacity (732 mAh g<sup>-1</sup><sub>Zn</sub> at a cut-off voltage of 0.4 V, twice as much as the best performer among the others) along with a stable discharge plateau (Figure 4.3a). The remaining three ZABs are below 308 mAh g<sup>-1</sup><sub>Zn</sub> at the cut-off voltage of 0.4 V. The superior Zn utilization rate (89.3%) demonstrated in depth of discharge serves as compelling evidence that DLKgel has contributed to prolonged discharging duration and increased energy density of ZAB. The high Zn utilization rate of DLKgel exceeds those in previously reported works (Table 4.1). Herein, the adverse effect of ZHS-generating reaction on air cathode is limited by preventing direct contact between ZnSO<sub>4</sub> gel layer and air cathode, contributing to increased Zn utilization rate.

**Table 4.1** Comparison of neutral ZAB batteries' performance.

| Methods                                                              | Catalyst                                                                 | Zn utilization (%) | Lifespan (hour)  | Current (mA cm <sup>-2</sup> ) | Ref |
|----------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------|------------------|--------------------------------|-----|
| PBS-derived neutral electrolyte                                      | Fe-N-C                                                                   | N.A.               | 26 (156 cycles)  | 1                              | 180 |
| Cathode electrocatalyst and gel electrolyte                          | Porous N-doped carbon tubes                                              | 76.2% at 60°C      | 50               | 2                              | 204 |
| Zn(OTf) <sub>2</sub> electrolyte                                     | No                                                                       | 83.1%              | 160 (320 cycles) | 1                              | 176 |
| Zinc acetate electrolyte                                             | No                                                                       | N.A.               | 60 (30 cycles)   | 1                              | 187 |
| Cathode electrocatalyst and NH <sub>4</sub> Cl/KCl electrolyte       | Fe <sub>SA+NC</sub> @NMPC                                                | N.A.               | 100 (600 cycles) | 5                              | 205 |
| Zinc/carbon nanotube fiber anode                                     | Pt and RuO <sub>2</sub>                                                  | 78.7%              | 35 (70 cycles)   | 0.04                           | 206 |
| Electrocatalyst and NH <sub>4</sub> Cl/KCl electrolyte               | NMCS-rGO-Co                                                              | N.A.               | 70 (420 cycles)  | 5                              | 207 |
| Electrocatalyst and NH <sub>4</sub> Cl/ZnCl <sub>2</sub> electrolyte | MnS <sub>0.10</sub> O <sub>1.90</sub> /Mn Co <sub>2</sub> S <sub>4</sub> | N.A.               | 140 (840 cycles) | 10                             | 208 |

|        |    |       |                 |     |           |
|--------|----|-------|-----------------|-----|-----------|
| DLKgel | No | 89.3% | 800 (40 cycles) | 0.1 | This work |
|        | No |       | 120 (60 cycles) | 1   | This work |

Figure 4.3b presents a comparative analysis of performances of ZABs with liquid KOH electrolyte and DLKgel in pure O<sub>2</sub> and air conditions. Substituting air with pure O<sub>2</sub> prolonged the lifespan of the KOH-based ZAB to over twelve hours. This is because the parasitic reactions between KOH electrolyte and atmospheric CO<sub>2</sub> in conventional alkaline ZABs are avoided. The susceptibility of alkaline electrolytes to CO<sub>2</sub> is also indicated by the fluctuation of the operating voltage of the KOH-based ZAB. In contrast, the DLKgel ZAB exhibits consistent results in both air and pure O<sub>2</sub> conditions. This consistency can also be seen from the galvanostatic charge/discharge (GCD) results of the second cycle (Figure 4.3c). In contrast, the charging and discharging capabilities of ZAB with KOH electrolyte experience notable degradation in ambient air (Figure 4.3d).

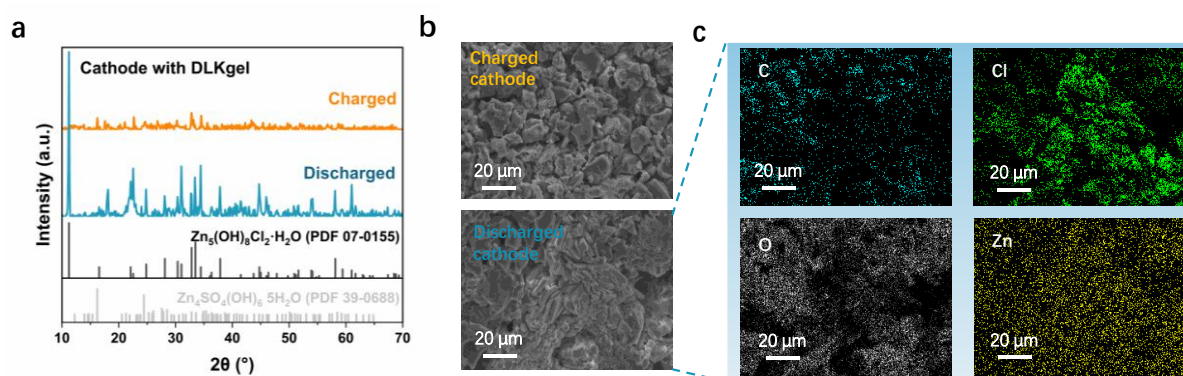


**Figure 4.4** (a) XRD patterns and (b) SEM images of air cathode obtained after charge and discharge with DLKgel, along with SEM mapping of discharged cathode (c) PDF: powder diffraction file, C: Carbon; Cl: Chlorine, O: Oxygen, Zn: Zinc.

As revealed by XRD results (Figure 4.4a), Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>·H<sub>2</sub>O (ZHC) was formed on air cathode due to participation of H<sub>2</sub>O in ORR during the discharging process, similar to the formation of ZHS in pure ZnSO<sub>4</sub> electrolyte. However, the formed ZHC on air cathode is not considered to have similar detrimental influence as ZHS, due to the intrinsic electron conductivity of ZHC as a semiconductor.<sup>209</sup> As demonstrated in XRD results of charged and discharged air cathodes, the patterns matching ZHC disappeared on the air cathode after the battery was recharged, proving that ZHC participated in the charging process and demonstrated desirable electrochemical reversibility. The absence of ZHS in the XRD profile of air cathode also indicated that phase separation, induced by the difference in kosmotropic property of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions, efficiently inhibited SO<sub>4</sub><sup>2-</sup> anions from reaching the air cathode. Thus,

reversible formation/decomposition of ZHC can be established during cycling in DLKgel electrolyte. The formed ZHC had a rhombohedral shape within the scale of micrometers according to SEM results (Figure 4.4b). The SEM mappings revealed the uniform distribution of Zn compounds on cathode surface (Figure 4.4c).

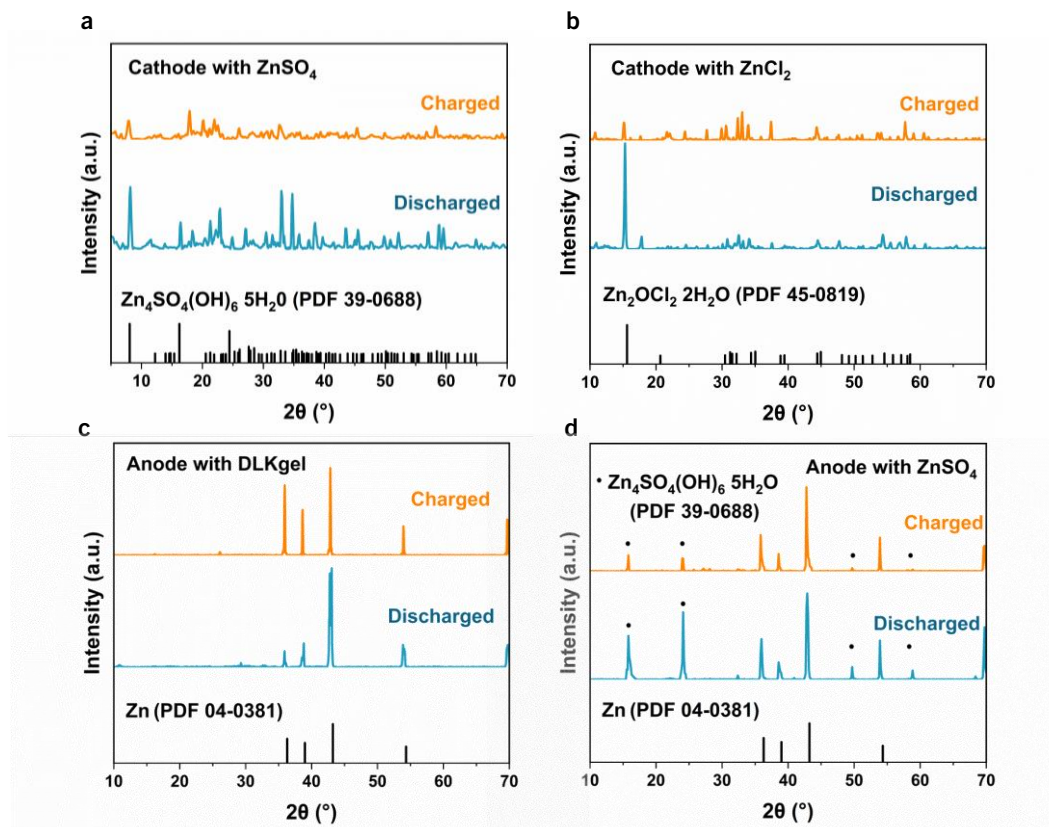


**Figure 4.5** XRD patterns of air cathodes obtained after charge and discharge with (a)  $\text{ZnSO}_4$  gel and (b)  $\text{ZnCl}_2$  electrolytes. And XRD patterns of zinc anode in ZAB after charging/discharging with two different electrolytes. (c) DLKgel electrolyte; (d)  $\text{ZnSO}_4$  gel electrolyte.

In contrast, when  $\text{ZnSO}_4$  electrolyte was used, the formation of ZHS on the air cathode was observed, resulting in irreversible by-products (Figure 4.5a). In ZAB using  $\text{ZnCl}_2$  gel,  $\text{ZnCl}_2$  will directly contact the zinc anode and induce water-consuming corrosion reactions on the anode.<sup>210</sup> Under a water-deficient environment,  $\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$  forms on the cathode instead of ZHC,<sup>211</sup> as supported by XRD patterns (Figure 4.5b). The efficiency of DLKgel in inhibiting generation of ZHS is further suggested through XRD profiles of the Zn anode. Pattern of by-product was absent on Zn anode after ZAB using DLKgel electrolyte was discharged (Figure 4.5c). Originating from the even stronger kosmotropic property of  $\text{OH}^-$  than  $\text{SO}_4^{2-}$ ,<sup>212</sup> the additionally generated phase separation between  $\text{OH}^-$  and  $\text{Cl}^-$  near air cathode could inhibit the potential pathway of  $\text{OH}^-$  anion from  $\text{ZnCl}_2$  gel layer to  $\text{ZnSO}_4$  gel layer during discharging.

In contrast, ZHS pattern was in the anode XRD patterns obtained from ZAB utilizing  $\text{ZnSO}_4$  electrolyte (Figure 4.5d).

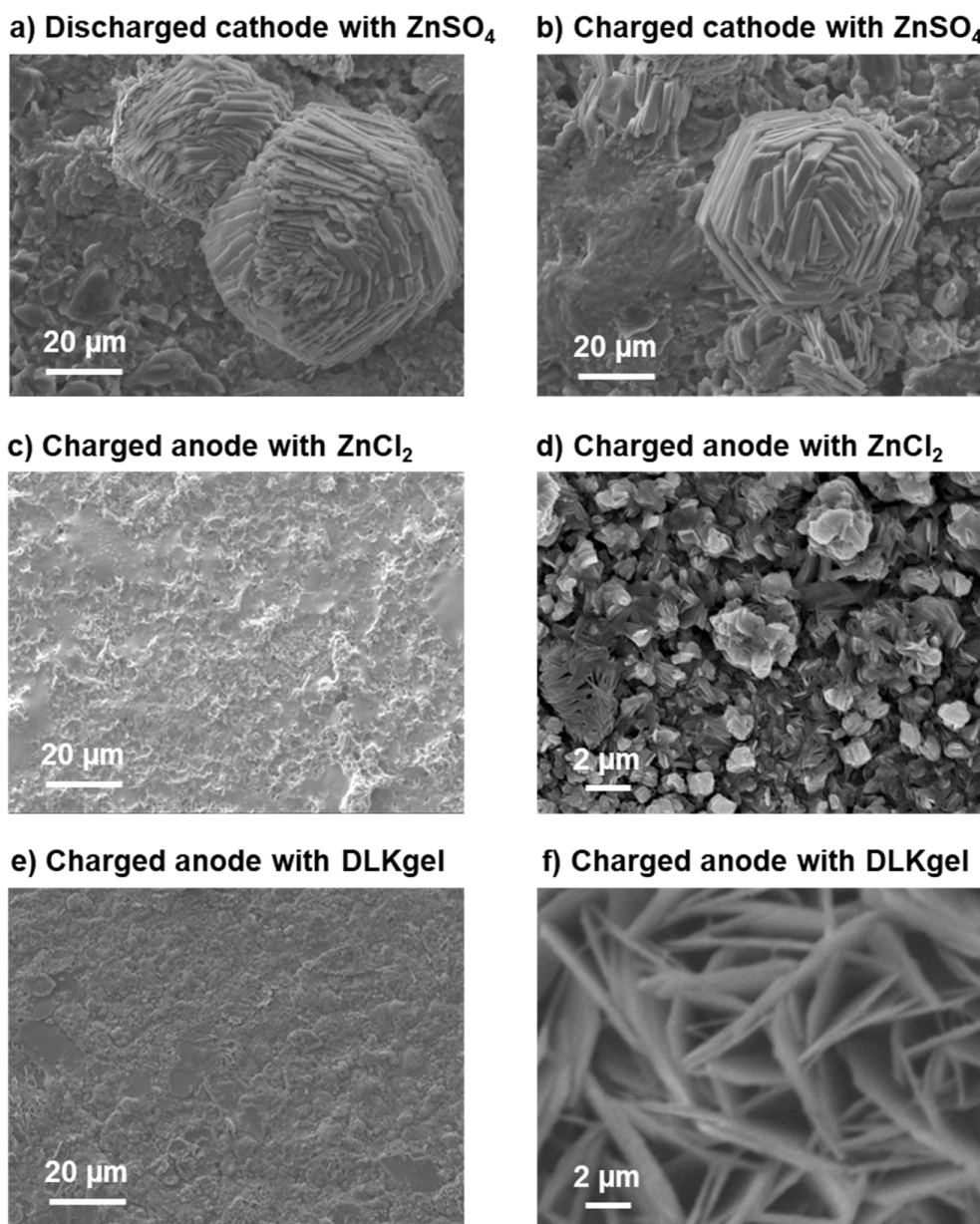


**Figure 4.6** SEM images of air cathode and Zn anode obtained after charging and discharging in ZAB with DLKgel,  $\text{ZnCl}_2$ , and  $\text{ZnSO}_4$  electrolytes. (a & b) Air cathode obtained after charging/discharging with  $\text{ZnSO}_4$ . (c & d) Charged Zn anode with  $\text{ZnCl}_2$ . (e & f) Charged Zn anode with DLKgel.

SEM observations of air cathode and Zn anode after charging and discharging show large-scale agglomeration of ZHS in ZAB with  $\text{ZnSO}_4$  electrolyte (Figure 4.6a). After ZAB was recharged, ZHS could still be observed, indicating its poor reversibility (Figure 4.6b). A chaotic and uneven distribution of crystal structures on anode surface was observed upon recharging of ZAB with  $\text{ZnCl}_2$  electrolyte (Figure 4.6c, d), indicative of passivation on Zn anode. In comparison, the charged anode surface of ZAB using DLKgel demonstrated better uniformity

and well-crystallized structure (Figure 4.6e, f), implying effective protection of DLKgel on Zn anode of ZAB.

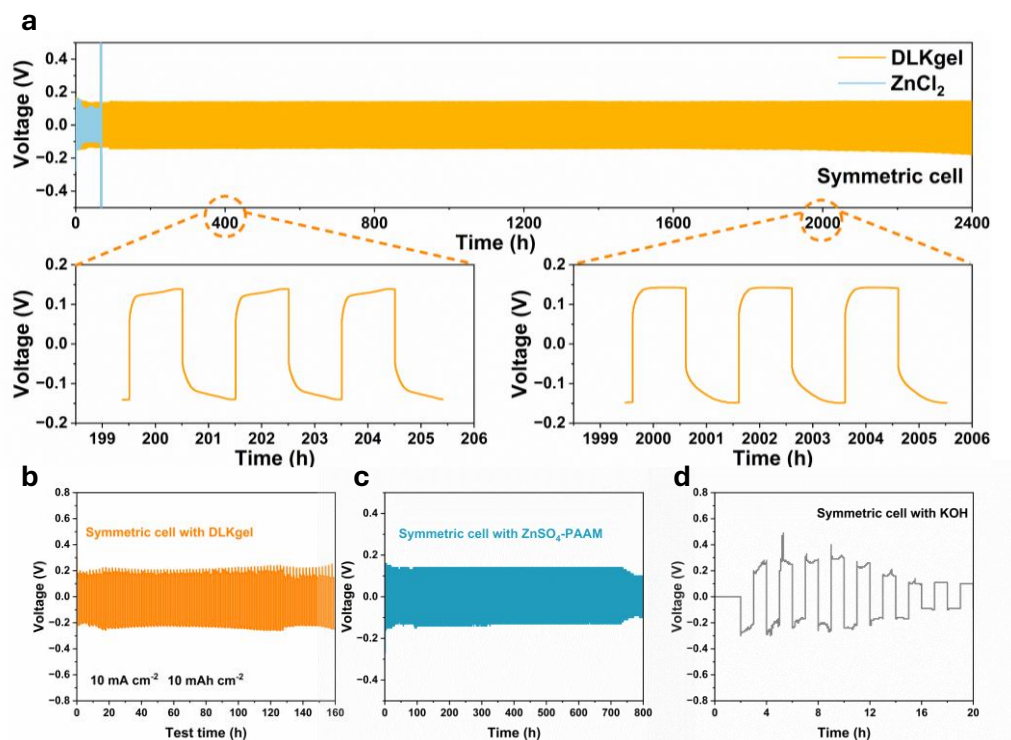


**Figure 4.7** Effect of electrolytes on Zn anode protections. Comparison of long-time cycling performances of Zn || Zn symmetric cells with (a) DLKgel and ZnCl<sub>2</sub> electrolytes at a current density of 2 mA cm<sup>-2</sup> and a capacity of 2 mAh cm<sup>-2</sup>. (b) Long-time cycling performance of Zn-to-Zn symmetric cell using DLKgel at a fixed current density of 10 mA cm<sup>-2</sup> and a constant capacity of 10 mAh cm<sup>-2</sup>, and symmetric cells using (c) ZnSO<sub>4</sub> gel electrolyte (d) KOH electrolyte at a current density of 2 mA cm<sup>-2</sup> and a capacity of 2 mAh cm<sup>-2</sup>.

DLKgel functions as an effective protection of Zn anode through separation between anode material and ZnCl<sub>2</sub> gel electrolyte using ZnSO<sub>4</sub> layer. To approve the extended battery long-term stability, a Zn-to-Zn symmetric cell using DLKgel is assembled to investigate the protection effect on Zn anode provided by the ZnSO<sub>4</sub> hydrogel. Symmetric cells with ZnCl<sub>2</sub>, ZnSO<sub>4</sub>, and KOH electrolytes were also fabricated for comparison (Figure 4.7). As depicted in Figure 4.7a, the symmetric cell with DLKgel sustains its operation for over 2400 hours (equivalent to 1200 cycles) at a constant current density of 2 mA cm<sup>-2</sup> and a fixed capacity of 2 mAh cm<sup>-2</sup>, with consistent output profiles observed both at 400 hours and 2000 hours. A stable charging and discharging voltage plateau occurs at 0.14 V and -0.14 V, affirming the superiority of the designed electrolyte (Inset of Figure 4.7a). DLKgel reduces dendrite-induced short circuits by maintaining uniform Zn plating and stripping. This directly contributes to the stable cycling performance observed over 2400 hours in Figure 4.7a. Suppression of DLKgel on Zn corrosion also contributes to the extended stability. At a higher current density of 10 mA

$\text{cm}^{-2}$  and capacity of  $10 \text{ mAh cm}^{-2}$ , the lifespan of symmetric cell exceeds 160 hours (Figure 4.7b), indicating the feasibility of DLKgel for fast charging and discharging applications. Conversely, the symmetric cell with  $\text{ZnCl}_2$  electrolyte (Figure 4.7a) degrades evidently since 15 hours with significant divergence after 65 hours. The symmetric cell with  $\text{ZnSO}_4$  electrolyte (Figure 4.7c) shows better cycling performance (cycle for around 700 hours) than the symmetric cell with  $\text{ZnCl}_2$ , due to the better compatibility of  $\text{SO}_4^{2-}$  to Zn anode. The superiority of DLKgel over  $\text{ZnSO}_4$  gel can be attributed to the cellulose gel component, which inhibits zinc dendrite formation through homogenization of  $\text{Zn}^{2+}$  ion flux and promotion of  $\text{Zn}^{2+}$  ion transfer.<sup>213,214</sup> Symmetric cell using the common liquid KOH gives the worst cycle performance among all four batteries (Figure 4.7d), mainly because of zinc electrode passivation and formation of dendrites.<sup>215</sup>

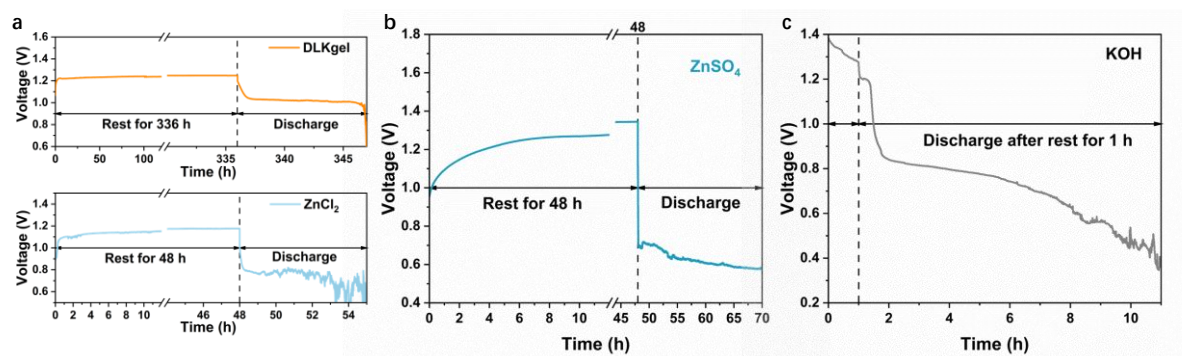


**Figure 4.8** Calendar aging effect for ZABs using (a-down)  $\text{ZnCl}_2$  (48-hour rest before discharge), (a-up) DLKgel (336-hour rest before discharge), (c)  $\text{ZnSO}_4$  (48-hour rest before discharge), and (d) KOH (1-hour rest before discharge) electrolytes.

Calendar aging strongly affects stability of aqueous batteries. The aging effects for ZABs utilizing  $\text{ZnCl}_2$  (resting for 48 hours before discharge) and DLKgel (resting for 336 hours before discharge) electrolytes discharge at a low current of  $0.1 \text{ mA cm}^{-2}$  are compared (Figure 4.8a). The ZAB using DLKgel maintained a stable open current voltage after a 336-hour rest period (equivalent to 14 days), followed by a consistent discharge plateau at approximately 1.0 V. In contrast, following only 48-hour rest, the ZAB with  $\text{ZnCl}_2$  electrolyte exhibited a radically reduced and uneven discharge voltage plateau and noticeable capacity degradation, indicative of inferior stability due to corrosion of Zn anode during the resting period. As for ZAB using  $\text{ZnSO}_4$ , it shares a similar trend with the  $\text{ZnCl}_2$  electrolyte, where the deterioration is due to relatively weak hydrophobicity of  $\text{ZnSO}_4$  which results in electrolyte evaporation (Figure 4.8b). Calendar aging effect of ZAB using liquid KOH (Figure 4.8c) was the worst due to generation of  $\text{K}_2\text{CO}_3$  during the rest of just one hour, underscoring the advantage of gel-type natural electrolytes for ZABs.

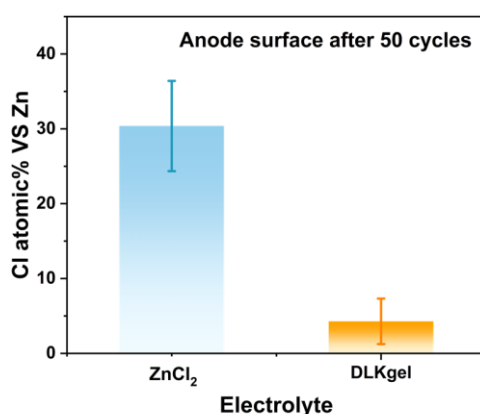
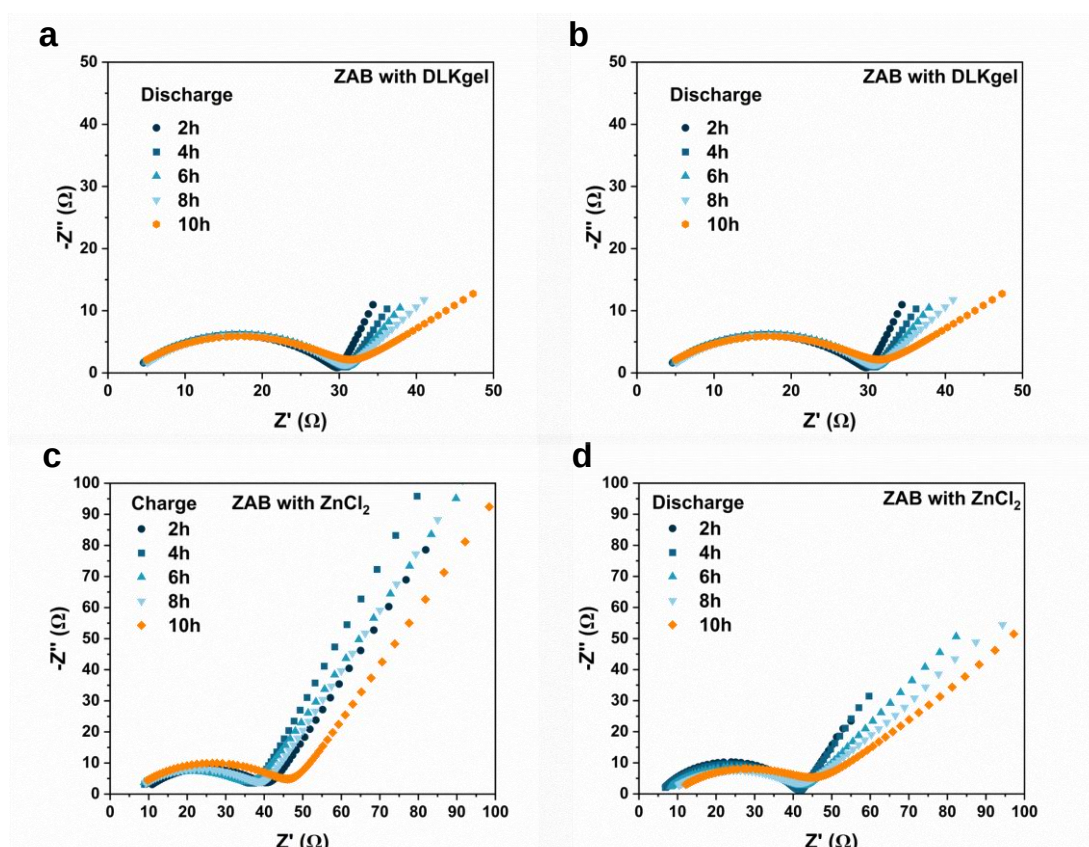


**Figure 4.9** Atomic portion of Cl compared to Zn on the anode surface with ZnCl<sub>2</sub> and DLKgel electrolytes after 50 cycles.

Elemental analysis (Figure 4.9) shows that DLKgel electrolyte results in a much lower concentration of Cl<sup>-</sup> on Zn anode surface compared to that of ZnCl<sub>2</sub> gel electrolyte after fifty charge and discharge cycles. This indicates efficient inhibition of Cl<sup>-</sup> transport provided by double-layer design.



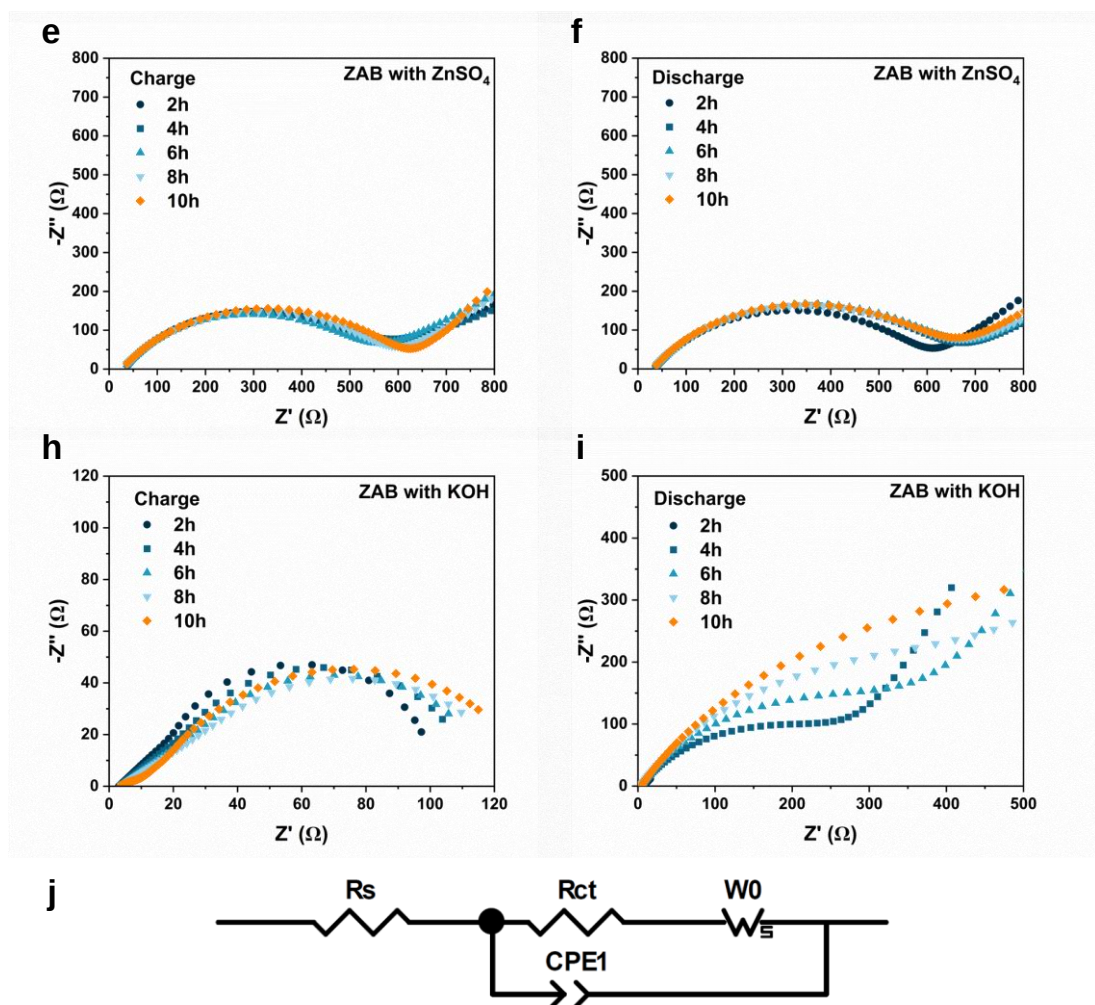


**Figure 4.10** Electrochemical impedance spectroscopy (EIS) fitting results of ZABs with different electrolytes during discharging/charging.

The charge transfer resistances are monitored during in charge and discharge process at a two-hour interval. The Nyquist plots are presented in Figure 4.10, with equivalent circuit attached as Figure 4.10j.

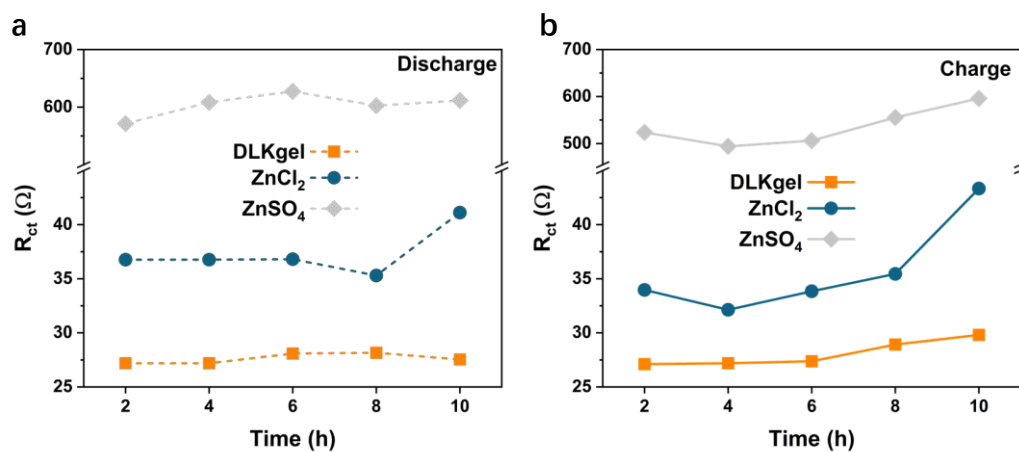


**Figure 4.11** Charge-transfer resistance ( $R_{ct}$ ) values obtained from fitted electrochemical impedance spectroscopy (EIS) results of ZABs with three types of gel electrolytes during the continuous (a) discharge and (b) charge processes according to Figure 4.10 a-f.

Figure 4.11a shows that ZAB using DLKgel has the lowest  $R_{ct}$  during discharging. The resistance remained almost unchanged along discharging duration, indicating that formation of ZHC on cathode surface does not elevate the  $R_{ct}$  due to its electrochemical reversibility. In comparison, ZABs using  $ZnCl_2$  and  $ZnSO_4$  electrolytes show larger  $R_{ct}$ . A similar trend is observed in the charging process (Figure 4.11b). In both cases, the increased  $R_{ct}$  of ZAB using  $ZnCl_2$  electrolyte after 10-hr cycle could be attributed to uneven surface structure of anode.  $R_{ct}$  for  $ZnSO_4$  and KOH electrolytes are particularly larger which could be related to the generation of irreversible by-products on cathode and anode (Figure 4.10 e-i).

The protection role offered by the distinct double-layer design is expected to boost the cycling stability of the aqueous ZAB. As illustrated in Figure 4.12a, ZAB using DLKgel can sustain smooth operation for over 800 hours at a current density of  $0.1 \text{ mA cm}^{-2}$ , surpassing that of  $ZnCl_2$  or  $ZnSO_4$  gel electrolytes (150 hours and 400 hours, respectively). Running at larger currents, ZAB using DLKgel can also maintain operation for more than 200 hours at  $0.5 \text{ mA cm}^{-2}$  and 120 hours at  $1.0 \text{ mA cm}^{-2}$  (Figure 4.12b).

When cycling at a high current density of  $10 \text{ mA cm}^{-2}$ , ZAB with DLKgel still operates for about one day (Figure 4.12c). The prolonged lifespan of ZAB utilizing DLKgel is competitive compared to those of reported neutral ZABs (Table 4.1).

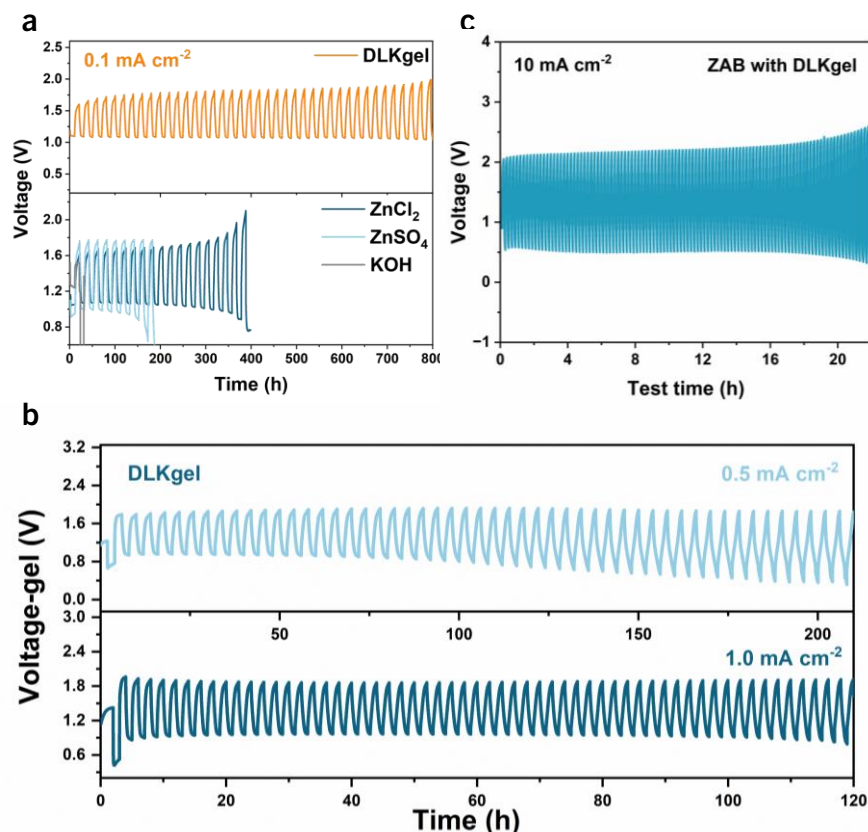


**Figure 4.12** ZAB performance and device integration. (a) Long-term cycling performance of ZABs with ZnCl<sub>2</sub>, ZnSO<sub>4</sub>, and DLKgel electrolytes at a current density of 0.1 mA cm<sup>-2</sup>. (b) Cycling performance of ZAB using DLKgel at two higher current densities. (c) Long-term cycling performance of ZABs with DLKgel electrolyte at a high current density of 10 mA cm<sup>-2</sup>.

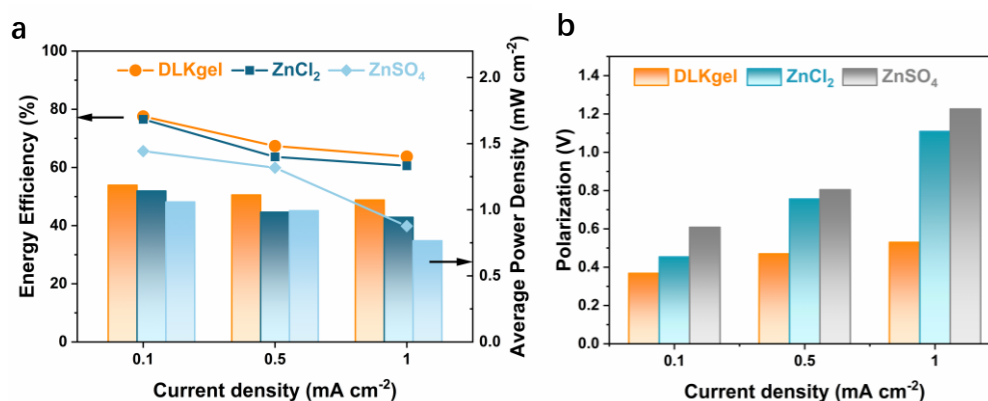


**Figure 4.13** ZAB cycling performance. (a) Charge/discharge energy efficiency and average power density of ZABs with the three electrolytes at various current densities at the 2<sup>nd</sup> cycle. (b) Voltage polarizations at three current densities at the 2<sup>nd</sup> cycle.

To underscore the enhanced output capability of ZABs using DLKgel compared to conventional liquid alkaline (KOH) and neutral (ZnSO<sub>4</sub> and ZnCl<sub>2</sub>) gel electrolytes, ZABs with these four electrolytes underwent cycling at three current densities under ambient air atmosphere. The DLKgel achieves the highest energy efficiency across current densities

including 0.1, 0.5, and 1 mA cm<sup>-2</sup> in the second cycle (Figure 4.13a). Regarding the power densities, ZAB with DLKgel delivers similar power with ZnCl<sub>2</sub> but more than the ZnSO<sub>4</sub> electrolytes (Figure 4.13a). If we compare the three gel electrolytes at a constant current density (0.1 mA cm<sup>-2</sup>) and the 2<sup>nd</sup> cycle, ZAB utilizing DLKgel corresponds to the lowest polarization during charging and discharging (Figure 4.13b and 4.14a), which is an important feature for metal-air batteries.

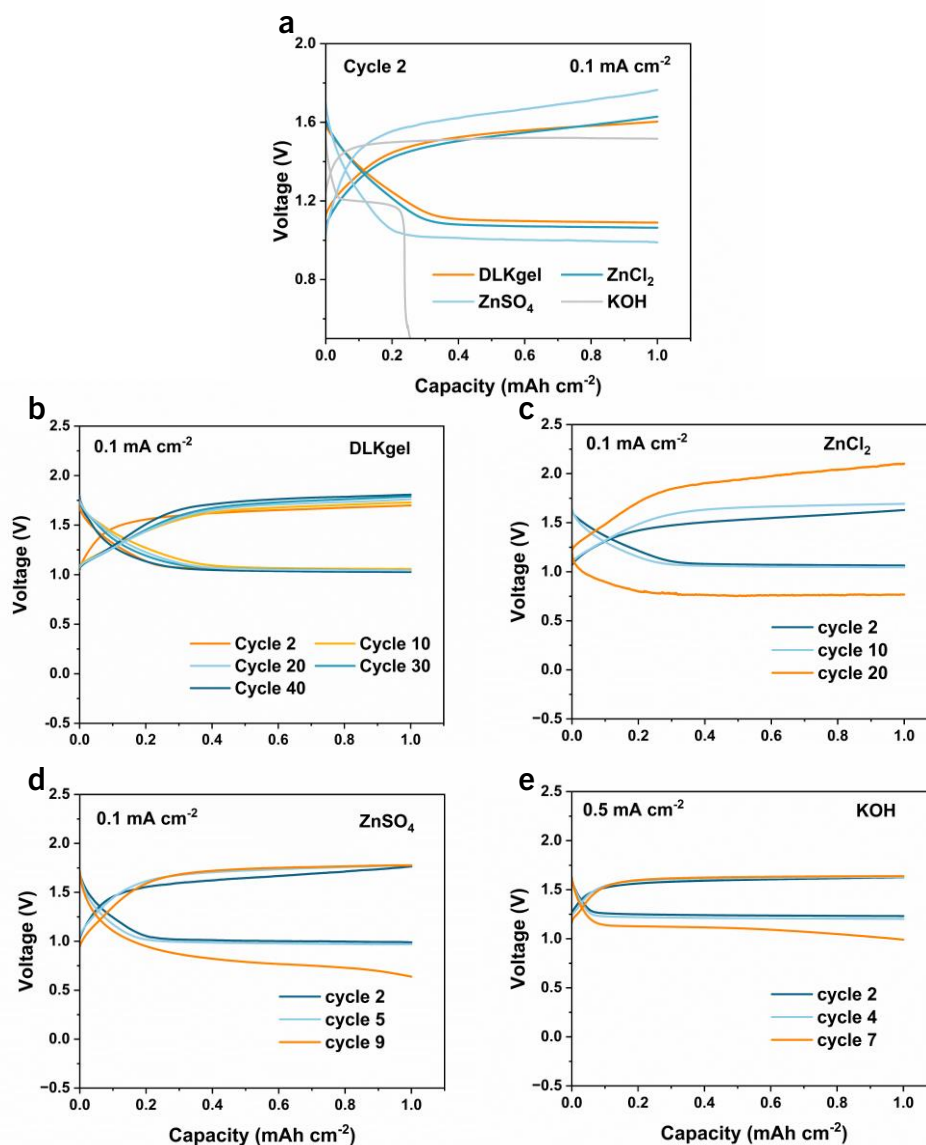


**Figure 4.14** (a) Comparison of galvanostatic voltage profiles of ZABs using DLKgel, ZnCl<sub>2</sub>, and ZnSO<sub>4</sub> electrolytes at a current density of 0.1 mA cm<sup>-2</sup> at the 2<sup>nd</sup> cycle. (b-e) Galvanostatic voltage profiles of ZAB using four different electrolytes at a current density of 0.1 mA cm<sup>-2</sup> for various cycles.

The polarization evolution in more cycles is further examined. ZAB using DLKgel demonstrated stable cycling with no significant increase of polarization within 40 cycles (Figure 4.14b). In contrast, the rest ZABs show increase in polarization after the tenth, ninth, or seventh cycles (Figure 4.14 c-e).

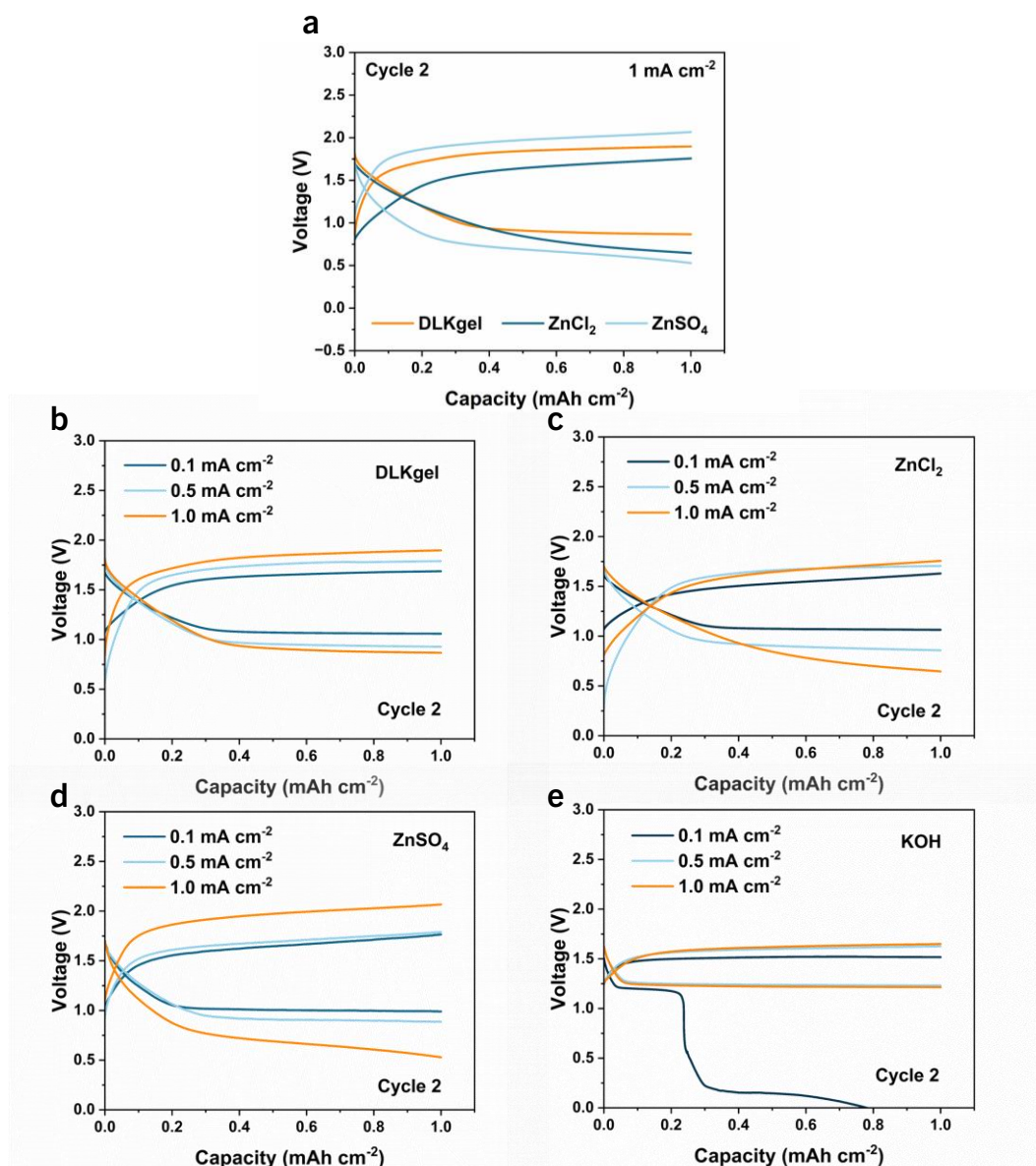


**Figure 4.15** (a) Comparison of galvanostatic voltage profiles of ZABs with DLKgel, ZnCl<sub>2</sub>, and ZnSO<sub>4</sub> gel electrolytes at a fixed current density of 1 mA cm<sup>-2</sup> at the 2<sup>nd</sup> cycle. Galvanostatic voltage profiles of ZAB using 4 different electrolytes at different current densities at the 2<sup>nd</sup> cycle. (b) ZAB with DLKgel electrolyte; (c) ZAB with ZnCl<sub>2</sub> electrolyte; (d) ZAB with ZnSO<sub>4</sub> electrolyte; (e) ZAB with KOH.

The polarization evolution under varying current densities is also compared. When current density is fixed at 1 mA cm<sup>-2</sup>, ZAB using DLKgel revealed the lowest polarization at the 2<sup>nd</sup> cycle (Figure 4.15a). A marginal increase in polarization appears in ZABs using DLKgel when the operating current increases from 0.1 to 1.0 mA cm<sup>-2</sup> during the second cycle, resulting in a slight decrease in energy efficiency (Figure 4.13a and 4.15b). In contrast, ZABs utilizing ZnCl<sub>2</sub> and ZnSO<sub>4</sub> electrolytes display noticeable polarization as the operating current density increases (Figure 4.15c, d). Particularly, for the conventional liquid KOH electrolyte where

generation of  $\text{K}_2\text{CO}_3$  is inevitable, the curve collapses at a low current density of  $0.1 \text{ mA cm}^{-2}$  after one cycle (Figure 4.15e). In our work, we did not employ any cathode catalyst. However, applying an extra electrocatalyst or the incorporation of redox mediators could further mitigate polarization and enhance the energy efficiency of ZABs utilizing DLKgel.<sup>216</sup>

The high stability and prolonged lifespan from ZABs utilizing DLKgel render them promising for powering wearable electronic devices, particularly those requiring extended usage.<sup>217</sup> Furthermore, the components of ZABs utilizing DLKgel are non-toxic and biocompatible. For example, ZHC, a byproduct of cathode ORR, is recognized as an efficient nutritional supplement.<sup>218</sup> Taking cues from various bio-compatible flexible battery applications<sup>219-222</sup>, we constructed a geographical information logging system based on a Global Positioning System (GPS) chip, powered by ZABs with DLKgel. The battery was engineered to deliver a consistent voltage of 3.3V, which can sustain the operation of the GPS chip in receiving and transmitting geographical data via Universal Asynchronous Receiver/Transmitter (UART) serial communication protocol.

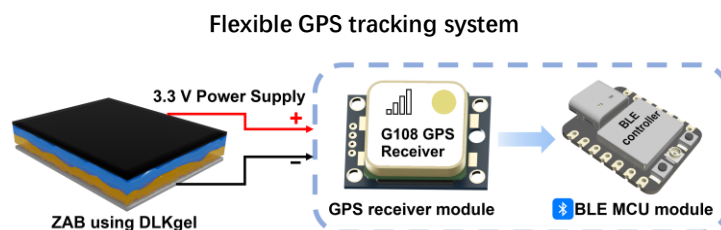


**Figure 4.16** Schematic of the flexible GPS tracking system powered by flexible ZAB using DLKgel, including key communication protocols used to fetch data from satellites and broadcast to mobile devices.

As illustrated in Figure 4.16, a GPS receiver module enables the reception of GPS location information from satellites at a frequency of 10 Hz from GPS/GNSS/Beidou satellites (more details of the connection between multiple devices are shown in Figure 4.17a). The received GPS location information is then transmitted to a Bluetooth Low Energy (BLE) microcontroller via the UART communication protocol.

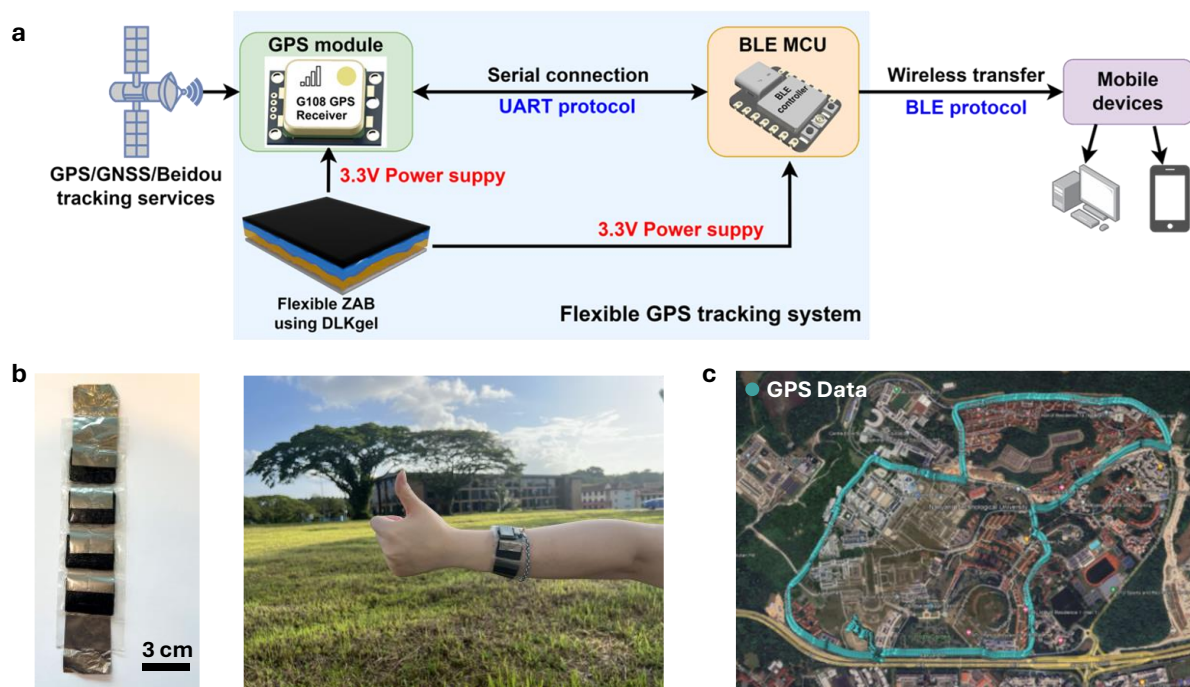


**Figure 4.17** Design, fabrication, and experiment of the flexible GPS tracking system powered by flexible ZAB using DLKgel. (a) Detailed schematic illustration of the assembling of flexible wearable GPS tracking system powered by flexible ZABs using DLKgel. (b) A wrist belt-shaped GPS recording device powered by the ZAB. (c) Demonstration of the wearable GPS device for dynamic tracking of the trip path (highlighted in cyan).

The flexible ZAB utilizing DLKgel supports both the GPS module and BLE microcontroller simultaneously, operating at a voltage of 3.3 V. Subsequently, the BLE microcontroller concurrently performs data analysis and Bluetooth services, dynamically broadcasting GPS location data to connected mobile devices. Users have the option to view or download the GPS data from either a mobile phone or a computer. Multiple ZABs with an electrode size of  $2 \times 3 \text{ cm}^2$  are connected in series to form a belt-like configuration, rendering flexibility and human comfort (Figure 4.17b). The compact and lightweight design of the integrated device makes it suitable for portable applications, occupying minimal space and exhibiting low weight.

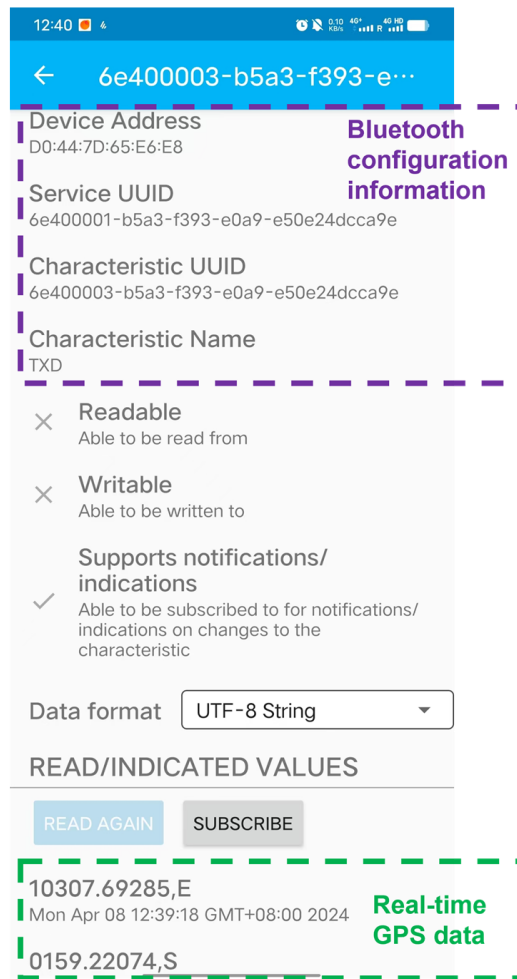


**Figure 4.18** GPS data receiver interface via Bluetooth service on the smartphone. Bluetooth configuration is highlighted in purple; GPS data in latitude (S) and longitude (E) is highlighted in green.

The flexible device facilitates dynamic monitoring of the tracking device's current location through mobile apps (Figure 4.18). To evaluate the longevity of ZAB, the device was tested for two round trips around the university campus, which lasted more than 40 min. The precise and comprehensive route data was recorded throughout the entire excursion (Figure 4.17c), affirming the extended operational duration of this portable device powered by ZAB with DLKgel. Such a low-cost battery holds potential utility in wearable technology, logistics, and numerous industries requiring prolonged flexible power supplies.

## 4.4 Conclusion

The introduction of DLKgel as a quasi-solid neutral electrolyte marks a significant advancement in ZABs. The unique properties of DLKgel, stemming from phase separation

induced by distinct kosmotropic characteristics, offer exceptional advantages in suppressing irreversible by-products and protecting against anode passivation. Such superiority over traditional alkaline and neutral electrolytes renders higher Zn utilization rate and extended battery lifespan. The successful integration of ZABs with DLKgel into a geographical information logging system showcases the practical utility and versatility of this technology. Leveraging DLKgel, we have achieved precise data capture and transmission, facilitating dynamic monitoring of location-based information. Looking ahead, the continued exploration and refinement of kosmotropic DLKgel holds immense potential for boosting the low-cost, flexible, and long-durability ZABs.

ZABs present a compelling alternative to traditional zinc batteries due to their high energy density, cost-effectiveness, environmental friendliness, long shelf life, high theoretical capacity, and stable discharge voltage. These attributes make them suitable for a wide range of applications, from small electronic devices to large-scale energy storage solutions. Continued advancements in ZAB technology could further enhance their performance and broaden their application spectrum, solidifying their role in the future of energy storage.

## Chapter 5 Conclusion and outlook

### 5.1 Conclusion

The research described in this thesis covers three major parts. The first section focuses on the design of hydrogel cellulose paper (HCP) as a separator for flexible zinc-ion batteries. The second section introduces an enhanced cathode material using a layer-expanding methodology for flexible zinc-iodine batteries. The third section presents a kosmotropism-based double-layer design for zinc-air batteries. This work advances the understanding of materials and structural designs for flexible aqueous zinc-ion batteries and proposes strategies to significantly improve their electrochemical performance. Detailed descriptions are provided in the subsequent chapters.

In the first chapter, hydrogel cellulose paper is investigated as the separator material for flexible zinc-ion batteries. Zn-MnO<sub>2</sub> batteries incorporating HCP demonstrate high redox efficiency, an extended lifespan, and excellent discharging capability under high current densities. Additionally, they exhibit stable electrochemical performance under various bending angles, confirming HCP's efficacy as a separator in flexible battery applications. Compared to existing state-of-the-art paper separator designs for ZIBs (Table 2.1), HCP is proved to be low-cost, simple in fabrication, efficient in extending the lifespan of flexible ZIBs, and ability to support high energy density ZIBs.

The second chapter investigates a layer-expanded material, EI-ZrP, as the cathode for flexible zinc-iodine batteries. EI-ZrP provides abundant channels for efficient zinc ion transport and effectively confines polyiodides, thereby mitigating the shuttle effect. The expanded interlayer spacing in EI-ZrP facilitates efficient ion transport and further suppresses the shuttle effect. The HCP-based zinc-iodine battery with the EI-ZrP/I<sub>2</sub> cathode demonstrates superior electrochemical properties, supporting a flexible BLE pressure sensor system. The layer-expanded cathode material concept provides valuable insights for advancing the development of efficient cathode materials tailored for flexible zinc-ion batteries (ZIBs). Furthermore, in comparison with other state-of-the-art research works (Table 3.3), the successful validation of my design in a practical electronic device marks a significant step toward the commercialization of flexible ZIB technology.

In the third chapter, DLKgel, a quasi-solid neutral electrolyte, is introduced to zinc-air batteries (ZABs). Leveraging phase separation induced by distinct kosmotropic characteristics,

DLKgel efficiently suppresses the formation of irreversible by-products and protects the anode from passivation. This enhancement results in a remarkable zinc utilization rate and an extended battery lifespan. ZABs incorporating DLKgel demonstrate the versatility of this technology by continuously powering a flexible wearable geographic information system. This application highlights the practical utility of DLKgel-based ZABs, offering significantly greater real-world value compared to other demonstration devices employing flexible ZABs (Table 4.1). With its simple manufacturing process, low cost, and high efficiency, DLKgel represents a significant advancement toward the practical application of flexible rechargeable ZABs.

Overall, the research underscores the potential of cellulose-based aqueous ZIBs for flexible energy storage applications. By integrating innovative materials including HCP, EI-ZrP, and DLKgel, this work addresses key challenges in the development of flexible batteries, paving the way for future advancements in wearable and portable electronic devices. The findings demonstrate that flexible cellulose-based ZIBs can maintain high performance and stability under mechanical stress, making them suitable for a wide range of applications where flexibility and durability are crucial. This research highlights the critical role of cellulose-based components in enhancing the mechanical properties and electrochemical performance of flexible batteries, positioning them as a promising solution for next-generation energy storage systems.

## **5.2 Outlook**

The development of power sources for flexible electronics is rapidly advancing, driven by continuous innovations in materials science and device engineering. To further enhance the performance of flexible aqueous Zn-ion batteries (FAZIBs), extensive investigations into advanced electrode materials and innovative electrolytes are required. Additionally, fabrication methods for FAZIBs should be examined to ensure a successful transition to scalable industrial production. In terms of integration with flexible electronics, the biocompatibility and safety of FAZIBs are also crucial considerations.

Firstly, the development of advanced electrode materials is paramount for improving FAZIB performance. Traditional electrode materials, while functional, often face limitations in capacity, stability, and flexibility. Future research should focus on exploring nanostructured materials, composite materials, and innovative fabrication techniques that can provide higher

energy densities, superior mechanical properties, and longer lifespans. Nanotechnology can significantly enhance the electrochemical performance of FAZIBs. Nanomaterials, such as nanowires, nanofibers, and nanotubes, offer larger surface areas and more efficient ion diffusion paths, thereby improving both capacity and rate capability.

Composite materials, which combine different constituents to synergize their properties, represent another promising research area. For instance, combining carbon-based materials with metal oxides or sulfides can enhance electrical conductivity, structural stability, and mechanical flexibility. Studies have demonstrated that composites such as graphene oxide/zinc oxide and carbon nanotube/vanadium oxide can significantly improve the overall performance of FAZIBs.

Introducing controlled defects in electrode materials can further enhance their electrochemical properties. Defect engineering, such as creating oxygen vacancies in metal oxides, can improve electrical conductivity and ion storage capacity. This approach is particularly useful for enhancing the performance of materials like zinc vanadates and manganese oxides, which are commonly used in Zn-ion batteries. In this thesis, the use of EI-ZrP as a cathode material for zinc-iodine batteries exemplifies how engineered electrode nanostructures can improve battery performance. Future research could further enhance EI-ZrP by incorporating more efficient intercalation materials into ZrP to expand layer spacing and improve ion transport efficiency.

Secondly, electrolytes play a crucial role in the performance and stability of FAZIBs. The current focus is on developing electrolytes that can provide high ionic conductivity, stability, and flexibility while preventing common issues such as dendrite formation and water splitting.

Quasi-solid-state electrolytes, which combine the advantages of both liquid and solid electrolytes, are being extensively studied. These electrolytes aim to provide the high ionic conductivity of liquid electrolytes along with the mechanical strength and stability of solid electrolytes. For example, gel polymer electrolytes (GPEs) have shown promise in maintaining flexibility while providing a stable ionic conduction path.

Incorporating ionic liquids into electrolytes can address several issues associated with aqueous electrolytes, such as water splitting and limited electrochemical stability windows. Ionic liquids are non-volatile and offer a wider electrochemical stability window, enhancing the overall performance and safety of the battery. Research has demonstrated that ionic liquid-

based electrolytes can improve the longevity and efficiency of Zn-ion batteries by reducing parasitic side reactions and dendrite formation.

Adding specific additives to electrolytes can significantly enhance their performance. For instance, incorporating metal-organic frameworks or certain organic compounds can help stabilize the electrolyte and prevent dendrite growth. These additives can also improve the mechanical properties of the electrolyte, making it more suitable for flexible applications.

Moreover, the structural design of electrolytes warrants further investigation. In the third chapter of this thesis, the superior performance of zinc-air batteries (ZABs) with the innovative double-layer designed DLKgel demonstrates the advantages of electrolyte structural engineering. DLKgel exemplifies a quasi-solid-state electrolyte, with both its constituents in a hybrid format. Future improvements on DLKgel could focus on enhancing interfacial connections between layers and incorporating additional electrolyte additives to boost performance. For example, commonly used catalysts for neutral ZABs could be added to DLKgel to achieve better performance and longer lifespan.

In the third place, flexible substrates are especially crucial for flexible batteries. Developing substrates that can support battery components without compromising their performance is essential. These substrates are expected to balance flexibility, durability, and thermal stability. In this thesis, cellulose paper is used as a raw material to synthesize a low-cost flexible substrate for supporting Zn batteries. The electrical conductivity of cellulose paper could be further improved to increase power density and decrease battery impedance. Additionally, the mechanical strength of cellulose paper could be enhanced to withstand continuous deformation in various applications.

Future research should emphasize material sustainability by using renewable and biodegradable materials for reinforcement, along with environmentally friendly processing techniques. Developing paper with not only improved mechanical strength but also additional functionalities, such as electrical conductivity, could address some limitations of existing cellulose paper solutions. Moreover, scaling up laboratory successes to commercial production will be crucial. Further research is needed to improve the commercial viability of paper batteries, addressing challenges related to cost, efficiency, and compatibility with existing manufacturing processes.

In the fourth section, scalability of FAZIBs could also be further investigated. For FAZIBs to become commercially viable, scalable and cost-effective manufacturing processes need to

be developed. This includes advancements in material synthesis, battery assembly, and packaging technologies. Current manufacturing methods reported by previous works remain highly laboratory style and lack massive production confirmation.

Printing technologies such as screen printing, inkjet printing, and 3D printing offer scalable and cost-effective approaches to manufacturing flexible zinc batteries. These methods allow for precise control over material deposition, enabling the fabrication of thin, flexible, and efficient battery components. In this thesis, Chapter 2 presents a printable cellulose-paper-based battery technology. Ongoing research aims to optimize the inks and substrates used in these printing processes to enhance the performance and reliability of FAZIBs.

Roll-to-roll (R2R) processing is another scalable manufacturing technique applicable to the production of FAZIBs. R2R processing is particularly suitable for producing large-area flexible batteries at a lower cost, making it a promising approach for commercial applications. Hence, the application of R2R processing for the scalable production of large-area HCP Zn-MnO<sub>2</sub> batteries warrants further investigation.

Packaging is critical for protecting battery components and ensuring their performance in flexible applications. Innovative packaging techniques that provide mechanical protection while maintaining flexibility are being developed. For example, encapsulating battery components in flexible, durable polymers can prevent damage from mechanical deformation and environmental exposure. While the investigation into flexible battery packaging is beyond the scope of this thesis, it is a crucial topic for future research. Identifying low-cost and stable packaging methods, especially for paper-based batteries, which are relatively new to industrial production, remains essential.

Finally, the integration of FAZIBs with flexible electronics is crucial for the development of wearable devices and other flexible technologies. This involves methods for embedding batteries within flexible circuits, connecting batteries to flexible sensors and displays, and ensuring reliable electrical connections under mechanical deformation. Advanced bonding and encapsulation techniques are being explored to enhance the durability and performance of these integrated systems.

Printed electronics technology could be further developed to enable the combined manufacture of both FAZIBs and flexible circuits, ensuring a more cohesive and efficient system. This approach can improve the coupling between the power source and the electronic components, leading to better overall performance and reliability of flexible devices.

The biocompatibility and comfortability of battery designs also remain a seldom visited research topic. Flexible medical devices often require thin-film batteries and stretchable batteries that can be smoothly integrated into textiles and skin patches. High battery safety is also a focus of demand in this industrial scenario. Research is exploring innovative designs such as serpentine interconnects and island-bridge structures that allow batteries to stretch and bend without losing functionality.

FAZIBs represent a significant advancement in the field of energy storage, offering a promising solution for flexible and wearable electronics. Future research directions will focus on developing advanced materials, innovative electrolytes, scalable manufacturing processes, and seamless integration techniques to enhance the performance, reliability, and commercial viability of these batteries. As research progresses, FAZIBs are expected to play a critical role in the evolution of flexible energy storage systems, significantly contributing to the advancement of wearable technologies and other flexible applications.

### **5.3 Potential market of FAZIBs and influencing factors**

#### **5.3.1 Competition of other battery technologies**

FAZIBs face significant competition from existing energy storage technologies, particularly LIBs. LIBs currently dominate the market due to their superior energy density and mature industrialization. To compete effectively, FAZIBs must demonstrate better performance in specific applications such as wearables, medical devices, and flexible electronics based on their advantages in safety, production cost, and biocompatibility.

#### **5.3.2 Regulatory considerations**

The commercialization of FAZIBs is influenced by evolving regulatory frameworks related to battery safety, environmental sustainability, and battery recycling. Compared to LIBs, FAZIBs have an advantage in the use of zinc which is more environmentally friendly. However, massive industrialization of FAZIBs will necessitate compliance with stringent manufacturing and safety standards, particularly in regions with advanced battery regulations (e.g., the European Union's Battery Directive). The increasing regulatory attention on ZIBs could slow down the pace of massive industrialization of FAZIBs.

### 5.3.2 Consumer acceptance

There is limited direct research specifically addressing consumer acceptance of FAZIBs, as they are still emerging technology. However, insights can be drawn from the increasing concern of customers over the intrinsic safety concerns of LIBs.<sup>223</sup> Consumer acceptance of FAZIBs depends on their advantages over LIB solutions. These key advantages include the intrinsic safety of FAZIBs, competitive pricing, and high biocompatibility. Currently, consumers are accustomed to the high energy density and rapid charge/discharge capabilities of LIBs. Effective marketing and clear communication of FAZIBs' advantages will be essential to bridge this perception gap.

### 5.4 Future Research plans

The next phase of this research on flexible zinc-based batteries focuses on enhancing the HCP to further improve its performance, particularly under extreme conditions. One promising approach is to reinforce the HCP using nanofibers such as carbon nanotubes (CNTs) or chemical modifications. This enhancement can be pursued in three key directions:

1. Improving electrical conductivity: Enhancing electrical conductivity will benefit the power density of the battery and reduce overall impedance, enabling more efficient energy delivery during operation.
2. Enhancing mechanical strength: Strengthening the mechanical properties of the HCP will further improve its capability to withstand continuous deformation, ensuring reliability and durability across a wide range of flexible applications.
3. Increasing Thermal Resistance: Improving the thermal stability of the HCP will expand its usability in diverse application scenarios, particularly in environments with extreme temperature variations.

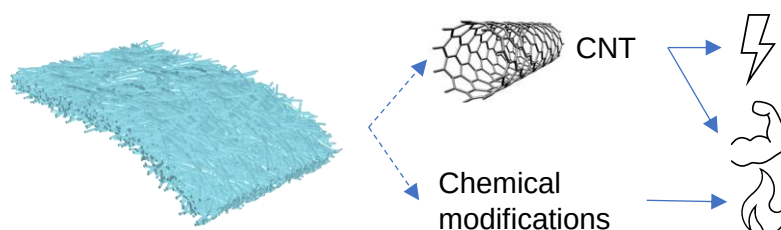


**Figure 5.1** Schematic illustration of using CNT/Chemical modifications to strengthen HCP.

After reinforcing the HCP, the subsequent research focus will shift toward developing viable large-scale production methods for flexible zinc-based batteries. Existing fabrication techniques, such as printing technologies, roll-to-roll processing, lithography, and deposition, require further investigation to evaluate their compatibility with flexible HCP-based zinc batteries. This includes assessing how these methods might impact battery performance, with particular attention to potential performance degradations during manufacturing.

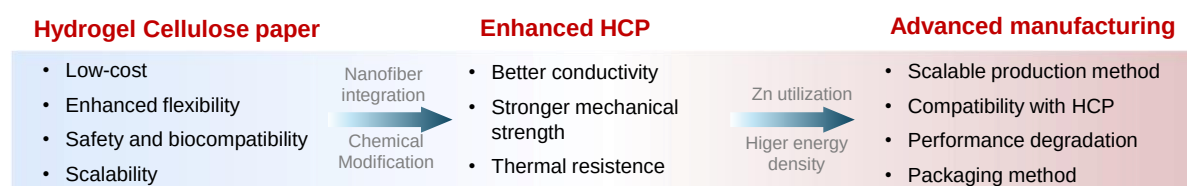


**Figure 5.2** Roadmap of developing HCP based flexible zinc battery technology, including the targets for next phase research works.

Additionally, the development of a flexible and compatible packaging method is critical. Such packaging must maintain the battery's mechanical flexibility, ensure its structural integrity, and provide robust protection against environmental factors, enabling reliable performance across various applications. Addressing these challenges will be a key step toward the commercialization of flexible zinc-based battery technology.

These improvements are aimed at pushing the boundaries of flexible zinc-based battery technology, paving the way for more robust and versatile energy storage solutions.

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