

**Design of Self-Aggregating and Recyclable Quasi-Solid-State Electrolyte
towards Dendrite-Free Zn Anode**

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Zn-based electrochemistries have received ever-increasing attention given their non-toxicity, easy recycling, biocompatibility, and abundant natural resources, which can solve the fundamental challenges of Li-based batteries and make promises in the application of grid-scale energy storage in the future. In particular, Zn-ion batteries coupled with quasi-solid-state electrolytes such as hydrogel electrolytes rather than conventional liquid electrolytes can bring less dendrite formation, thermal runaways, and electrolyte volatilization along with higher energy density. Herein, my current research work reports a gelatin-based hydrogel electrolyte using commercially available Jell-O powder, which is able to regulate the cycling behavior of Zn anodes by inhibiting the growth of Zn dendrite formation. Numerous characterizations and electrochemical techniques prove that gelatin chains can twin into helical structure and self-assemble to form a 3D triple matrix during sol-gel transition, which promotes better electrochemical performance than single molecules. In the meantime, the Jell-O QSSE can promote the binding of anions in the Zn^{2+} solvation sheath while reducing the content of free anions, thereby decreasing their contribution to the current density and inhibiting the formation of Zn dendrites. The as-assembled Zn//Zn symmetric cells using Jell-O QSSE can sustain long-term cycling of 2000 h, 1500 h, 250 h, and 120 h at 1, 10, 20, and 50 mA cm^{-2} with an areal capacity of 1 mAh cm^{-2} , respectively. Moreover, Zn//Cu coin cells show excellent reversibility with a high average CE of 98.61% for more than 100 stable cycles. To validate the practicality of Jell-O QSSE, Zn// MnO_2 full cells are assembled, showing an ultrahigh capacity retention of 88.7% after 1000 cycles with a high average CE of 99.64%. Different cathode materials such

as sodium vanadate (β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$, NVO) was applied as well, which similarly show excellent cycling stability and capacity retention, indicating good compatibility of Jell-O QSSE to various cathode materials. Finally, the recycling of used Jell-O QSSE was demonstrated via a suction filtration method. The filtered Jell-O QSSE was applied again in the assembly of Zn//Zn symmetric cells, showing an excellent cycling stability of more than 1200 h, making Jell-O QSSE much more promising than conventional ZnSO_4 electrolyte in the application of aqueous Zn-ion batteries.

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Chapter 1 Introduction: The Energy Crisis

Global carbon emissions have persistently surged since the 1970s, peaking at unprecedented levels in the past five years. This rise is largely attributable to the accumulation of greenhouse gases in the atmosphere, a consequence of human-driven expansion and the extensive reliance on fossil fuels (Liu et al., 2024). In turn, this intensifies global warming, leading to elevated average temperatures, crises in food and water supplies, and the depletion of fossil fuel reserves. To expedite the transition from consuming non-renewable fossil fuels to adopting sustainable but intermittent energy alternatives such as wind and solar power, there is a burgeoning demand for next-generation energy storage systems with superior versatility, efficiency, and energy density (Lee et al., 2011; Li & Lu, 2017; Q. Liu et al., 2020). Lithium-ion batteries (LIBs) have received ever-increasing attention and development since their first commercialization by Sony Co. 30 years ago (Etacheri et al., 2011; Li et al., 2018). Due to their relatively high energy density and long calendar life, LIBs have become the practical “go-to” solution for versatile applications such as portable electronics and electric vehicles (EVs), re-shaping people’s lifestyles (Assat & Tarascon, 2018; Frith et al., 2023; Wang et al., 2024). However, LIBs have faced criticism for the high costs, flammability, and reliance on lithium (Li) and cobalt (Co) elements – elements with comparatively low crustal abundance and gradually depleting reserves (Fu et al., 2017; Hou et al., 2020; Hu, 2016). Although numerous strategies have been developed recently to reduce the costs of LIB by up to 40% (Ji et al., 2024; T. Yang et al., 2024), safety issues remain a fundamental challenge: thermal runaways are uncontrollable during the use of LIBs, and heavy metal elements (e.g., Ni and Co) may further

pose safety hazards during the recycling of spent LIBs (Deng et al., 2018; B. Liu et al., 2020; Liu et al., 2018).

Compared to LIBs, various aqueous multivalent ion batteries (Zn^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , etc.) possess higher safety and comparable theoretical energy density, thus attracting extensive exploration recently. Among all these technologies based on multi-electron redox couples, Zn-based chemistries stand out as a competitive contender for large-scale EES, where metallic Zn is used as the anode material, boasting ultrahigh theoretical gravimetric (820 mAh g^{-1}) and volumetric (5854 mAh cm^{-3}) capacities, relatively low redox potential (-0.762 V vs. the standard hydrogen electrode, S.H.E), non-toxicity, excellent intrinsic safety, environmental benignity, high crustal abundance, and affordability (H. Dou et al., 2024; Dou et al., 2022; Hao et al., 2020; M. Xu et al., 2022). However, batteries using Zn-based chemistries are still hampered by significant challenges such as severe parasitic reactions (e.g., HER), narrow electrochemical stability window (ESW), and the notorious Zn dendrite growth, which open many research directions to achieve high-performance Zn-based batteries. Among all strategies to circumvent the aforementioned obstacles, electrolyte engineering appears as a cost-effective option given the crucial role of electrolyte in controlling Zn^{2+} transport between electrodes and regulating Zn^{2+}/Zn nucleation on the anode surface (Cao et al., 2023; Kang et al., 2020; T. C. Li et al., 2023; Y. Li et al., 2023; Sun et al., 2022; Tian et al., 2022; D. Wang et al., 2023; Yu Wang et al., 2023; Yanyan Wang et al., 2023; Wu et al., 2023; Xie et al., 2023; Xing et al., 2023; Zheng et al., 2023; Zhou et al., 2022). Aqueous zinc-ion batteries (AZIBs), a

representative of advanced Zn-based batteries, have garnered substantial scientific attention in recent years.

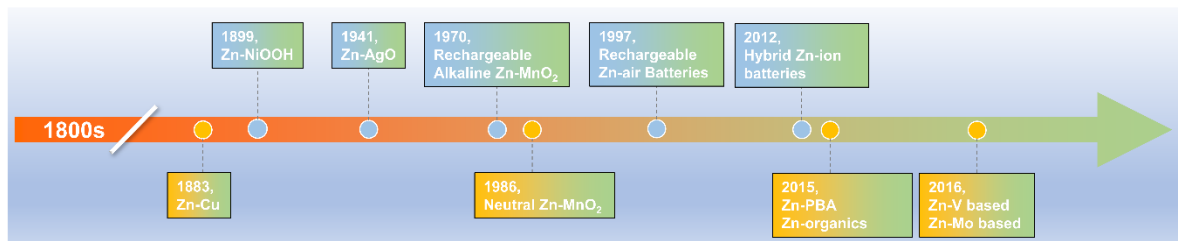
Herein, by designing and incorporating a gelatin-based, novel quasi-solid-state electrolyte into an AZIB in this work, we aim to advance the transition to a more sustainable energy ecosystem. This innovative approach supports the shift from fossil fuels to renewable energy by enhancing the efficiency, safety, and longevity of next-generation battery systems, which are essential for grid-scale energy storage.

Chapter 2 Literature Review: Fundamentals of Aqueous Zinc-Ion Batteries

2.1 Zn-Based Batteries

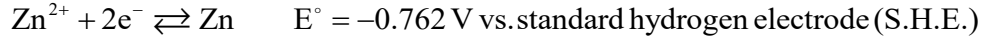
Figure 1.

Historic development for different Zn-based batteries



As illustrated in Figure 1, the utilization of Zn as an anode material traces its origins to the Voltaic pile, the earliest electrochemical cell created by Alessandro Volta in the early 19th century (Mainar et al., 2018). Over time, Zn has been incorporated into various battery chemistries, including Zn-NiOOH, Zn-MnO₂, Zn-V, and Zn-PBA, many of which have

achieved commercial success and remain widely applied today. In general, the anodic chemistry of most Zn-based batteries is based on the Zn/Zn^{2+} redox couple:



As for the cathodic redox, the choice of the type or structure of cathode material is critical. By coupling various cathode materials, such as porous carbon materials and manganese oxide, different Zn-based batteries including Zn-air batteries and aqueous Zn-ion batteries can be achieved. Compared to most other Zn-based batteries, aqueous Zn-ion batteries (AZIBs) offer several compelling advantages due to their unique electrochemical properties and facile structural design. Unlike many conventional Zn-based batteries, which are limited to single-use due to irreversible reactions, AZIBs are inherently rechargeable, demonstrating superior cycling stability and extended lifespan when coupled with optimized electrolytes and electrode materials. The excellent rechargeability makes AZIBs highly suitable for applications requiring long-term, repetitive usage (Xu et al., 2012). Furthermore, AZIBs employ aqueous electrolytes that are non-toxic, non-flammable, and environmentally benign, thus reducing safety hazards and ecological impact compared to systems utilizing organic solvents (H. Dou et al., 2024). The cost-effectiveness of AZIBs is another significant benefit; by relying on Zn, an abundant, economically accessible, and non-toxic material, alongside inexpensive water-based electrolytes, AZIBs offer an affordable solution for large-scale energy storage, such as grid applications where cost-efficiency is paramount (Li, Ma, et al., 2019; Ma et al., 2023). Last but not least, AZIBs achieve high power densities and deliver improved energy efficiency, allowing rapid charge and discharge while maintaining stability across a broad temperature

range, which enhances their adaptability for diverse operational conditions and further underscores their potential for sustainable and scalable energy storage solutions.

2.2 Aqueous Zn-Ion Batteries (AZIBs)

The origins of AZIBs date back to the 1980s, when Yamamoto and Shoji (1986) employed a mildly acidic 2 M ZnSO_4 electrolyte to achieve a rechargeable Zn/MnO_2 battery configuration. In 2012, Xu et al. (2012) formally introduced the concept of AZIBs, elucidating the electrochemical mechanisms underlying the function of both cathodes and anodes. Since then, AZIBs have garnered substantial interest within the scientific community, leading to a remarkable rise in research publications focusing on design and modification strategies for AZIB technologies.

As mentioned in section 2.1, like most Zn-based batteries, the charge storage mechanism in AZIBs relies on the migration of Zn^{2+} ions between the Zn anode and a cathode material capable of reversibly intercalating Zn^{2+} ions. However, in contrast to the widely utilized zinc-manganese oxide primary battery, AZIBs adopt weakly acidic or neutral zinc salts, such as ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, as their electrolytes. This electrolyte configuration effectively mitigates the formation of ZnO on the Zn anode and suppresses the irreversible production of $\text{Mn}(\text{OH})_2$ and MnOOH on the cathode (Blanc et al., 2020). As one of the multivalent metal-ion batteries, AZIBs capitalize on the redox properties of Zn, whereby the oxidation of Zn to Zn^{2+} facilitates the transfer of two electrons. This dual-electron transfer capability affords AZIBs a high theoretical volumetric specific capacity of 5851 mAh cm^{-3} and a theoretical gravimetric capacity of 820 mAh g^{-1} (Xie et al., 2018). While multivalent systems theoretically

enhance specific capacity, most metals (e.g., Mg, Al) typically form passivating, inert products within aqueous electrolytes, leading to significant challenges in charge-discharge efficiency. To counteract this, carbon-based materials are frequently employed as cathodes in aqueous multivalent metal-ion batteries. Nevertheless, Zn exhibits a comparatively low redox potential (-0.762 V vs. S.H.E.), imparting substantial corrosion resistance, which enables AZIBs to uniquely operate with both aqueous and non-aqueous electrolytes (Song et al., 2018). Moreover, AZIBs' capability for assembly under ambient conditions substantially reduces manufacturing costs and efforts. Collectively, these attributes position AZIBs as a highly promising candidate for applications in grid-scale energy storage and residential battery systems, offering distinct advantages over conventional energy storage technologies.

In AZIBs, aqueous electrolytes offer considerable benefits, including inherent safety, environmental sustainability, ease of preparation, and reduced costs when compared to organic electrolyte systems. Although organic electrolytes exhibit superior stability against oxygen evolution and provide a broader electrochemical window, the redox potential of Zn is significantly more positive than that of other commonly used metals such as Li (-3.045 V vs. S.H.E.) and Na (-2.714 V vs. S.H.E.) (X. Li, L. Wang, et al., 2023). As a result, even when coupled with high-voltage cathode materials, organic AZIBs achieve output voltages of only 2 – 3 V, thus offering limited improvements in energy density over aqueous AZIBs (Li et al., 2022). Moreover, aqueous electrolytes demonstrate an ionic conductivity of approximately 1 S cm⁻¹, which far exceeds that of organic electrolytes (1 – 10 mS cm⁻¹) by nearly two orders of magnitude. The interfacial transfer resistance between aqueous electrolytes and electrode

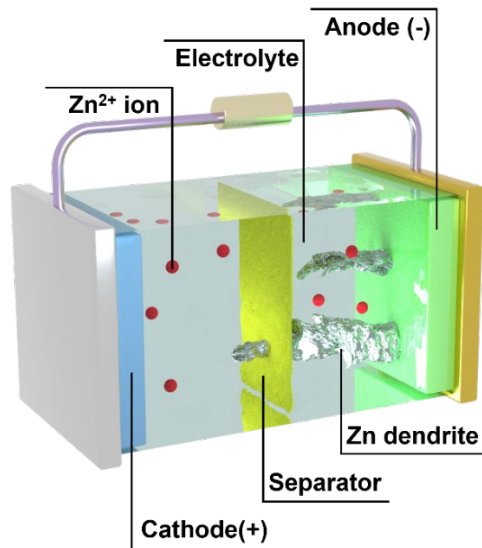
materials is also substantially lower than that found in organic systems, further enhancing AZIBs' ionic transport and efficiency (X. Li, L. Wang, et al., 2023).

2.3 Configuration, Challenges, and Design Strategies for AZIBs

The typical configuration of an AZIB is shown in Figure 2, which consists of a cathode, a metallic Zn anode, a glass fiber or cellulose separator, and an aqueous electrolyte. To satisfy the stringent requirements of large-scale energy storage applications, cathode materials for AZIBs must possess both high reversible charge capacity and excellent cycling stability. Equally important are the characteristics of resource abundance and environmental compatibility. Presently, the principal categories of cathode materials under investigation encompass manganese-based oxides, vanadium-based oxides, polyanionic compounds, Prussian blue analogues (PBAs), organic materials, and transition metal disulfides.

Figure 2.

Schematic of a typical aqueous zinc ion battery



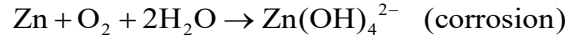
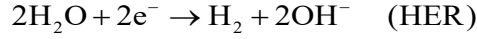
The transition metal manganese (Mn) demonstrates a range of valence states (Mn^{2+} , Mn^{3+} , Mn^{4+} , Mn^{7+}), which contribute to its exceptional ion storage properties (Guo et al., 2022). Notably, manganese dioxide (MnO_2) in its 4+ valence state is particularly suited for large-scale production due to its straightforward synthesis, abundance, cost-effectiveness, and environmental compatibility (Ke et al., 2024). In conventional alkaline primary batteries, MnO_2 cathodes undergo irreversible reactions, yielding Mn(OH)_2 and MnOOH as byproducts (Blanc et al., 2020). Conversely, in the acidic aqueous electrolytes of AZIBs, MnO_2 is the preferred cathode material, as it facilitates reversible electrochemical reactions. MnO_2 exhibits various structural configurations, including tunnel structures (e.g., α , β , γ), layered structures (e.g., δ type), and spinel structures (e.g., λ type), interconnected by MnO_6 octahedra that share edges or vertices. However, during charge-discharge cycles, these MnO_2 crystal structures can readily transform into one another, leading to stress accumulation and structural collapse, which ultimately contribute to capacity fading over extended cycling (Jia et al., 2020). Additional factors limiting MnO_2 's practical application include (1) the formation of Mn^{2+} due to MnO_2 dissolution in aqueous environments, (2) its inherently poor conductivity, which impedes ion diffusion, and (3) the negative impact of these issues on overall electrochemical performance.

As a transition metal, vanadium (V) can similarly adopt multiple oxidation states (V^{2+} , V^{3+} , V^{4+} , and V^{5+}), enabling valence shifts throughout redox reactions. Vanadium-based oxides have garnered ever-increasing attention as cathode materials for AZIBs due to the reversible Zn^{2+} intercalation facilitated by vanadium's intermediate oxidation states (Ding et al., 2021).

Current studies on V-based cathodes primarily focus on layered structures such as MV_2O_5 , where $M = Zn, Mg, Ca, Na, V_2O_5$, and other vanadium oxides (Tolstopyatova et al., 2024). Generally, V-based oxide cathodes exhibit high discharge capacity, impressive rate performance, and stable cycling at elevated current densities. However, these materials are susceptible to dissolution under low current density conditions (X. Dou et al., 2024). Furthermore, although V-based oxides offer various morphologies and structural configurations, such as layered or tunnel structures. Cathodes that rely on the V^{5+}/V^{4+} redox couple typically yield low discharge potentials; therefore, extensive investigation is required to refine the electronic structure and optimize the electrolyte composition or concentration to enhance the oxidation potential (C. Xu et al., 2022).

Zn metal stands out as a highly promising anode material due to its large theoretical specific capacity (820 mAh g^{-1} or 5851 mAh cm^{-3}), favorable redox potential ($-0.762 \text{ V vs. S.H.E.}$), chemical stability in aqueous electrolytes, natural abundance, low cost, and nonflammable nature (F. Wang et al., 2018). Nevertheless, the Zn anode faces significant challenges, including dendrite formation, metal corrosion, passivation, and the hydrogen evolution reaction (HER) during prolonged cycling. Key factors influencing Zn deposition include electric field intensity and ion distribution. Zn^{2+} ions typically nucleate at energetically favorable sites during electrodeposition, initiating the growth of small Zn dendrites. Once these dendritic tips form, charge accumulation at the tips generates intense electric fields, further attracting Zn^{2+} ions to preferentially deposit and extend the dendrites (Yang et al., 2022). The formation of Zn dendrites not only reduces cell lifespan but also presents a potential short-

circuit risk. Additionally, these dendrites increase the anode/electrolyte interface area, which promotes undesirable HER and Zn corrosion reactions, as illustrated below:



Consequently, the Coulombic efficiency (CE) is lowered, and the internal pressure of battery cells is increased. The local rise in OH^- concentration also results in the formation of insulating byproducts, which passivate the plating/stripping processes of Zn anodes. This corrosion and passivation lead to self-discharge issues and the depletion of active material (Thieu et al., 2023). Importantly, both dendrite formation and corrosion contribute to reshaping the Zn anode's surface morphology, further degrading its structure. These persistent challenges, including dendrite formation, hydrogen evolution reaction (HER), surface corrosion/passivation, and morphological changes, are intricately connected, constituting complex, life-limiting factors for AZIBs. Regulating Zn plating/stripping behavior is therefore essential for developing a highly rechargeable, dendrite-free anode, aimed at achieving high-capacity and long-cycle-life AZIBs (Yan et al., 2022).

The use of metallic Zn as an anode material in AZIBs dates back to 1799, when Italian physicist Alessandro Volta developed the earliest voltaic cell by alternating circular Zn and Ag plates separated by a saltwater-soaked cloth. Beyond AZIBs and Zn- MnO_2 batteries, metallic Zn has found widespread application in various alkaline electrolyte batteries, including zinc-silver (Zn- Ag_2O), zinc-nickel (Zn- NiOOH), and zinc-air (Zn- O_2) batteries (Lim et al., 2021). However, in alkaline aqueous solutions, Zn is susceptible to side chemical reactions and water

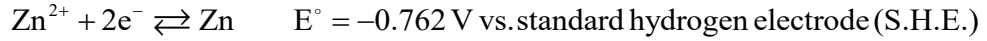
consumption, leading to irreversible charge-discharge cycles and reduced CE (N. Wang et al., 2021). In acidic or neutral aqueous electrolytes, Zn demonstrates stable redox behavior due to its high hydrogen evolution potential, which also mitigates dendrite formation and passivation, thereby enhancing AZIBs' reversibility and stability (Zhu et al., 2024). Recent studies have suggested several approaches to improve the electrochemical performance of Zn anodes: (1) optimizing the structure of the current collector, (2) constructing a functional interface layer, and (3) refining electrolyte composition and concentration. These strategies aim to regulate Zn^{2+} dissolution and deposition, suppress dendrite formation, and improve CE.

As a critical component in AZIBs, a wide variety of Zn-based inorganic and organic salts have been utilized in electrolytes. The type and concentration of Zn salts and additives within AZIB electrolytes exert a significant influence on their charge-discharge performance (Bai et al., 2024). Currently, Zn salts that have been identified for use in AZIBs include ZnSO_4 , $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, ZnCl_2 , $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, and ZnF_2 , with ZnSO_4 and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ being the most commonly utilized salts (Pavlica et al., 2009). Near-neutral or mildly acidic aqueous electrolytes (pH 4 – 5) offer numerous advantages including low cost, nontoxicity, high ionic conductivity ($> 40 \text{ mS cm}^{-1}$), and the ability for battery assembly in ambient air (Kundu et al., 2016; Kundu et al., 2018). Quasi-solid-state electrolytes (QSSEs) and all-solid-state electrolytes (ASSEs) have also been developed to mitigate cathode dissolution, prevent Zn dendrite formation, and reduce corrosion by lowering water molecule reactivity. However, these electrolytes suffer from limited ionic conductivity. Thus, further research is required to engineer an electrolyte with superior ionic conductivity, a widened

electrochemical stability window, ultrahigh chemical stability, high Zn^{2+} ion diffusivity, and cost-effectiveness (Lv et al., 2022).

2.4 Basic Working Principles of AZIBs

A comprehensive understanding of the electrode mechanisms is fundamental to advancing high-performance AZIBs. For the Zn anode, as mentioned earlier, the operational mechanism is relatively straightforward, involving a reversible redox reaction during charge and discharge cycles as shown below:



In contrast, the cathode's working mechanism is significantly more complex and remains a subject of debate, largely due to variations in material types and crystallinity, which renders this an area of active research (Wang et al., 2019; Zheng et al., 2019). This section aims to consolidate current insights into AZIB energy storage mechanisms, which can be classified into cationic redox, anionic redox, and redox reactions involving active functional group based on redox chemistry.

2.4.1 Cationic Redox

Cationic redox represents a principal mechanism in AZIBs, involving the redox of transition metals within cathode materials (Wan & Niu, 2019). Depending on the cathode used, this process encompasses oxidation state transformations such as $\text{Mn}^{4+} \rightleftharpoons \text{Mn}^{3+} \rightleftharpoons \text{Mn}^{2+}$, $\text{V}^{5+} \rightleftharpoons \text{V}^{4+} \rightleftharpoons \text{V}^{3+}$, $\text{Mo}^{4+} \rightleftharpoons \text{Mo}^{3+}$, and $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$, which occur during the reversible insertion and extraction of charge carriers like Zn^{2+} and H^{+} ions. This redox mechanism is

widely applicable to layered and tunnel-structured materials, including V-based compounds (Ding et al., 2018; He et al., 2017; Wan & Niu, 2019; Xia et al., 2018), PBAs (Zhang et al., 2015), Mo-based materials (Li, Yang, et al., 2019), and polymorphic forms of MnO_2 (Pan et al., 2016; Y. Wu et al., 2020).

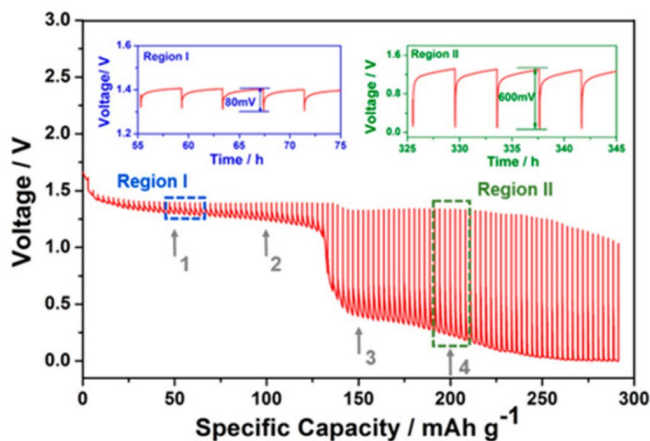
Zn^{2+} ions possess an ionic radius (0.74 Å) comparable to that of Li^+ (0.76 Å), which favorably supports the intercalation of Zn^{2+} into the crystal lattices of host materials (Zhou et al., 2019). In aqueous electrolytes, Zn^{2+} ions form hydrated cations by coordinating with six water molecules, resulting in a larger effective radius of approximately 4.3 Å (Ming et al., 2021). Cathode materials with expansive interlayer spacings and/or tunnel dimensions enable the facile insertion and extraction of these hydrated Zn^{2+} ions during charge-discharge cycles, accompanied by a reversible cationic redox process of transition metals (Sambandam et al., 2018). Importantly, the intercalated water molecules mitigate electrostatic interactions between Zn^{2+} ions and the host structure, facilitating efficient ion transport. In cases where interlayer or tunnel spaces are restricted, Zn^{2+} ions must undergo dehydration before insertion. For instance, the narrow tunnels in VO_2 allow only dehydrated Zn^{2+} ions to intercalate and deintercalate (Ding et al., 2018).

Beyond Zn^{2+} ions, proton (H^+) insertion and extraction are also recognized as viable mechanisms due to the presence of protons in mildly acidic electrolytes. Wan, Zhang, Dai, et al. (2018) demonstrated that H^+ and Zn^{2+} ions could be co-intercalated into and extracted from the $\text{NaV}_3\text{O}_8 \cdot 1.5\text{H}_2\text{O}$ cathode. For MnO_2 cathodes, however, H^+ and Zn^{2+} insertion/extraction proceeds as a two-step process. Sun et al. (2017) proposed this stepwise mechanism using

electrodeposited ϵ -MnO₂. In the galvanostatic intermittent titration technique (GITT) curve (Figure 3), rapid ionic diffusion with minimal voltage fluctuation in Region I suggested H⁺ intercalation, while significant overpotential in Region II indicated Zn²⁺ intercalation, which proceeds at a slower diffusion rate.

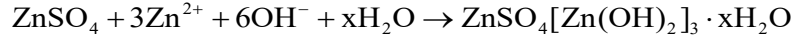
Figure 3.

Discharge galvanostatic intermittent titration technique (GITT) profiles of the Zn//MnO₂@CFP cell (50 mA g⁻¹ for 120 s followed by a 4 h rest).



Note. Reprinted from “Zn/MnO₂ battery chemistry with H⁺ and Zn²⁺ coinsertion”, by Sun et al., 2017, *Journal of the American Chemical Society*, 139(29), 9775-9778. Copyright 2017 by American Chemical Society.

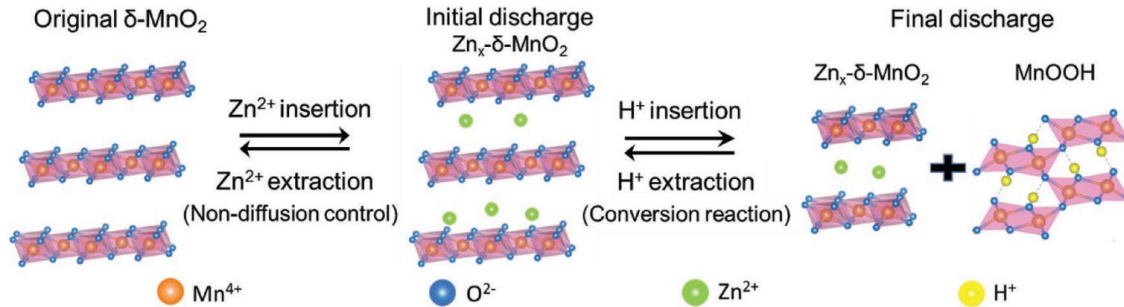
Notably, H⁺ insertion increases the local OH⁻ concentration near the cathode, precipitating Zn₄SO₆(OH)₆·5H₂O (ZSH) flakes on the surface, as shown in the following equation:



Upon recharging, H^+ extraction dissolves these ZSH products. Recently, Jin et al. (2019) proposed an alternative joint charge storage mechanism for $\delta\text{-MnO}_2$ in $\text{Zn}(\text{TFSI})_2$ electrolyte confirming that the initial discharge is dominated by non-diffusion-controlled Zn^{2+} intercalation with minimal phase change, followed by diffusion-controlled H^+ conversion reactions in subsequent cycles (Figure 4).

Figure 4.

Joint non-diffusion controlled Zn^{2+} intercalation and H^+ conversion reaction mechanism in $\delta\text{-MnO}_2$.



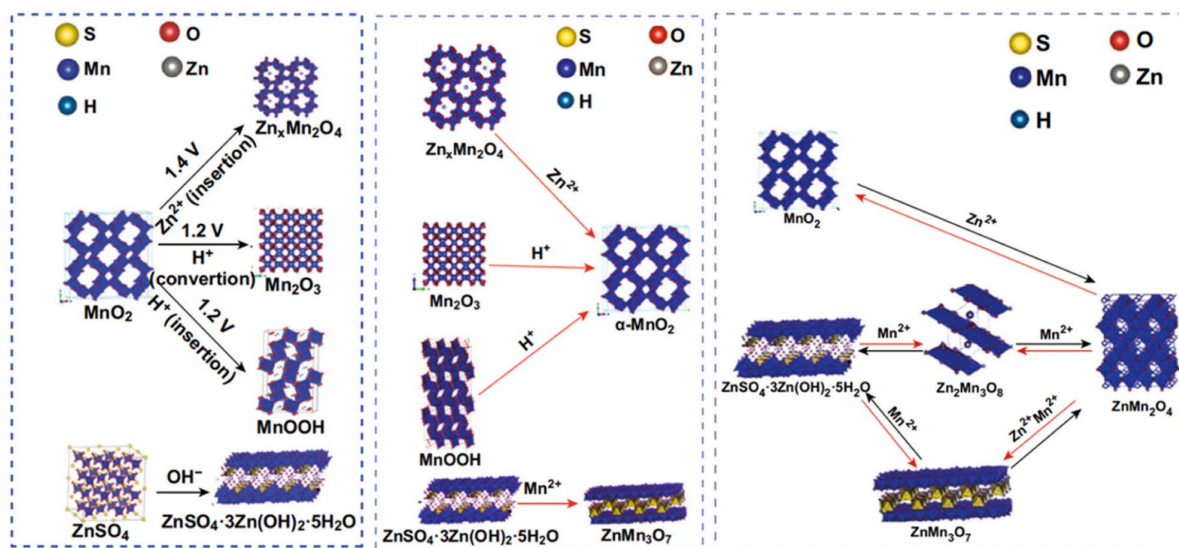
Note. Reprinted from “Joint Charge Storage for High-Rate Aqueous Zinc-Manganese Dioxide Batteries”, by Jin et al., 2019, *Advanced Materials*, 31(29), 1900567. Copyright 2019 by Wiley-VCH.

Recent studies by Zhou et al. (2021) on $\alpha\text{-MnO}_2$ also indicated that Zn^{2+} and H^+ insertion/extraction induce a reversible formation of Zn_xMnO_2 , MnOOH , and Mn_2O_3 during the first discharge/charge process. Interestingly, ZSH byproduct formation triggers a reaction with Mn^{2+} to yield a new ZnMn_3O_7 phase upon initial charging, with Mn^{2+} participating in

subsequent cycles to produce various Zn-Mn oxides, such as ZnMn_2O_4 , ZnMn_3O_7 , and $\text{Zn}_2\text{Mn}_3\text{O}_8$, via dynamic phase transitions, as shown in Figure 5 (Yongfeng Huang et al., 2019).

Figure 5.

Phase evolution of $\alpha\text{-MnO}_2$ cathode during the first discharge process, first charge process, and repeated charge/discharge cycles after the first cycle, respectively.



Note. Adapted from “Novel Insights into Energy Storage Mechanism of Aqueous Rechargeable Zn// MnO_2 Batteries with Participation of Mn^{2+} ”, by Yongfeng Huang et al. 2019, *Nano-Micro Letters*, 11(1), 49. Copyright 2019 by Springer Nature.

More recently, a two-electron $\text{Mn}^{2+}/\text{Mn}^{4+}$ redox reaction mechanism has been proposed, wherein H^+ and Zn^{2+} initially intercalate into MnO_2 , forming trivalent MnOOH and ZnMn_2O_4 , which then react with ZnSO_4 electrolyte to produce soluble Mn^{2+} and ZSH. This dissolution-

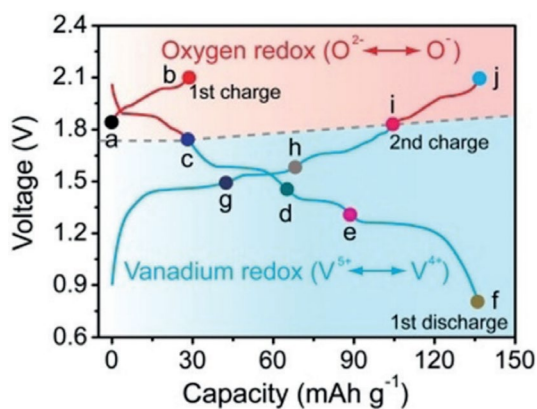
deposition characteristic has been leveraged to develop innovative Zn/MnO₂ flow batteries (X. Guo et al., 2020; Li et al., 2020; Zhai et al., 2020). Collectively, the energy storage mechanism of MnO₂ is intricate and remains actively debated; advanced characterization techniques are essential for a thorough understanding.

2.4.2 Anionic Redox

An anionic redox mechanism, involving elements such as oxygen, sulfur, and nitrogen, has been identified as an accompanying process in AZIBs. Wan et al. (2019) uncovered a dual-redox mechanism involving both cationic vanadium and anionic oxygen in a VOPO₄ cathode. As illustrated in Figure 6, oxygen oxidation occurred at the conclusion of the initial charging process, signifying the transition of lattice oxygen from O²⁻ to O^{•-}.

Figure 6.

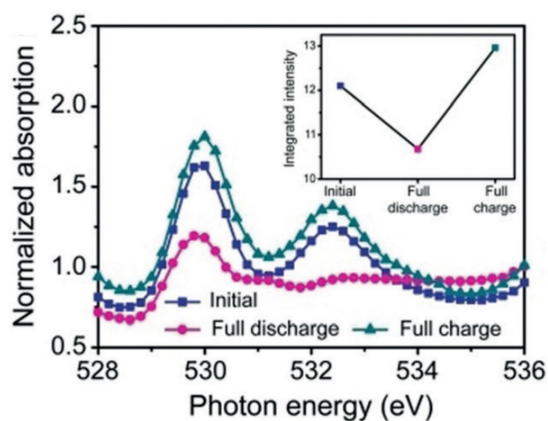
Charge/discharge curves of Zn//VOPO₄ batteries at 0.05 A g⁻¹.



Note. Reprinted from “Reversible Oxygen Redox Chemistry in Aqueous Zinc-Ion Batteries”, by Wan et al., 2019, *Angewandte Chemie International Edition*, 2019, 58(21), 7062-7067. Copyright 2019 by Wiley-VCH.

Conversely, O^- was reduced back to O^{2-} during the subsequent discharge cycle from 2.1 to 1.7 V. The reduced oxygen intensity in X-ray absorption spectra (SXAS) at the fully discharged state was attributed to the reduction of vanadium, whereas the enhanced signals at the fully charged state, relative to the initial state, indicated the oxidation of oxygen (Figure 7).

Figure 7. Oxygen SXAS spectra (inset shows the integrated intensity).

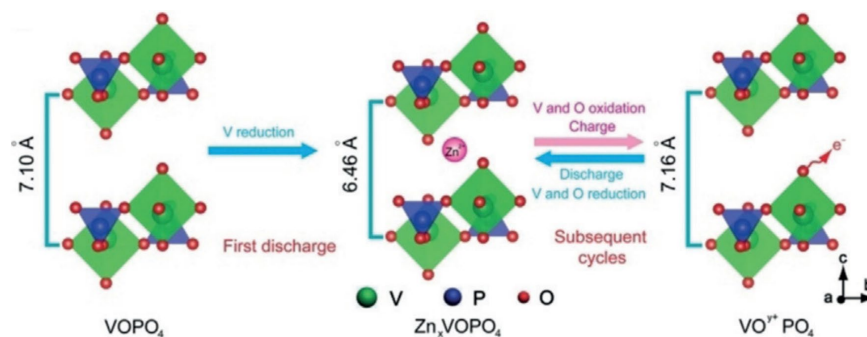


Note. Reprinted from “Reversible Oxygen Redox Chemistry in Aqueous Zinc-Ion Batteries”, by Wan et al., 2019, *Angewandte Chemie International Edition*, 2019, 58(21), 7062-7067. Copyright 2019 by Wiley-VCH.

The overall redox process is comprehensively illustrated in Figure 8. It is notable that oxygen redox chemistry not only contributes to additional specific capacity but also raises the average operating voltage of Zn/VOPO₄ batteries.

Figure 8.

Oxygen and vanadium redox mechanism during charge/discharge processes.



Note. Reprinted from “Reversible Oxygen Redox Chemistry in Aqueous Zinc-Ion Batteries”, by Wan et al., 2019, *Angewandte Chemie International Edition*, 2019, 58(21), 7062-7067. Copyright 2019 by Wiley-VCH.

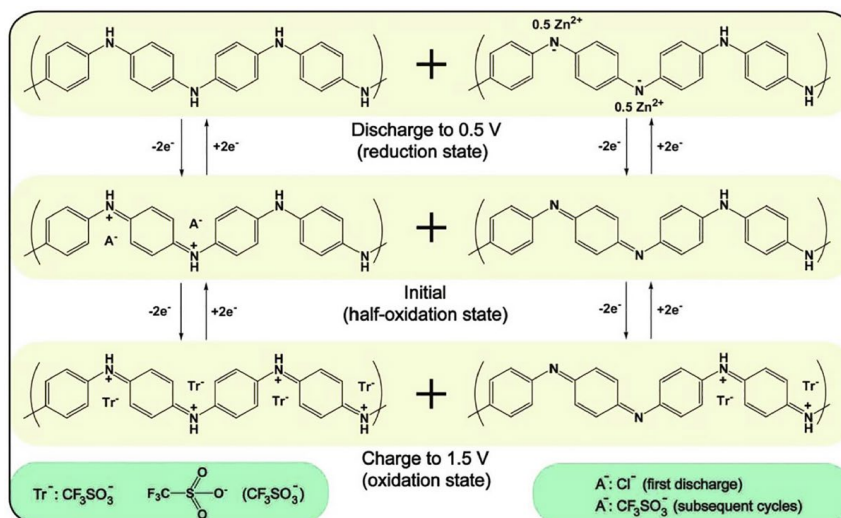
A similar dual-ion mechanism was also detected in a surface-oxidized vanadium nitride (VN_xO_y) cathode, which involved a concurrent reversible reaction of cationic redox ($V^{3+} \leftrightarrow V^{2+}$) during Zn²⁺/H⁺ intercalation/de-intercalation and pseudo-capacitance-like surface anionic redox ($N^{3+} \leftrightarrow N^{2+}$) during OH⁻ release/uptake (Fang et al., 2019). Crucially, the lower electronegativity of nitrogen compared to oxygen reduces the ionic bond strength between Zn²⁺ and oxygen, thereby facilitating the rapid and reversible diffusion of Zn²⁺. Consequently, the VN_xO_y cathode exhibited excellent rate performance of 200 mAh g⁻¹ at 30 A g⁻¹, along with remarkable cycling stability over 2000 cycles.

2.4.3 Redox of Active Functional Groups

Recently, a diverse range of organic compounds enriched with functional groups has been investigated as potential cathode materials for AZIBs. These materials include polyaniline (PANI) (Ma et al., 2018; Wan, Zhang, Wang, et al., 2018; D. Wang et al., 2018), quinone (Liang et al., 2017), calix[4]quinone (C4Q) (Zhao et al., 2018), sulfur heterocyclic quinone dibenzo[n,i]thianthrene-5,7,12,14-tetraone (Wang et al., 2020), poly(benzoquinonyl sulfide) (Dawut et al., 2018), and pyrene-4,5,9,10-tetraone (PTO) (Guo et al., 2018). The electrochemical mechanisms of these organic cathodes predominantly involve the redox reactions of active functional groups within their chain structures, such as $C=N-$ and $C=O$ (carbonyl) groups (Cui et al., 2020). For instance, in PANI, both $C=N-$ and protonated $C=NH^+$ groups have been identified as electrochemically active sites capable of storing Zn^{2+} ions (Wan, Zhang, Wang, et al., 2018). As depicted in Figure 9, during the initial discharge, the protonated $=NH^+$ groups undergo reduction to $-NH-$ groups, while the $C=N-$ groups in the polymer backbone are reduced to electronegative $-N^-$ species, which effectively adsorb Zn^{2+} ions. During partial charging, the $-NH-$ and $-N^-$ groups revert to their original $=NH^+$ and $C=N-$ forms, respectively.

Figure 9.

Proposed redox mechanism of PANI/CFs.



Note. Reprinted from “An Aqueous Rechargeable Zinc-Organic Battery with Hybrid Mechanism”, by Wan et al., 2018, *Advanced Functional Materials*, 2018, 28(45), 1804975. Copyright 2018 by Wiley-VCH.

Although still in an early stage, these pioneering investigations could open up new avenues for developing innovative organic cathode materials enriched with functional groups, capable of undergoing active redox interactions with Zn^{2+} ions.

Chapter 3 Recent Advances in Hydrogel Electrolytes for AZIBs

As we mentioned in previous chapters, despite the competitiveness of AZIBs among all battery technologies due to their ultrahigh theoretical gravimetric (820 mAh g^{-1}) and volumetric (5854 mAh cm^{-3}) capacity, relatively low redox potential (-0.762 V) vs. S.H.E, non-toxicity, excellent intrinsic safety, environmental benignity, high crustal abundance, and affordability, AZIBs are still hampered by numerous challenges such as severe parasitic reactions (e.g., HER), narrow electrochemical stability window (ESW), and notorious Zn dendrite growth, which open up research directions to achieve better, high-performance AZIBs. Among all strategies to circumvent the abovementioned obstacles, electrolyte engineering appears as a cost-effective option given the crucial role of electrolyte in controlling Zn^{2+} transport between electrodes and regulating Zn^{2+}/Zn nucleation on the anode surface (Cao et al., 2023; Kang et al., 2020; T. C. Li et al., 2023; Y. Li et al., 2023; Sun et al., 2022; Tian et al., 2022; D. Wang et al., 2023; Yu Wang et al., 2023; Yanyan Wang et al., 2023; Wu et al., 2023; Xie et al., 2023; Xing et al., 2023; Zheng et al., 2023; Zhou et al., 2022). Electrolytes used in AZIBs can be categorized into liquid-state, quasi-solid-state, and all-solid-state electrolytes. Liquid- and all-solid-state electrolytes represent single-phase systems composed solely of either liquid solutions or solid materials, such as polymers and ceramics, respectively (Ge et al., 2024). On the other hand, quasi-solid-state electrolytes (QSSEs) combine an aqueous solution with a solid matrix, thus encompassing both liquid and solid phases. While liquid-state electrolytes generally exhibit superior ionic conductivity compared to the other types, their fluidic nature imposes stringent requirements on battery packaging, and issues such as leakage and volatilization are still of

concern (Lv et al., 2022). Even minor scratches or punctures during battery operation can lead to encapsulation failure (H. Dong et al., 2021). In the context of flexible applications, liquid electrolytes are prone to being squeezed, which leads to uneven deposition and an increased risk. This limitation makes liquid electrolytes unsuitable for flexible and wearable applications.

All-solid-state electrolytes (ASSEs) mitigate many of the concerns associated with liquid electrolytes; however, they still fall short in electrochemical performance due to their low ionic conductivity at room temperature and substantial interfacial resistance (Liang et al., 2020; Zhao et al., 2020; Zheng et al., 2020). Additionally, their inherent brittleness poses challenges for large-scale production. In contrast, quasi-solid-state electrolytes (QSSEs) have garnered considerable attention for use in flexible and wearable batteries and electronics, as they combine the benefits of both liquid- and solid-state electrolytes. They offer a favorable balance of ionic conductivity, improved interfacial properties, and mechanical deformability (Fan et al., 2022). Furthermore, QSSEs can serve as separators with optimal mechanical stiffness and elasticity, effectively blocking dendrite growth and thereby reducing the risk of short-circuiting (Huang et al., 2023).

Moreover, side reactions caused by free water, a major challenge in AZIBs using liquid electrolytes, can be mitigated by employing QSSEs. This is possible due to the presence of abundant hydrophilic functional groups that can modify the solvation structure of Zn^{2+} ions and confine water molecules (Y. Wang et al., 2023). Additionally, QSSEs are versatile and highly tunable, allowing them to be tailored into multifunctional materials (Y. Guo et al., 2020).

As a result, there has been a surge in QSSE research, with hydrogel electrolytes (HEs) emerging as particularly promising candidates.

3.1 Hydrogel Electrolytes

Hydrogels are three-dimensional (3D) crosslinked networks composed of hydrophilic polymers, capable of absorbing substantial amounts of water within their structure. These materials exhibit an impressive capacity to absorb over 1000% of their weight in water without dissolving. As such, hydrogels have recently garnered significant attention in the development of polymer electrolytes due to their ability to retain considerable quantities of ionic solutions within the polymer matrix, which contributes favorably to both ionic conductivity and mechanical properties. Furthermore, the distinctive porous microstructure of hydrogels facilitates efficient contact between electrodes and electrolytes, thereby enhancing ion transport and promoting effective electrochemical processes. The mechanical, chemical, thermal, and electrochemical properties of hydrogel electrolytes (HEs) can also be easily tailored by modifying the hydrogel matrix, introducing copolymers or hybrid materials, and incorporating ionically conductive fillers (X. Li, D. Wang, et al., 2023; Ma et al., 2023).

3.2 Classification of Hydrogel Electrolytes

Hydrogel electrolytes, owing to their numerous aforementioned merits, have emerged as suitable electrolyte materials for AZIBs. Key advantages of hydrogel electrolytes include their high interfacial stability between the electrode and electrolyte, biocompatibility, suppression of oxidative decomposition within the battery, excellent mechanical properties, and high ionic conductivity (K. Wu et al., 2020).

These hydrogel electrolytes can be broadly categorized into two main types: natural hydrogels and synthetic hydrogels. Synthetic hydrogels demonstrate high mechanical strength, enhanced stability, and reduced impurity levels. Polymers such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), polyacrylic acid (PAA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and polyacrylamide (PAM) are among the synthetic hydrogels that have been extensively applied in AZIBs. Compared to synthetic hydrogels, natural hydrogels appear to be more attractive due to their excellent sustainability and biocompatibility. Derived from biopolymers such as cellulose, gelatin, and chitosan, natural hydrogels are highly biocompatible and environmentally friendly, making them suitable for applications involving wearable or implantable energy devices (Ma et al., 2023).

3.3 Natural Hydrogel Electrolytes

Natural hydrogel electrolytes can be broadly categorized into two types: (1) polysaccharide-based hydrogel electrolytes and (2) protein-based hydrogel electrolytes (Radjendirane et al., 2024). Polysaccharide-based hydrogel polymer electrolytes (HPEs) possess several advantages over conventional liquid electrolytes, such as high ionic conductivity, superior mechanical properties, nonvolatility, and remarkable stability. Examples of polysaccharides that have been studied for their use in HPEs include chitosan, cellulose, alginate, and carrageenan. On the other hand, protein-based HPEs also exhibit numerous benefits, including excellent ionic conductivity, favorable mechanical attributes, and inherent biocompatibility. Furthermore, proteins can be chemically modified to acquire specific properties, such as enhanced affinity

for particular ions, thereby improving the overall performance of the electrolyte. The potential application of proteins such as gelatin, collagen, and silk fibroin as hydrogel polymer electrolytes has been extensively explored.

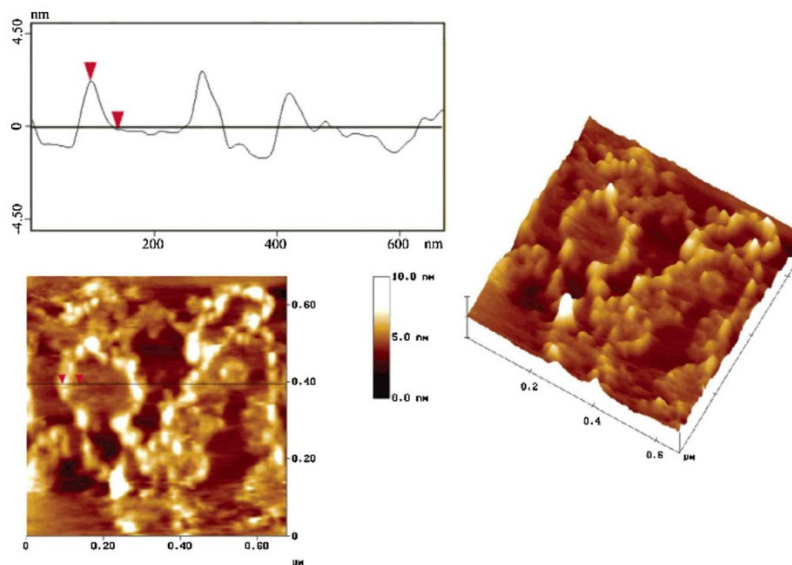
3.4 Polysaccharides-Based Natural Hydrogel Electrolytes for AZIBs

3.4.1 Cellulose

The advancement of low-cost, eco-friendly, and durable energy storage systems is of paramount importance. Cellulose, one of the most abundant renewable resources on Earth, presents a promising solution. Cellulose hydrogels are composed of cellulose molecules dissolved in water, forming long polysaccharide chains of repeating glucose units linked by hydrogen bonds (Gong et al., 2024). Glatz et al. (2019) utilized a cellulose membrane to develop a dual-ion AZIB comprising a zinc metal anode, a 1,4-bis(diphenylamino)benzene (BDB)-based cathode, and a cellulose-based hydrogel membrane. This AZIB exhibited a capacity of 112 mAh g^{-1} , retaining approximately 82% capacity after 500 cycles and about 75% after 1000 cycles. Similarly, Weng et al. (2004) explored the gelation behavior of cellulose in NaOH/thiourea compared to neat cellulose. Wide-angle XRD analysis indicated that cellulose in the hydrogel state exhibited no crystallinity, indicating a lack of inter- and intra-molecularly packed chains. Top-view height scan images showed cellulose spread over a substrate immersed in water, with nanoparticles averaging $47.7 \pm 5.9 \text{ nm}$, forming peak-valley structures due to their interconnections. The height of these peaks was measured at 2.36 nm (Figure 10), with an average nanoparticle size of $45.9 \pm 8.5 \text{ nm}$, consistent with that in pure water.

Figure 10.

AFM image of the gel from the 5 wt% cellulose solution spread on the substrate after being dispersed in pure water.



Note. Adapted from “Thermal Gelation of Cellulose in a NaOH/Thiourea Aqueous Solution”, by Weng et al., 2004, *Langmuir*, 20(6), 2086-2093. Copyright 2004 by American Chemical Society.

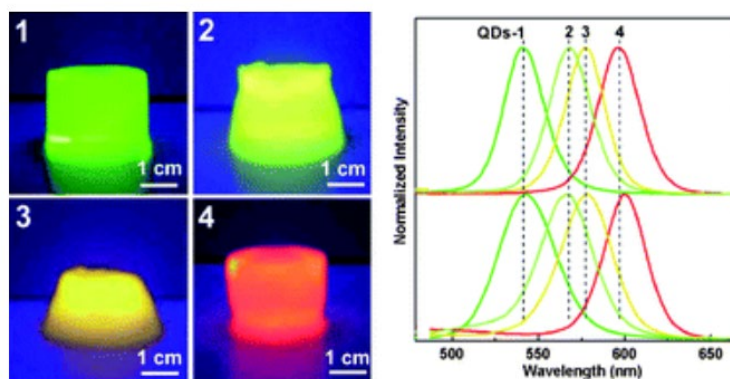
Notably, the cellulose hydrogel formed stable networks in NaOH/thiourea, in contrast to its instability in pure water, creating hydrogel lumps with a stable 3D topology on the substrate.

Moreover, Chang et al. (2009) synthesized a novel cellulose quantum dot (QD) hydrogel electrolyte, investigating the photoluminescent properties of the cellulose-QD hydrogel under visible light and UV exposure. Photoluminescence studies revealed emission peaks for

CdSe/ZnS at 541 nm, 568.5 nm, 577 nm, and 596 nm, while the cellulose-QD hydrogel exhibited peaks at 549.5 nm, 566.5 nm, 577 nm, and 599 nm, as depicted in Figure 11.

Figure 11.

The appearances of the cellulose-QD hydrogels under a 302 nm UV lamp (left), and PL spectra of CdSe/ZnS (core/shell) QDs in buffer solution (right, top) with emission peaks at 541 nm, 568.5 nm, 577 nm, 596 nm, and in the cellulose-QD hydrogel (right, bottom) with emission peaks at 549.5 nm, 566.5 nm, 588 nm with a laser line at 400 nm used for excitation. The average diameters of the QDs nanocrystals are 2.8 nm (green), 3.0 nm (yellowish-green), 3.2 nm (yellow), and 3.6 nm (red).



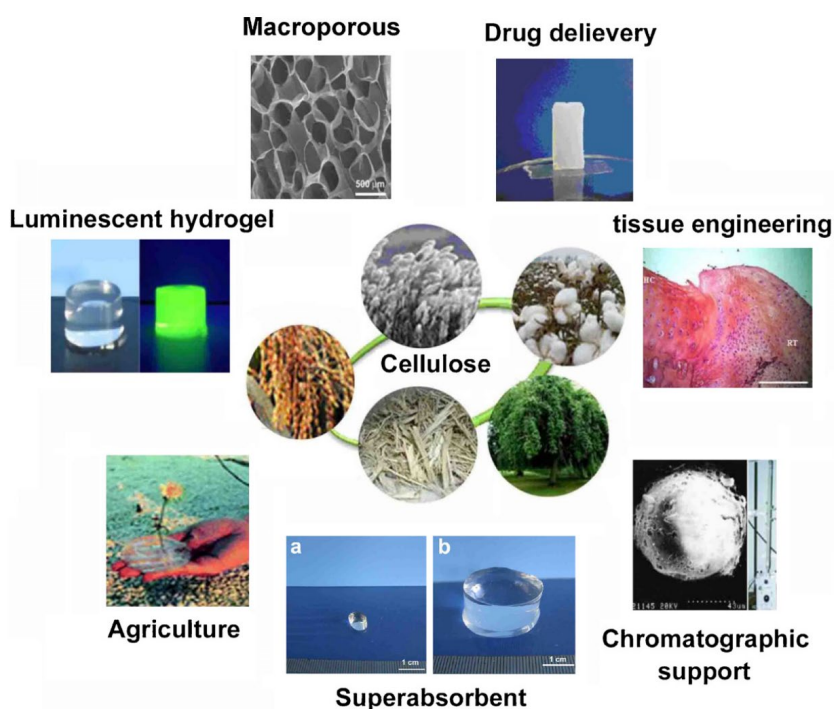
Note. Reprinted from “Strongly fluorescent hydrogels with quantum dots embedded in cellulose matrices”, by Chang et al., 2019, *Journal of Materials Chemistry*, 19(41), 7771-7776. Copyright 2009 by Royal Society of Chemistry.

These emissions were facilitated by a 400 nm excitation laser, with average nanocrystal QD sizes of 2.8 nm, 3.0 nm, 3.2 nm, and 3.6 nm for green, yellow-green, yellow, and red samples,

respectively. The versatile applications of cellulose hydrogels span various fields, including superabsorbents, drug delivery systems, tissue engineering, chromatographic support, agriculture, and luminescent and microporous structures (Chang & Zhang, 2011).

Figure 12.

Applications and developments of cellulose-based hydrogels.



Note. Reprinted from “Cellulose-based hydrogels: Present status and application prospects”, by Chang and Zhang, 2011, *Carbohydrate Polymers*, 84(1), 40-53. Copyright 2010 by Elsevier.

In the evolving landscape of energy storage, superabsorbent cellulose hydrogels show considerable potential for use in AZIBs, offering high water content capability and compatibility with other polymers to create mechanically robust crosslinked hydrogel networks.

3.4.2 Starch

Starch, one of the most prevalent carbohydrates in plants, is stored in the form of granules in chloroplasts of leaves and amyloplasts of seeds, tubers, and pulses. It is a polysaccharide composed of glucose units connected through α -D-(1-4) and α -D-(1-6) glycosidic bonds. Starch consists of approximately 70% amylose, which is amorphous, and 30% amylopectin, which has a crystalline structure. Starch-based hydrogels offer numerous advantages, including abundance as a natural and renewable resource, excellent water retention capability, and low cost. However, their limitations include the need for chemical enhancement to improve water retention and a limited surface area (Qamruzzaman et al., 2022; Zhang et al., 2024). In recent studies, Zuo et al. (2022) developed an AZIB incorporating a starch/PAM hydrogel electrolyte, prepared through a simple solution polymerization approach. This hydrogel exhibited improved ionic conductivity ($26.5 \times 10^{-3} \text{ S cm}^{-1}$), which was significantly higher compared to PAM hydrogels without starch. The AZIB displayed a high specific capacity of 202.6 mAh g^{-1} at 0.1 A g^{-1} , with a moderate energy density of 148.2 Wh kg^{-1} and a capacity retention of 98.6% after 600 cycles. Discharge capacities at current densities ranging from 0.1 A g^{-1} to 4.0 A g^{-1} were also stable, highlighting the electrolyte's potential for flexible energy storage systems. Furthermore, incorporating Zn and KOH salts led to an impressive ionic conductivity

of $115.1 \times 10^{-3} \text{ S cm}^{-1}$, outperforming other polymer electrolytes such as PAA-KOH, BC-KOH, and PVA-KOH. Starch's lower cost, compared to other synthetic polymers such as PVA, PAM, and PAA, adds to its appeal, making it a cost-effective and sustainable option for hydrogel electrolytes. In addition, starch offers functional benefits, such as acting as a thickening agent and providing shear resistance, which helps prevent short-circuit issues in AZIBs and enhances their reliability in energy storage applications.

3.4.3 Kappa-Carrageenan

Kappa-carrageenan (KCR) is a naturally derived polymer with mucopolysaccharide structures, chemically represented by the formula $\text{C}_{24}\text{H}_{36}\text{O}_{25}\text{S}_2$. By employing various crosslinking methods, such as methacrylation, its rheological, morphological, and mechanical properties can be effectively tuned. This polymer is primarily used in the food and healthcare sectors as a gelling, emulsifying, solidifying, and thickening agent, and it is sourced from red algae (*Rhodophyceae*). KCR has a notable gelling ability when cooled under specific salt conditions, attributed to the presence of hydrogen and ionic bonds. Structurally, it is composed of alternating units of 3-linked β -D-galactose-4-sulfate and 4-linked 6-enhydro- α -galactopyranose, each carrying a negative charge per repeating disaccharide unit (Fan et al., 2011; Zakaria et al., 2023).

Beyond traditional uses, KCR shows potential as a promising solid-polymer electrolyte for energy storage applications of AZIBs such as supercapacitors and Al-air batteries. Huang et al. developed an AZIB using KCR as a conductive polymer electrolyte, achieving an energy density of 400 Wh kg^{-1} and a power density of 7.9 kW kg^{-1} . The resulting AZIB exhibited a

specific capacity of approximately 291.5 mAh g⁻¹ at 0.15 A g⁻¹, maintaining 95% of its capacity after 300 cycles under continuous bending, highlighting its flexibility and capacity retention. The KCR hydrogel electrolyte demonstrated a high ionic conductivity of 33.2×10^{-3} S cm⁻¹, which is higher compared to other polymer electrolytes commonly used in AZIBs. Additionally, blending KCR with other biopolymers further enhanced ionic conductivity. The cyclic voltammetry of the AZIB featuring KCR hydrogel revealed oxidation peaks at 1.238 V and 1.364 V, while two discharge plateaus indicated the insertion/extraction of H⁺ or Zn²⁺ ions. Capacities of 287.1 and 278.5 mAh g⁻¹ were achieved, surpassing conventional AZIBs (Y. Huang, J. Liu, et al., 2019) (Yuan Huang, Jiuwei Liu, et al., 2019). This investigation underscores the potential of a novel KCR-based polysaccharide hydrogel as an optimal hydrogel electrolyte for AZIBs, paving the way for advanced energy storage solutions.

3.4.4 Sodium Alginate

Alginate is a water-soluble polymer extracted from green phytoplankton, primarily composed of monomers such as (1-4)-D-mannuronic acid (M) and (1-4)- α -L-gluronic acid (G), which may appear as homopolymeric (MM or GG blocks) or heteropolymeric (MG or GM blocks) sequences. Sodium alginate (SA) is known for its stable crosslinked framework, which is facilitated by carboxyl groups that form electrovalent bonds with bivalent cations (L. Wang et al., 2021; T. Wang et al., 2023). In a study conducted by Shang et al. (2021), an aqueous Zn-I₂ battery was developed using SA-based hydrogels enriched with abundant carboxyl and hydroxyl functional groups, which were capable of cross-linking with Zn²⁺ cations, thereby facilitating uniform transport of Zn²⁺ ions while effectively blocking I₃⁻ anions. The fabricated

Zn-I₂ batter exhibited a notable reversible capacity of 120 mAh g⁻¹, with a capacity retention of 72% after 100 hours of resting, significantly outperforming the conventional aqueous electrolyte-based AZIBs, which delivered 90 mAh g⁻¹ with only 16% capacity retention after 10 hours. Furthermore, the Zn(Ac)₂-hydrogel Zn-I₂ battery achieved impressive CE of 99.3% at 0.2 A g⁻¹ for over 200 cycles, and 99.5% at 2 A g⁻¹ for over 2000 cycles, underscoring the potential of hydrogel electrolytes as a promising alternative to conventional electrolyte materials.

3.4.5 Guar Gum

Guar gum is also commonly chosen for its non-toxic nature, mechanical stability, and intrinsic safety. Since natural polymers have limited ionic conductivity, they are often blended with other polymers to create composite hydrogels that overcome these limitations. J. Wang et al. (2021) developed a guar gum/sodium alginate/ethylene glycol (GG/SA/EG) hydrogel electrolyte for a flexible AZIB, with Zn foil serving as the anode and MnO₂ as the cathode. This GG/SA/EG-based AZIB demonstrated a specific capacity of 181.5 mAh g⁻¹, with a capacity retention of approximately 91.52% for over 1000 cycles. In terms of electrochemical performance, the AZIB delivered 354.9 mAh g⁻¹ at 0.15 A g⁻¹ and 137.0 mAh g⁻¹ at a high current density of 6 A g⁻¹. Interestingly, pure guar gum and a guar gum/sodium alginate (GG/SA) blend form gels at -20 °C, whereas the GG/SA/EG hydrogel forms a gel at room temperature due to the existence of ethylene glycol, which decreases the freezing tendency of the hydrogel effectively. In another study, R. Xu et al. (2022) developed an AZIB using a guar gum-cellulose hydrogel electrolyte, which showed excellent ionic conductivity of 4.73×10^{-2}

S cm⁻¹ and a specific capacity of 309.1 mAh g⁻¹. This system demonstrated full capacity retention after 200 cycles and a high CE of 99%, surpassing the performance of other gum-based electrolytes.

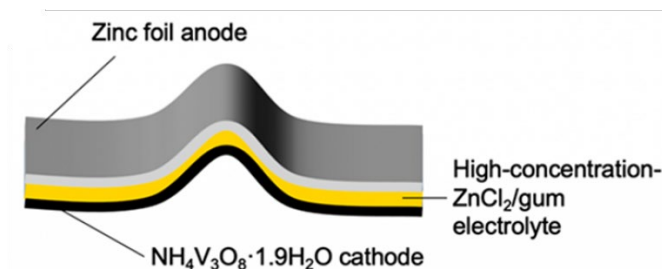
3.4.6 Xanthan Gum

Xanthan Gum (XG) is another complex extracellular polysaccharide derived from the bacterium *Xanthomonas campestris*. Its structure consists of a branched trisaccharide side chain composed of β -D-(1,2)-mannose linked to β -D-(1,4)-glucuronic acid, terminating in β -D-mannose, with a primary chain made of β -D-(1,4)-glucose (Gils et al., 2009). The alkyl groups present in the side chains give XG its high water absorption capability. When dissolved in an aqueous solution, XG shows excellent conductivity, salt tolerance, and mechanical strength, making it well-suited for applications in AZIBs (Zhang et al., 2018). It also helps mitigate self-oxidation and inhibits Zn dendrite formation during charge/discharge cycles.

Chen et al. (2020) were the first to create a subzero AZIB using an NH₄V₃O₈ cathode and an antifreezing hydrogel electrolyte made from XG and zinc chloride (ZnCl₂), as shown in Figure 13.

Figure 13.

Schematic illustration of high-concentration quasi-solid-state electrolyte (HCSE) battery: Zn/XG-
ZnCl₂/NH₄V₃O₈.



Note. Reprinted from “Quasi-Solid-State Zinc Ion Rechargeable Batteries for Subzero Temperature Applications”, by Chen et al., 2020, *ACS Applied Energy Materials*, 3(9), 9058-9065. Copyright 2020 by American Chemical Society.

The formation of XG was confirmed using Fourier Transform Infrared (FTIR) spectroscopy, where a prominent peak at 3270 cm⁻¹ corresponded to the axial deformation of the O-H bond. Additional peaks at 1601, 2879, and 1705 cm⁻¹ were attributed to different C-O, C-H, and other molecular stretching and deformation vibrations. The glass transition temperature of XG was approximately 290 °C. The resulting flexible AZIB retained 90.3% of its capacity after 800 cycles at both 20 °C and 0 °C, while the XG-based hydrogel electrolyte with ZnCl₂ exhibited ionic conductivity of 13.8 × 10⁻³ S cm⁻¹. The XG hydrogel also demonstrated good mechanical properties, such as resistance to bending and twisting, ensuring flexibility without cracking at -20 °C (Figure 14).

Figure 14.

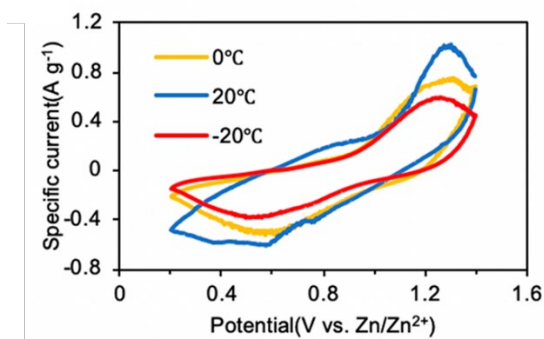
Mechanical deformation of XG electrolyte under bending, twisting, and adhesion.



Note. Reprinted from “Quasi-Solid-State Zinc Ion Rechargeable Batteries for Subzero Temperature Applications”, by Chen et al., 2020, *ACS Applied Energy Materials*, 3(9), 9058-9065. Copyright 2020 by American Chemical Society.

The improved battery performance was due to effective ion transport through the hydrogel electrolyte at subzero temperatures, as shown in Figure 15.

Figure 15. Cyclic voltammetry (CV) studies of HCSE battery from 20 to -20 °C.

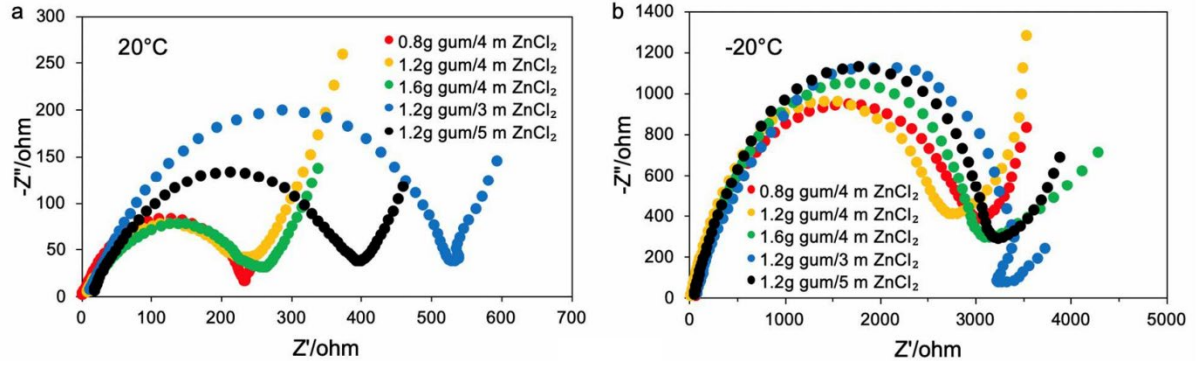


Note. Reprinted from “Quasi-Solid-State Zinc Ion Rechargeable Batteries for Subzero Temperature Applications”, by Chen et al., 2020, *ACS Applied Energy Materials*, 3(9), 9058-9065. Copyright 2020 by American Chemical Society.

Wang and Chen (2021) also developed a flexible AZIB for low-temperature applications, using an $\text{NH}_4\text{V}_3\text{O}_8$ cathode and Zn anode, with XG hydrogel sandwiched in between as the electrolyte. Different concentrations of XG and ZnCl_2 salt (e.g., 1.2 g of XG combined with 3 M, 4 M, or 5 M ZnCl_2 , as well as 0.8 g and 1.2 g of XG with 4 M ZnCl_2 at 20 °C and -20 °C) were used to conduct electrochemical impedance spectroscopy (EIS) (Figure 16a, b).

Figure 16.

EIS of XG-ZnCl₂ electrolyte at (a) 20 °C and (b) -20 °C



Note. Adapted from “A flexible zinc-ion battery based on the optimized concentrated hydrogel electrolyte for enhanced performance at subzero temperature”, by Wang and Chen, 2021, *Electrochimica Acta*, 395, 139178. Copyright 2021 by Elsevier.

It was observed that the electrolyte with 1.2 g of XG in 4 M ZnCl₂ solution had the lowest charge transfer resistance, indicating stable performance even at – 20 °C. Moreover, the mechanical properties of XG hydrogels mixed with Fe³⁺ ions were also investigated, revealing that an increase in XG content led to reduced tensile strength, agglomeration, and structural defects due to irregular crosslinking. The key advantage of XG lies in its stability and compatibility with homogeneous sulfate salt solutions, in contrast to synthetic polymers such as PEO and PVDF-HFP. Furthermore, the drawbacks of XG can be addressed through optimizing concentration, which highlights its potential in advancing energy storage technology.

3.5 Protein-Based Natural Hydrogel Electrolytes for AZIBs

3.5.1 Gelatin

Gelatin is a biocompatible polymer derived from animal bones, skin, and connective tissues, created through the covalent bonding of monomers. Its structure, rich in amino and carboxyl groups, makes it suitable as an electrolyte material for energy storage devices like supercapacitors and batteries, as it can accommodate various inorganic ions. As a result, gelatin-based HEs offer high ionic conductivity (Choudhury et al., 2009). By adjusting the water content during production, the mechanical strength of gelatin can be modified after solidification, providing flexible batteries with enhanced structural support and stability.

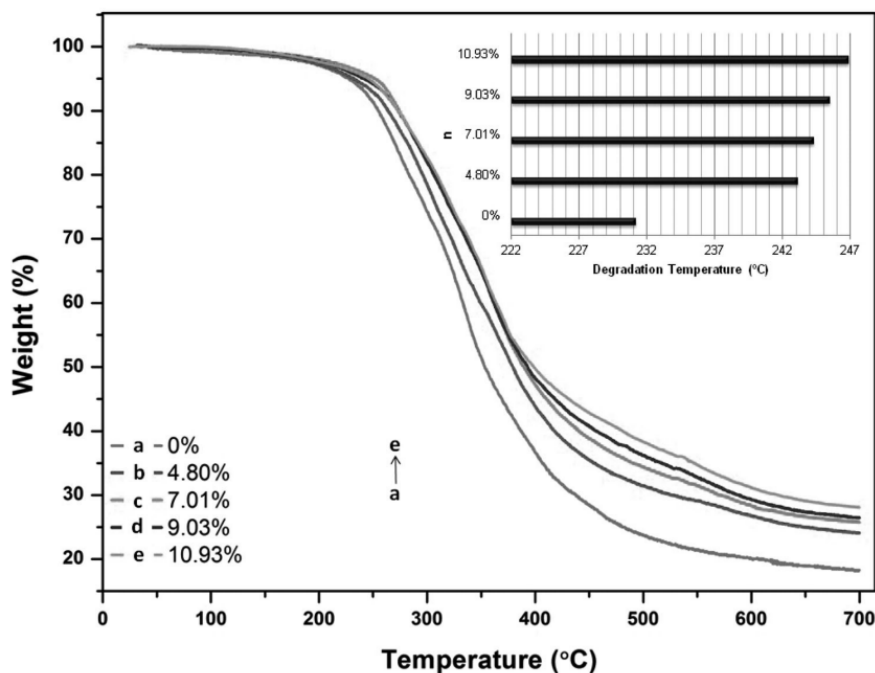
Gelatin is commonly used in flexible batteries due to its ease of assembly, high salt conductivity, affordability, environmental friendliness, and biodegradability (Ulubayram et al., 2002; Z. Wang et al., 2018). Rapid cooling promotes the formation of helical segments as gelatin molecules, initially dispersed randomly in an aqueous solution at temperatures above the gelation temperature (T_g), assemble through hydrogen bonding. As the gelatin cools, these disordered molecules form hydrogen bonds, transitioning to a more ordered structure. This leads to the creation of triple helix segments, which then coil together to form the gelatin-based solid electrolyte (GSE). Liu et al. (2021) fabricated a Zn//MnO₂ AZIB using a gelatin-based electrolyte. Using Mn²⁺ ions and gelatin as co-additives in a ZnSO₄ environment, the performance of the assembled AZIB was significantly improved. Zn dendrite formation was also suppressed by altering Zn's crystal growth orientation, from the (112) plane to the (103) and (002) planes, which are less prone to dendrite formation. The Zn//MnO₂ battery exhibited

extended cycle life and improved capacity retention (80% after 1000 cycles), demonstrating the synergistic effect of the gelatin-based electrolyte and Mn^{2+} in enhancing electrochemical performance for a ZnSO_4 system. Han et al. (2018) also utilized gelatin to develop a quasi-solid-state Zn metal battery, noting that the porous structure of gelatin hydrogels and their high electrolyte retention capacity enabled the gelatin hydrogel electrolyte to achieve an ionic conductivity of $6.15 \times 10^{-3} \text{ S cm}^{-1}$. The electrolyte demonstrated increased compressive strength when subjected to lower C. cooling temperatures, achieving twice the strength when cooled at 5 °C compared to 25 °C. Chronoamperometry (CA) testing indicated reduced Zn dendrite formation due to the lower deposition currents between the Zn electrode and electrolyte. Gelatin solid electrolytes also exhibited shrinkage when salt concentrations surpassed 1.5 M, driven by osmotic pressure, which peaked at a 56% shrinkage ratio at 3.5 M salt concentration. Water absorption and overhydration were identified as the primary factors for swelling and shrinking behaviors, with water content significantly dropping to 45.35% at 2.5 M salt concentration. Further increases in salt concentration did not substantially alter the water content, and this reduction proved beneficial for improving the thermal stability, mechanical strength, and safety of gelatin solid electrolytes under extreme conditions while enhancing cycling stability by reducing free water molecule effects (Huang et al., 2021).

Moreover, Alves et al. (2013) investigated the thermal stability of GSEs, observing that thermal degradation, evidenced by weight loss, began at temperatures above 225 °C across all samples (Figure 17).

Figure 17.

Thermogravimetric analysis curves of different concentrations of prepared gelatin- $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -based electrolytes.

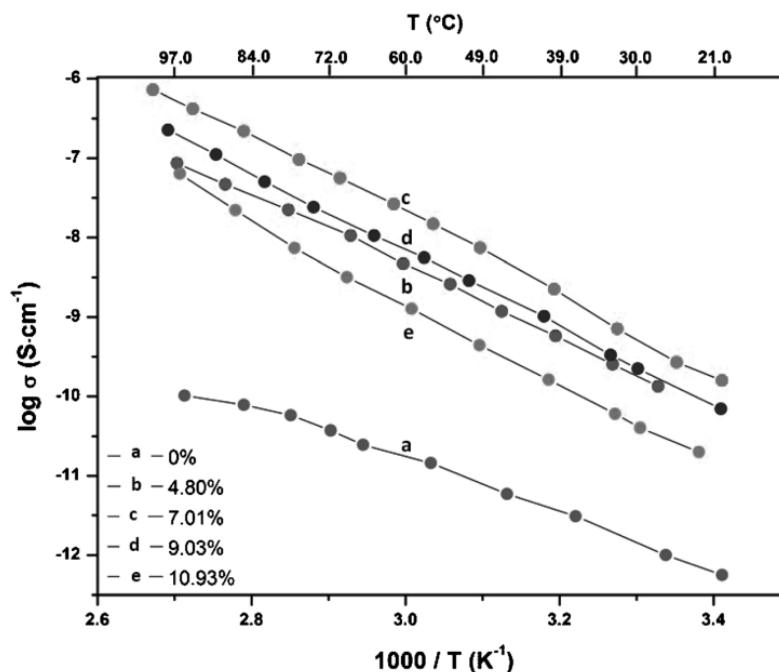


Note. Reprinted from “Gelatin_nZn(CF₃SO₃)₂ Polymer Electrolytes for Electrochromic Devices”, by Alves et al., 2013, *Electroanalysis*, 25(6), 1483-1490. Copyright 2013 by Wiley-VCH.

Higher salt concentrations increased the stabilization of the gelatin matrix, improving ionic conductivity to an optimal level at 7.01 wt% salt addition. Without $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, the ionic conductivity of the gelatin sample was about 1.0×10^{-12} S at room temperature, increasing to 1.0×10^{-10} S cm⁻¹ at 95 °C. With 7.1% $\text{Zn}(\text{CF}_3\text{SO}_3)_2$, the conductivity values improved further,

reaching $3.09 \times 10^{-10} \text{ S cm}^{-1}$ at room temperature and $4.60 \times 10^{-7} \text{ S cm}^{-1}$ at 95 °C. However, further increasing the salt concentration led to reduced conductivity, likely due to the formation of complexes hindering ion mobility, as indicated in Figure 18.

Figure 18. Conductivity plots with respect to the inverse of temperature for gelatin- $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ -based electrolytes



Note. Reprinted from “Gelatin_n $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ Polymer Electrolytes for Electrochromic Devices”, by Alves et al., 2013, *Electroanalysis*, 25(6), 1483-1490. Copyright 2013 by Wiley-VCH.

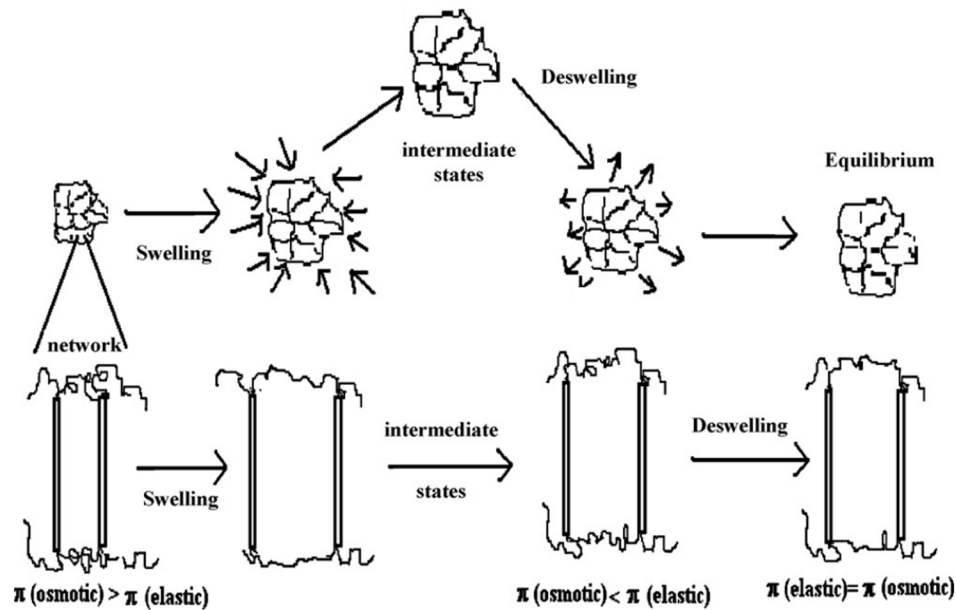
Furthermore, Zhu et al. (2018) innovatively developed a photoluminescent micro-battery featuring a gelatin-based electrolyte. The charge/discharge profiles revealed plateaus, indicating consistent electrochemical activity. This micro Zn-metal battery, comprising a Zn anode, MnO₂ cathode, and gelatin electrolyte infused with CdTe quantum dots (QDs), achieved an energy density of approximately 21 mWh cm⁻³ and a capacity of 110 μAh cm⁻² at a current rate of 0.2 mA cm⁻². Increasing the current to 0.4 mA cm⁻² resulted in a reduced capacity of 60 μAh cm⁻², though the system maintained stability for over 200 cycles with high CE. The micro Zn metal battery emitted blue light when using pure gelatin, while incorporating water-soluble CdTe QDs enabled modulation of the emitted color. The gelatin-based electrolyte exhibited substantial hydrophilicity, resulting in enhanced ionic transport and superior ionic conductivity compared to standard polymer hydrogels.

3.5.2 Agar Gum

Agar gum is a naturally occurring polycationic biopolymer, characterized by a molecular structure consisting of repeating disaccharide units of $-(1-3)-\beta\text{-D-galactose-(1-4)-3,6-anhydro-}\alpha\text{-L-galactose}$. It features various structural defects due to C6 substitutions within the anhydride. The presence of methoxyl groups plays a key role in determining the temperature at which agar hydrogel forms (Boral et al., 2010). Typically, agar hydrogels exhibit a glass transition temperature (T_g) of approximately 40 °C, and they melt at a temperature T_m of around 85 °C. The swelling and deswelling behavior of agar hydrogels is driven by osmotic pressure and the elasticity of its components, enabling agar gum to form temperature-reversible hydrogels that swell or shrink as required (Figure 19).

Figure 19.

Agar hydrogel membranes swelling-deswelling kinetics driven by osmotic and elastic components of osmotic pressure.

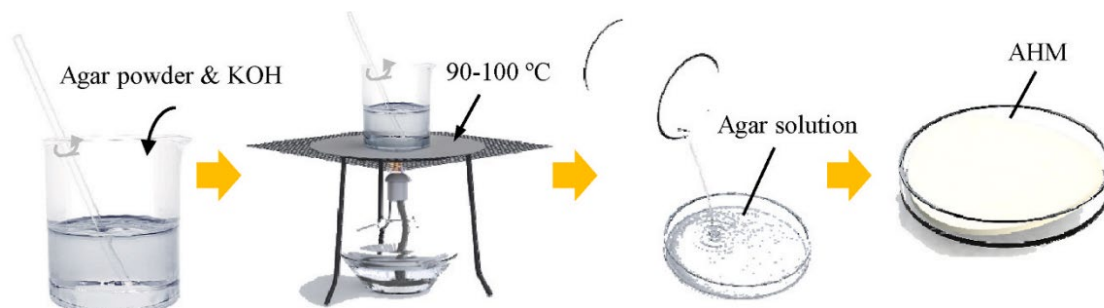


Note. Reprinted from “Syneresis in agar hydrogels”, by Boral et al., 2010, *International Journal of Biological Macromolecules*, 46(2), 232-236. Copyright 2010 by Elsevier.

The preparation of agar hydrogel involves sequential steps of stirring, heating, cooling, and solidification, as illustrated in Figure 20 (M. Wei et al., 2022).

Figure 20.

Schematic illustration of agar hydrogel membrane preparation.



Note. Reprinted from “Zn-dominated interphase inhibits the anodic parasitic reactions for Al-air batteries using Zn^{2+} @Agar hydrogel membrane”, by M. Wei et al., 2022, *Journal of Power Sources*, 545(15), 231974. Copyright 2022 by Elsevier.

The resulting agar hydrogel demonstrated excellent elastoplastic properties, with no signs of fracture when subjected to a 180° bend under a 500 g load, reflecting its strong mechanical characteristics suitable for use in electrolyte applications (Baek et al., 2019; Khoobakht et al., 2024).

Jenson et al. (2019) also fabricated a battery utilizing an agar hydrogel electrolyte incorporating acetylene black, where the anode and cathode were suspended within the electrolyte. The system was separated using an agar hydrogel containing NaCl (1.5 M). The anode in the setup was hydrazine-based, while the cathode employed lithium perchlorate. The battery achieved an energy density of 0.5 J L^{-1} and a cell capacity of $0.0053 \text{ mAh g}^{-1}$ at a concentration of 8 mM.

3.6 Design Metrics of Advanced Natural Hydrogel Electrolytes for AZIBs

The design of advanced hydrogel electrolytes for AZIBs is primarily driven by the need to address the drawbacks of traditional liquid electrolytes and to improve battery safety and performance (Radjendirane et al., 2024). To enhance battery functionality, high ionic conductivity ($> 10 \text{ mS cm}^{-1}$) is crucial, as it ensures efficient ion transport within the electrolyte. This property can be influenced by factors such as the polymer network structure, ion dissociation within the hydrogel matrix, and the water content. Additionally, a broad electrochemical stability window (ESW) of over 2.2 V is necessary to prevent decomposition at electrode operating voltages, thus improving energy density. Mechanical robustness ($>1 \text{ MPa}$) and flexibility are key to maintaining the structural integrity of the hydrogel and ensuring consistent contact with the electrodes during cycling. These attributes can be tuned through adjustments to crosslinking density, polymer composition, and the incorporation of reinforcing fillers or fibers. Efficient Zn^{2+} ion transport (transference number > 0.6) minimizes internal resistance, facilitating faster ion migration and enhancing battery performance. Another essential property is high water retention ($>1000\%$), which helps maintain ionic conductivity and prevents the electrolyte from drying out, thereby improving overall ionic mobility. Furthermore, hydrogel electrolytes must be compatible with zinc anodes to minimize dendritic growth, ensuring uniform zinc deposition and improving cycling stability. Advanced hydrogels should also possess self-healing properties, anti-freezing capability, and an entangled network structure, contributing to high stability over extended cycling periods. In sum, designing advanced hydrogel electrolytes for high-performance AZIBs requires careful consideration of

hydrogel chemistry and structural innovations to meet the evolving requirements for conductivity, stability, and mechanical resilience.

3.7 Summary

In conclusion, recent advancements in hydrogel electrolytes have demonstrated their potential as a transformative solution for addressing the challenges facing AZIBs. Hydrogels offer a unique combination of high ionic conductivity, robust mechanical properties, and tunable chemistry, making them particularly well-suited for enhancing battery safety, performance, and longevity. By mitigating issues such as Zn dendrite growth, parasitic reactions, and narrow electrochemical stability window, hydrogel electrolytes provide a promising path forward for developing high-performance AZIBs. The versatility of hydrogel electrolytes, including natural and synthetic variants, enables the creation of multifunctional materials tailored to specific application requirements, such as flexible and wearable energy storage devices. Moreover, advancements in electrolyte engineering—focusing on structural modifications, crosslinking strategies, and integration with various biopolymers—are paving the way for the next generation of AZIBs with improved electrochemical stability and durability. Future research should continue to explore novel hydrogel formulations and their integration with innovative electrode materials to fully realize the potential of AZIBs as a safe, cost-effective, and sustainable energy storage solution.

Chapter 4: Methods

This chapter delves into the fundamental principles and operational mechanisms of essential material characterization techniques and electrochemical characterization methodologies that were employed. The materials used, battery assembly procedures, electrolyte preparation, and synthesis of various cathode materials employed in this research, including alpha manganese oxide (α -MnO₂) and sodium vanadate (β -Na_{0.33}V₂O₅, NVO), are also discussed.

4.1 Material Characterization

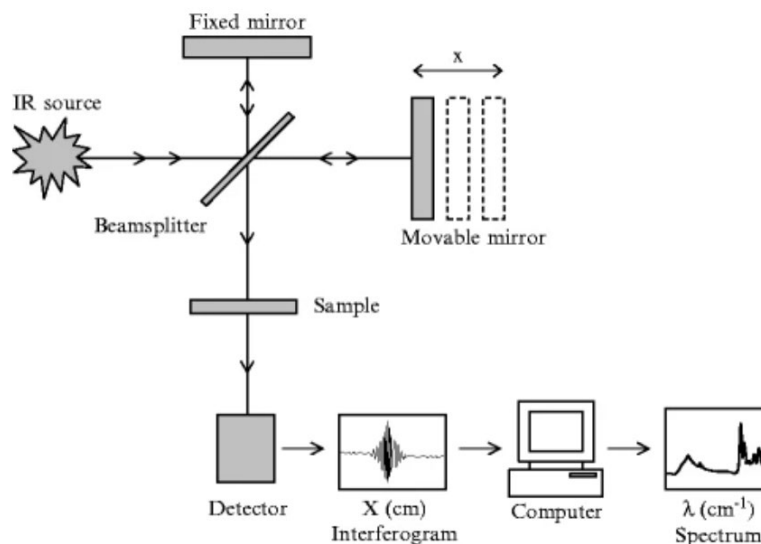
4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is an analytical technique commonly employed to identify organic, polymeric, and occasionally inorganic materials (Berthomieu & Hienerwadel, 2009). The FTIR analysis leverages infrared radiation to examine test samples and evaluate their chemical properties. During the analysis, infrared radiation, typically ranging from 10,000 to 100 cm⁻¹, is directed through the sample, where some of the radiation is absorbed while the remainder is transmitted. The absorbed energy is subsequently converted into rotational and vibrational motions within the sample molecules. The detected signal is presented as a spectrum, generally spanning from 4000 cm⁻¹ to 400 cm⁻¹, which represents a unique molecular fingerprint of the sample. Given that each molecule or chemical structure produces a distinctive spectral signature, FTIR analysis is an invaluable technique for precise chemical identification.

FTIR employs a Michelson interferometer, as depicted in Figure 21 (Ojeda & Dittrich, 2012).

Figure 21.

Instrumental setup for FTIR spectroscopy.



Note. Reprinted from “Fourier Transform Infrared Spectroscopy for Molecular Analysis of Microbial Cells”, by Ojeda and Dittrich, 2012, *Microbial Systems Biology: Methods and Protocols*, 187-211. Copyright 2012 by Springer Nature.

This configuration comprises a semi-transparent beam-splitter and two reflectors – one stationary and the other movable. Light from the source is directed into the interferometer as a collimated beam, which is incident on the beam-splitter at an oblique angle, resulting in the division of the light into transmitted and reflected components. These two beams are subsequently reflected by the stationary and movable mirrors, respectively, and then recombine at the semi-transparent mirror, producing an interference pattern. Depending on the position of

the moving mirror, which determines the optical path difference, various interference patterns are formed. The resulting intensity for each wavenumber is calculated using a Fourier transform, which is executed at high speed by a computer, ultimately yielding the infrared spectrum. In this research work, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) measurements were conducted using a Bruker Vertex 70 spectrometer with wavenumbers ranging from 500 to 4000 cm^{-1} , a resolution of 4 cm^{-1} , and a scan rate of 32 scans per spectrum.

4.1.2 Raman Spectroscopy

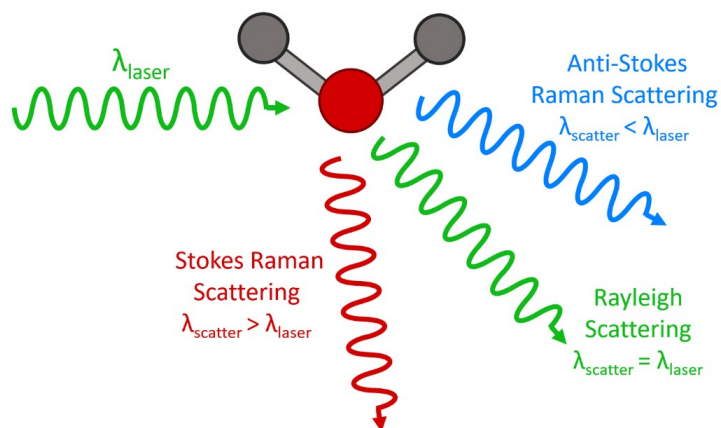
Raman spectroscopy is a powerful analytical technique used to probe the vibrational energy modes of materials by analyzing scattered light (Mulvaney & Keating, 2000). Named after Indian physicist C. V. Raman, who, alongside K. S. Krishnan, first observed Raman scattering in 1928, this method offers detailed chemical and structural information about a sample. It enables the identification of substances through their unique Raman "fingerprint," derived from the detection of Raman-scattered light.

When light interacts with molecules, the oscillating electromagnetic field of a photon polarizes the molecular electron cloud, briefly exciting the molecule to a higher-energy virtual state (N et al., 2023). This transient state, often described as a photon-molecule complex, is inherently unstable. Consequently, the molecule rapidly re-emits the photon as scattered light. In most cases, the scattered photon retains the same energy as the incident photon, resulting in elastic scattering, known as Rayleigh scattering. This process, which conserves the energy of the interacting photon and molecule, is the dominant form of light scattering. In contrast, Raman

scattering is an inelastic process where energy is exchanged between the photon and the molecule. This occurs in approximately one in 10 million photons. When a molecule absorbs energy and transitions to a higher vibrational level, the scattered photon loses energy, leading to an increase in wavelength—this is referred to as Stokes Raman scattering. Conversely, if a molecule releases energy by relaxing to a lower vibrational level, the scattered photon gains energy, resulting in a shorter wavelength, known as Anti-Stokes Raman scattering.

Figure 22.

Different types of scattering that can occur when light interacts with a molecule



Note. From *Raman Spectroscopy for Detecting Neurological Disorders: Progress and Prospects*, by M. N et al., in *Theranostic Applications of Nanotechnology in Neurological Disorders* (p. 219-250).

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Although quantum mechanics predicts equal probabilities for Stokes and Anti-Stokes scattering, the Boltzmann distribution dictates that most molecules exist in their ground vibrational state at room temperature. Consequently, Stokes scattering is more prevalent and produces a stronger signal. For this reason, Raman spectroscopy predominantly measures the Stokes Raman scatter to provide insights into molecular vibrations and sample composition. This technique's sensitivity to vibrational modes makes it a critical tool for characterizing materials in fields such as aqueous Zn-ion battery research.

The wavelength of Raman-scattered light is influenced by the excitation wavelength, making direct comparison of spectra obtained with different lasers impractical. To address this, the Raman scatter position is expressed as a Raman shift, which quantifies the displacement from the excitation wavelength as follows:

$$\Delta\bar{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right)$$

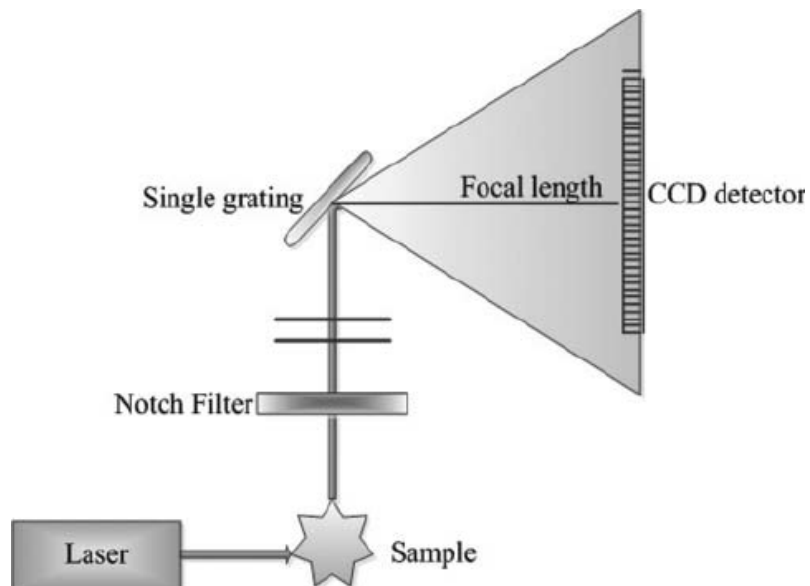
where $\Delta\bar{\nu}$ is the Raman shift in cm^{-1} , λ_0 is the wavelength of the excitation laser in nm, and λ_1 is the wavelength of the Raman scatter in nm.

In a conventional Raman back-scattering setup (Figure 23), the laser and spectrometer are positioned on the same side of the sample (Yang & Ying, 2011). The laser illuminates the sample to induce the Raman effect, and the back-scattered light is collected. Before analysis, the Rayleigh and anti-Stokes components are filtered out, leaving the Stokes component for measurement. The filtered back-scattered light is directed into a Czerny-Turner spectrograph for wavelength sorting. Initially, the light is focused onto an entrance slit, then onto a

collimating mirror, which aligns the light and directs it to a diffraction grating. The grating separates the light into its constituent wavelengths. Finally, a focusing mirror refines the light's focus onto a CCD detector, where the Raman signal is recorded for analysis.

Figure 23.

Schematic diagram of a dispersive Raman spectrometer



Note. Reprinted from “Applications of Raman Spectroscopy in Agricultural Products and Food Analysis: A Review”, by Yang and Ying, 2011, *Applied Spectroscopy Reviews*, 46(7), 539-560.

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4.1.3 Contact Angle Measurement

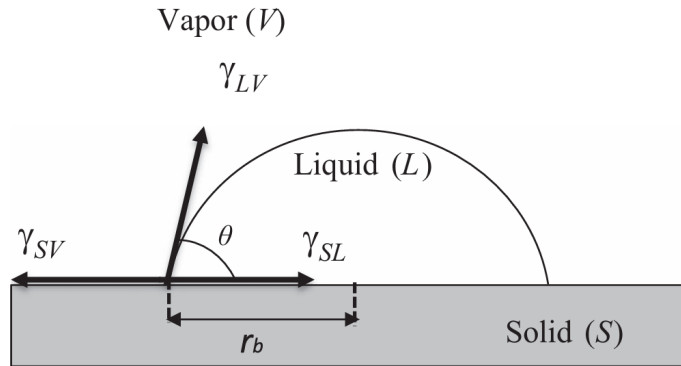
The contact angle, denoted as θ , serves as a metric for evaluating the wettability of a liquid on a solid surface. Geometrically, it is defined as the angle formed at the tri-phase boundary where the liquid, solid, and gas phases converge. This interfacial phenomenon is characterized by the well-established Young's equation below, which elucidates the equilibrium at the contact point between the solid, liquid, and gas phases (Kwok & Neumann, 1999).

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

The equilibrium contact angle of wetting, often termed Young's contact angle (θ), arises from the interplay among various interfacial tensions: γ_{LV} , which represents the liquid's surface tension; γ_{SL} , indicating the interfacial tension between the solid and liquid phases; and γ_{SV} , corresponding to the surface tension or surface free energy of the solid. This relationship is illustrated in Figure 24 (Erbil, 2014).

Figure 24.

Profile of a drop of liquid on a solid surface. Contact angle, contact radius, and three interfacial tensions, γ , between solid, liquid, vapor phases



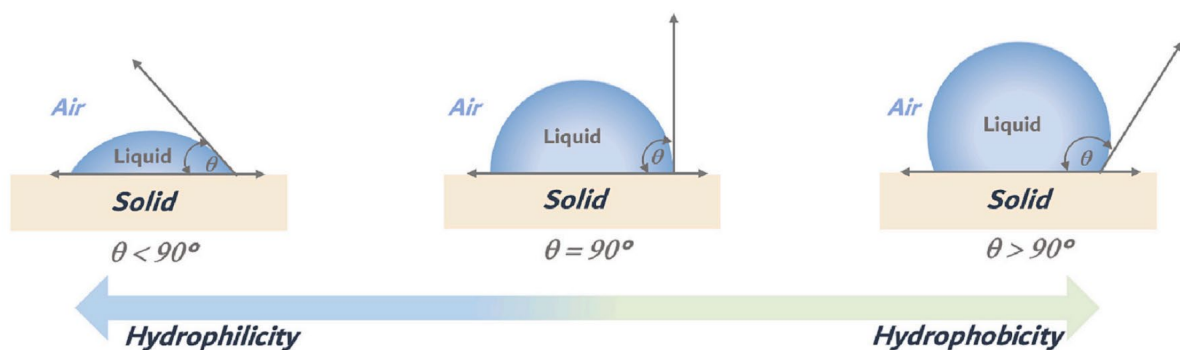
Note. Reprinted from “The debate on the dependence of apparent contact angles on drop contact area or three-phase contact line: A review”, by Erbil, 2014, *Surface Science Reports*, 69(4), 325-365.

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Wettability describes the propensity of a liquid to disperse across a given surface. It is often assessed by employing water as the probe liquid in a static contact angle measurement. Typically, surfaces that promote the spreading of liquid into a flatter droplet are characterized as possessing high wettability or favorable wetting properties. Conversely, surfaces where the liquid tends to form a spherical shape are considered to exhibit low wettability or poor wetting behavior. In practical applications, these distinctions in wettability correspond to particular contact angle ranges, as depicted in the diagram in Figure 25 (El-bahi et al., 2023).

Figure 25.

Schematic illustration of contact angles on uniform solid surface and its relation to surface properties.



Note. Reprinted from “Advancing phosphate ore minerals separation with sustainable flotation reagents: An investigation into highly selective biobased depressants”, by El-bahi et al., 2023, *Advances in Colloid and Interface Science*, 317, 102921. Copyright 2023 by Elsevier.

Contact angle measurements facilitate the evaluation of a surface’s hydrophilicity or hydrophobicity, which is frequently crucial in determining the efficacy of surface modification. When a droplet spreads across the surface, yielding a contact angle of less than 90° , the surface is classified as hydrophilic. In contrast, if the droplet resists spreading and forms an angle greater than 90° , the surface is deemed hydrophobic.

The simplest way of measuring the contact angle of a sessile drop is with a contact angle goniometer. A droplet is deposited by a syringe which is positioned above the sample surface, and a high-resolution camera captures the image from the profile or side view. The image can

then be analyzed either by eye or more often by image analysis software (e.g., ImageJ). This type of measurement is also referred to as a static contact angle measurement. The contact angle is affected not only by the surface chemistry but also by the roughness of the surface. In this research work, contact angles of electrolytes toward the Zn anode were measured by a SL200B/K Automatic Contact Angle Meter, and the obtained images were analyzed using a KRUSS Scientific DSA25 Drop Shape Analyzer.

4.1.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopes (SEMs) employ an electron beam to visualize specimens at nanometric resolution. In the electron source, electrons are generated from a filament and subsequently collimated into a coherent beam. This beam is precisely directed onto the sample's surface via a series of focusing lenses within the electron column. SEM generally features multiple operational modes, including backscattered electron (BSE) imaging, secondary electron (SE) imaging, and energy dispersive X-ray spectroscopy (EDX) (Vernon-Parry, 2000).

Backscattered electrons (BSEs) are high-energy electrons that are scattered from the sample, experiencing only minimal energy loss during the process. They originate from deeper regions within the sample, typically several microns beneath the surface, and exhibit significant interaction with the material. BSEs provide valuable compositional information but generally yield lower-resolution images. These electrons are reflected back as a result of elastic interactions between the incident beam and the sample atoms. BSEs imaging exhibits significant sensitivity to variations in atomic number; materials with higher atomic numbers

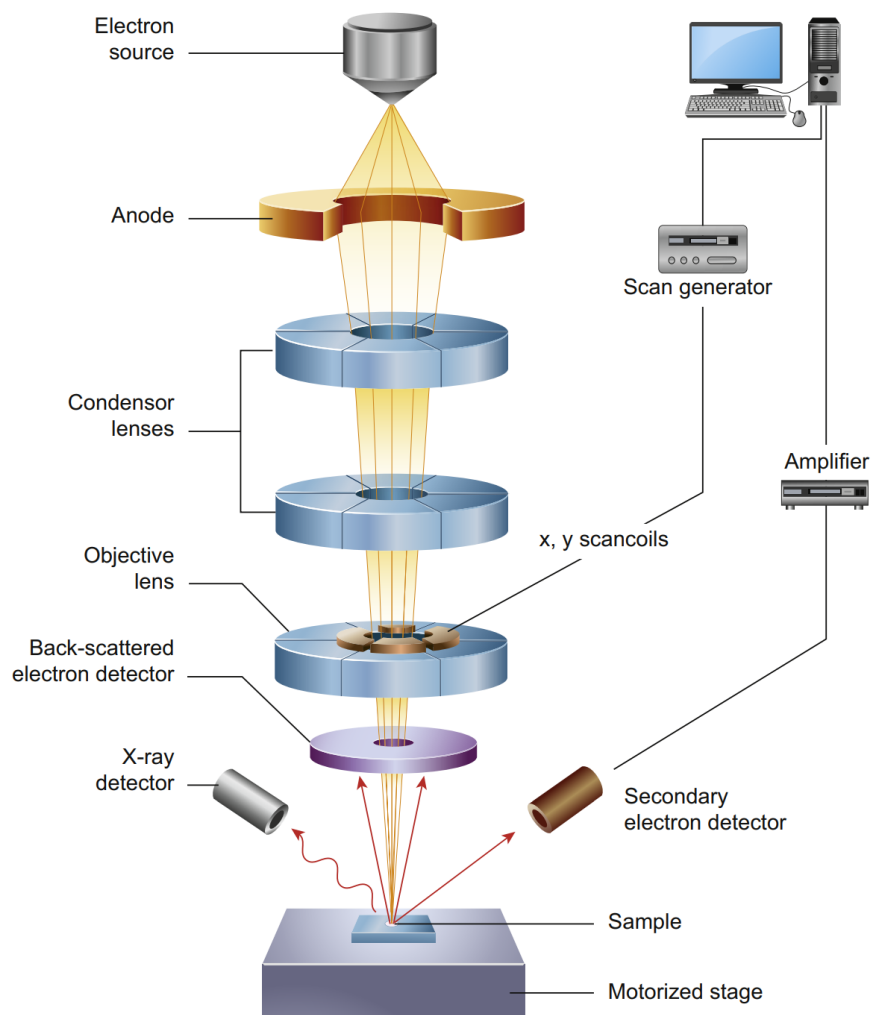
appear with increased brightness in the image. Furthermore, BSE imaging can yield essential insights regarding the crystallographic characteristics, surface topography, and magnetic properties of the specimen under analysis. SEs are emitted from a region just a few nanometers beneath the sample's surface, and they possess lower energy relative to BSEs. Due to their sensitivity to surface characteristics, SEs are particularly effective for providing detailed topographic information. These electrons are generated from the atoms of the sample as a consequence of inelastic interactions occurring between the incident electron beam and the sample material. X-ray is produced when the sample is struck by high-energy electrons, resulting in the ejection of core electrons and leaving an unoccupied energy level. Subsequently, an electron from an outer shell transitions to fill this vacancy, releasing photons with quantized energy, which forms the X-ray emission. Since each element possesses a distinct set of energy levels, the emitted X-ray signal can be detected by an EDX detector, enabling the mapping of elemental distribution or quantifying the abundance of elements within the sample.

Figure 26 illustrates the typical configuration of SEM, which includes an electron gun comprising the electron source and accelerating anode, a series of electromagnetic lenses for electron focusing, a vacuum chamber containing the specimen stage, and various detectors designed to capture the signals emitted from the sample (Rabha & Saikia, 2020). Basically, electrons are generated at the electron gun and accelerated by an electric field (~ 5 to 20 kV) towards the sample within a high-vacuum environment. By detecting the emitted signals, including SEs for topographical imaging, BSEs for compositional contrast, and characteristic

X-rays for elemental analysis, with various detectors, the surface structure and morphology of the sample can be characterized with high resolution (~ 10 nm). In a standard SEM image, the electron signals from regions of interest are converted into electrical current, and the resulting image brightness corresponds to the intensity of this current. In this thesis, SEM measurements were performed using a Zeiss UltraPlus Field Emission SEM (FESEM) with an accelerating voltage of 10 kV.

Figure 26.

Schematic representation of the essential components of a SEM.



Note. From *Advanced micro- and nanoscale characterization techniques for carbonaceous aerosols*, by S. Rabha and B. K. Saikia, in *Handbook of Nanomaterials in Analytical Chemistry* (p. 449-472). Copyright 2020 by Elsevier. Reprinted with permission.

4.1.5 Focused Ion Beam Scanning Electron Microscopy (FIB-SEM)

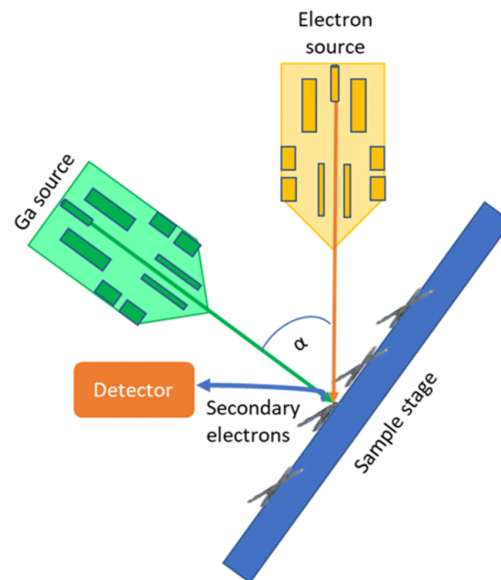
The Focused Ion Beam Scanning Electron Microscope (FIB-SEM) is an advanced technology that has evolved from the conventional Scanning Electron Microscope (SEM). The primary distinction between SEM and FIB-SEM lies in the nature of the beam utilized; instead of employing an electron beam as in SEM, FIB-SEM uses a focused ion beam (FIB). These two methodologies are largely analogous, except for the substitution of the electron beam with an ion beam. Additionally, FIB-SEM technology is capable of producing images with significantly enhanced resolution, reaching down to the nanometer scale. In the FIB system, a focused ion beam is employed to precisely interact with the sample's surface. Both the energy and movement of this ion beam are meticulously controlled at nanometer-level precision, enabling various applications such as fabricating microscopic components or removing ultrathin layers of material/tissue for further analysis.

The FIB typically composed of gallium ions, is focused and directed onto the surface of the sample to achieve various functions, such as material ablation, milling, or deposition, which is controlled with high precision at the nanometer scale (Dwiranti et al., 2021). This precise ion bombardment can be utilized to remove ultrathin layers, cross-section specific areas, or fabricate microstructures directly on the sample. Meanwhile, the electron beam functions similarly to a traditional SEM, providing high-resolution imaging of the sample surface by detecting signals such as secondary or backscattered electrons. The dual-beam configuration (Figure 27) allows for real-time imaging and nanoscale manipulation, enabling detailed surface characterization as well as precise material modification within the same instrument, making

it an essential tool for nanofabrication and advanced material analysis. In this research work, all FIB-SEM measurements were performed using a FEI Scios FIB microscope with liquid Ga ion source in depth of 10 μm at a beam intensity of 3 nA.

Figure 27.

Schematic illustration of a FIB-SEM system.



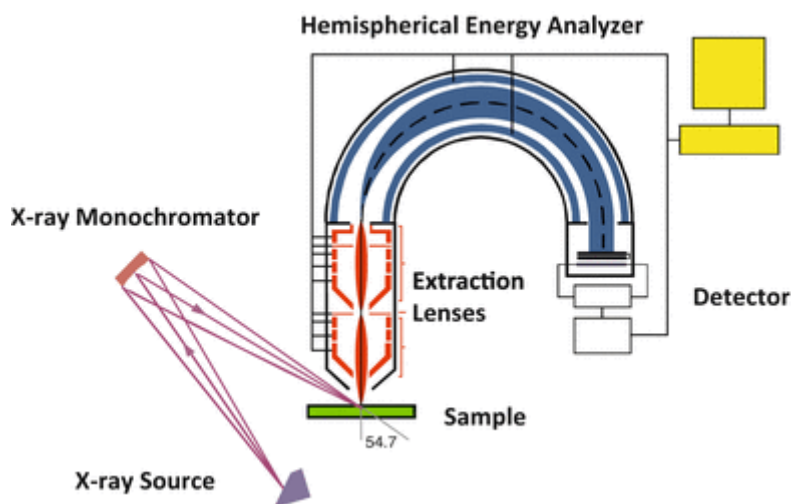
Note. Reprinted from “Imaging the inner structure of chromosomes: contribution of focused ion beam/scanning electron microscopy to chromosome research”, by Dwiranti et al., 2021, *Chromosome Research*, 29(1), 51-62. Copyright 2021 by Springer Nature.

4.1.6 X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive analytical technique in which a material's surface is irradiated by X-rays, causing the ejection of electrons whose kinetic energies are subsequently analyzed. XPS can be employed either to ascertain the elemental composition or to characterize the chemical/electronic states of particular elements. A schematic illustration of the instrumentation of the X-ray photoelectron spectrometer is shown in Figure 28 (Haasch, 2014). When X-rays are directed onto a sample, the electrons within the material, upon absorbing sufficient energy, are emitted from the sample with a characteristic kinetic energy. The kinetic energies of these emitted electrons are subsequently analyzed by a detector, resulting in the generation of a spectrum that represents their energies and relative quantities. As electrons of distinct kinetic energies traverse varied paths within the detector, the system is able to distinguish between them, allowing the computer to generate the corresponding spectra.

Figure 28.

Schematic of a typical modern high resolution X-ray photoelectron spectrometer.



Note. From *X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy*, by R. T. Haasch, 2014, in *Practical Materials Characterization* (p. 93-132). Copyright 2014 by Springer Nature. Reprinted with permission.

The identification of atoms present within a compound under investigation through XPS is determined using the following equation:

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$$

Here, E_{binding} is the binding energy, which refers to the energy associated with an electron's attraction to the nucleus; E_{photon} is the photon energy, which pertains to the energy of the X-ray photons utilized by the spectrometer; E_{kinetic} is the kinetic energy, which represents the energy of electrons emitted from the sample; and ϕ is the work function, which serves as an

instrumental correction factor, representing the minimum energy necessary to remove an electron from an atom. With both the work function and photon energy known and the kinetic energy measured by the detector, the binding energy remains as the only unknown variable, which can then be calculated. Electrons located in orbitals farther from the nucleus require less energy for ejection, resulting in lower binding energies for such higher orbitals. Moreover, electrons residing in different subshells (e.g., s, p, d) exhibit distinct energies. By providing insight into the energy of emitted electrons, XPS facilitates the determination of the material's elemental composition. In this research work, the surface and depth profiles of XPS were carried out on Thermo Fisher K-Alpha system under a vacuum of 2×10^{-6} Pa with Ar^+ bombardment. For depth profiling, the Argon cluster ion gun with 1 k eV ion energy was used to sputter $1 \times 1 \text{ mm}^2$ areas centered around the analyzed areas ($200 \times 200 \text{ }\mu\text{m}^2$). The results were analyzed using CasaXPS and the spectra were fitted using the Tougaard background (BG) type.

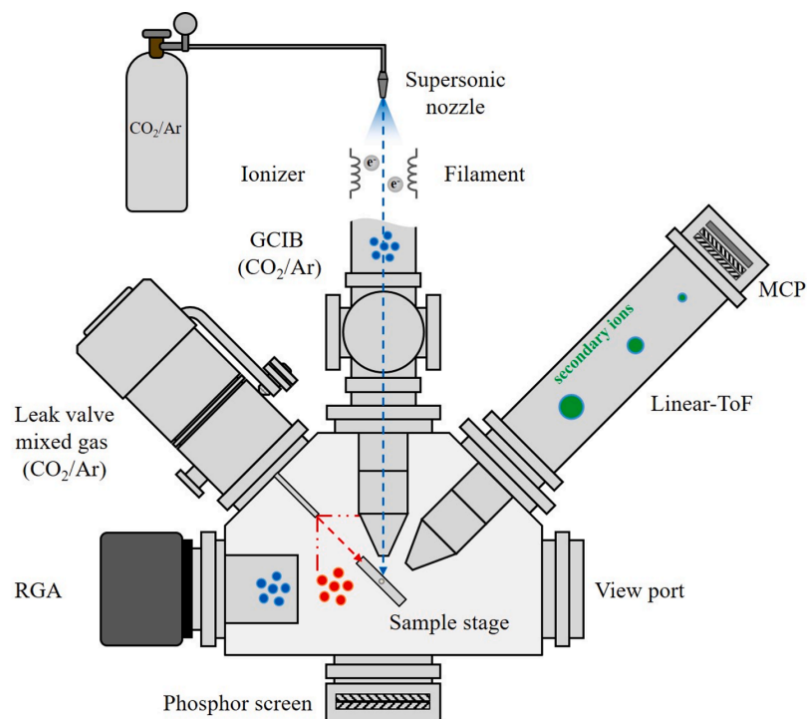
4.1.7 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a sophisticated analytical technique used to explore the structural and compositional characteristics of a sample's surface. This method boasts high sensitivity and selectivity, outperforming many other analytical techniques, which makes it exceptionally effective for detecting both molecular ions of organic substances and specific contaminants at the outermost surface layers (Lee et al., 2022). ToF-SIMS is also capable of identifying both organic and inorganic compounds across a broad range of particle sizes, from micrometer to centimeter scale, and is applicable to elements with atomic numbers ranging from 1 to 92 (hydrogen to uranium). Furthermore, ToF-SIMS

combines its high-resolution imaging functionality with superior spatial resolution, enabling the precise mapping of the spatial distribution of identified substances on the surface. By incorporating a sputtering ion beam, ToF-SIMS also facilitates qualitative depth profiling, which allows for the assessment of chemical composition along the depth axis without requiring prior knowledge of the sample. This depth analysis is especially useful for elucidating the variability in material composition as a function of etching depth. The combination of high sensitivity, molecular ion detection, broad elemental applicability, spatial imaging, and depth profiling makes ToF-SIMS an invaluable tool for comprehensive surface characterization and failure analysis in various research settings. Figure 29 presents a schematic representation of the ToF-SIMS equipment, featuring a bismuth primary ion source alongside a reflectron-type mass spectrometer (Lee et al., 2022). The sputtering ion source, which includes an argon gas cluster ion beam (GCIB), is employed to selectively etch away the uppermost layers of the sample, thereby enabling depth-specific and spatially-resolved analysis of the sample at various locations. In this research work, ToF-SIMS was carried out using TOF.SIMS5-100 and the signal was collected with the sputtering of Cs^+ ion beam (1 k eV ion energy, ~ 40 nA measured sample current) during the period of 1200 seconds in the area of $50 \times 50 \mu\text{m}^2$.

Figure 29.

Schematic illustration of the ToF-SIMS equipment



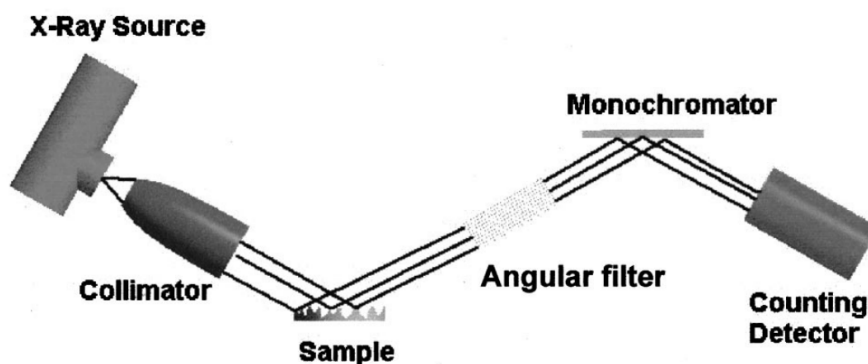
Note. Reprinted from “Characteristics of a mixed-gas cluster ion beam for time-of-flight secondary ion mass spectrometry”, by Lee et al., 2022, *Applied Surface Science*, 572, 151467. Copyright 2022 by Elsevier.

4.1.8 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a versatile and non-destructive analytical technique widely used to investigate the crystalline structure of materials. By analyzing the diffraction patterns produced when a monochromatic X-ray beam interacts with a crystalline sample, XRD provides critical information about phase identification, lattice parameters, crystallinity, and particle size. The schematic illustration of an X-ray diffractometer is shown in Figure 30 (Schiels et al., 2002).

Figure 30.

Schematic illustration of an X-ray diffractometer



Note. Adapted from “Overview of polycapillary X-ray optics”, by Schields et al., 2002, *Powder Diffraction*, 17(2), 70-80. Copyright 2012 by Cambridge University Press.

Here, X-rays are produced by a radiation source (usually Cu K α for lab-source diffractometer) and subsequently pass through a collimator. Upon reaching the sample crystals, the incident X-rays may undergo diffraction into various directions. The diffracted X-ray signal is then gathered by a detector, which measures the intensity of the radiation. Throughout the measurement process, either the X-ray source or the sample holder will rotate, capturing data at each angular position.

The foundation of XRD lies in Bragg’s Law, which describes the condition for constructive interference of X-rays scattered by atomic planes within a crystal (Jauncey, 1924). Bragg’s Law is expressed as:

$$n\lambda = 2d \sin \theta$$

where n is the order of reflection (an integer), λ is the wavelength of the incident X-ray beam, d is the interplanar spacing (distance between adjacent crystal planes), and θ is the Bragg angle (angle of incidence). This relationship allows the determination of d when the diffraction angle 2θ is measured. Once d is determined, Miller Indices (h, k, l) are used to describe the orientation of these crystal planes. Miller indices are determined from the reciprocals of the fractional intercepts of a plane with the crystal axes. For instance, a plane intersecting the x -axis at a , y at $b/2$, and z -axis at infinity would be assigned Miller indices $h = 2, k = 1, l = 0$, corresponding to the (210) plane. Miller indices are essential for indexing diffraction peaks and analyzing crystal orientations. Moreover, the XRD is a powerful tool for estimating the size of crystalline domains using the Scherrer Equation, which relates the broadening of diffraction peaks to the crystallite size. The Scherrer Equation is given by,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where D is the average crystallite size, K is the shape factor, λ is the wavelength of the incident X-rays, β is the full width at half maximum (FWHM) of the diffraction peak (in radians), and θ is the Bragg angle. In this research work, XRD measurements were carried out using a Rigaku MiniFlex 600 benchtop general purpose diffractometer with a Cu $K\alpha$ X-ray source ($\lambda = 0.154$ nm). The range of incident angles ranged from 5 to 90° with a scan rate of 0.2° s⁻¹.

4.1.9 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is a thermal analysis technique used to measure the change in mass of a material as a function of temperature or time under a controlled atmosphere.

It provides insights into thermal stability, composition, and decomposition behavior of materials by monitoring mass changes during processes such as decomposition, volatilization, oxidation, or reduction. Figure 31 shows a schematic illustration of TGA (Prime et al., 2009).

Schematic illustration of the working principle of TGA.

Note. From *Thermogravimetric Analysis (TGA)*, by R. B. Prime et al., 2009, in *Thermal Analysis of Polymers: Fundamentals and Applications* (p. 241-317). Copyright 2009 by Wiley-VCH. Reprinted with permission.

transitions such as step changes indicating mass loss events or plateaus representing thermal stability. Derivative thermogravimetric (DTG) curves further help identify transition points by highlighting the rate of mass change. TGA is widely used for determining thermal stability, quantifying moisture or volatiles, studying oxidative or reductive behavior, and analyzing compositional properties across a variety of materials including polymers, ceramics, metals, and composites. In this research work, TGA analysis was used to verify the composition of synthesized cathode materials. All TGA measurements were carried out using a TGA55 Premium Performance Thermogravimetric Analyzer in a nitrogen environment. For both the alpha manganese oxide and sodium vanadate cathode materials, the temperature was first ramped from 25 °C to 100 °C, held isothermal for 10 minutes, and then ramped from 100 °C to 800 °C, all at a constant rate of 10 °C min⁻¹.

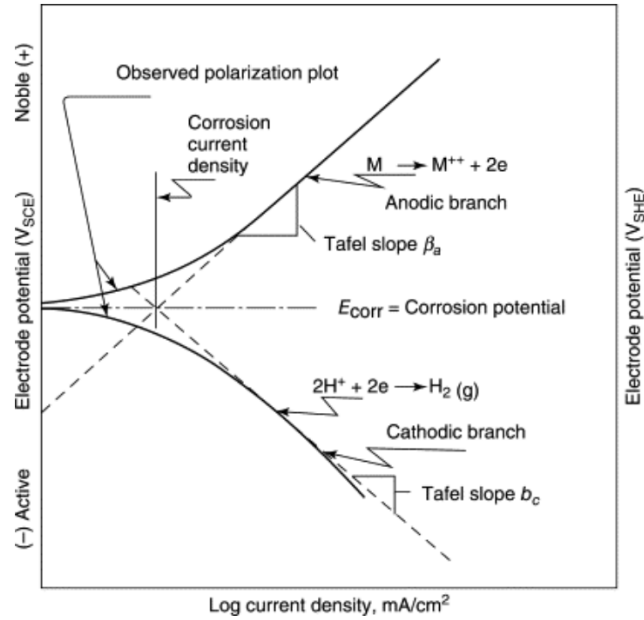
4.2 Electrochemical Characterization

4.2.1 Tafel Plot

The Tafel plot is a graphical representation of the relationship between the overpotential (η) and the logarithm of the current density ($\log j$) in electrochemical systems. In corrosion studies, a Tafel plot is frequently used to find the corrosion rate as well as the corrosion current (Bard & Faulkner, 2001). A typical Tafel plot is shown below (Papavinasam, 2008).

Figure 32.

A typical Tafel plot.



Note. From *Electrochemical polarization techniques for corrosion monitoring*, by S. Papavinasam, 2008, in *Techniques for Corrosion Monitoring* (p. 49-85). Copyright 2009 by Elsevier. Reprinted with permission.

The Tafel equation is expressed as:

$$\eta = a + b \log |j|$$

where η is the overpotential (the deviation of the electrode potential from its equilibrium value, $\eta = E - E_{eq}$), j is the current density, a is the intercept related to the exchange current density

(j_0), and b is the Tafel slope used to determine the kinetics of charge transfer via the following equation:

$$b = \frac{2.3RT}{\alpha nF}$$

Here, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K), α is the charge transfer coefficient, n is the number of electrons transferred, and F is the Faraday's constant (96485 C mol^{-1}). Notably, the Tafel equation is a simplified version of the Butler-Volmer (BV) equation, which describes the current density as function of overpotential:

$$j = j_0 \left[\exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(\frac{-\alpha nF\eta}{RT}\right) \right]$$

At high overpotentials ($> \pm 70 \text{ mV}$), one of the exponential terms become dominant, while the other decreases. Thus, we can then neglect one of the terms, which transforms the BV equation into the linear Tafel relationship. In the context of AZIBs, the Tafel plot is widely used to identify corrosion rates and the effectiveness of protective layers/electrolyte additives in suppressing parasitic reactions. In this research work, Tafel curves were collected by a Bio-Logic VSP-300 electrochemical workstation using a three-electrode system, where Zn foil was the working electrode, Pt plate was the counter electrode, and Ag/AgCl was the reference electrode. The scan rate was 5 mV s^{-1} .

4.2.2 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry (LSV) is an electrochemical technique where the electrode potential is linearly varied over time while recording the corresponding current response. In an LSV

experiment, the potential of the working electrode is scanned linearly from an initial potential (E_i) to a final potential (E_f) at a particular scan rate ($\nu = \frac{dE}{dt}$). As the potential varies, redox reactions occur on the electrode surface, generating a current. The magnitude of the current depends on the reaction kinetics and mass transport processes. The relationship between potential and current is then recorded by a potentiostat to generate a voltammogram. This data is analyzed to extract detailed information on peak currents, peak potentials, and related electrochemical characteristics. A typical LSV plot for a non-diffusion limited redox systems

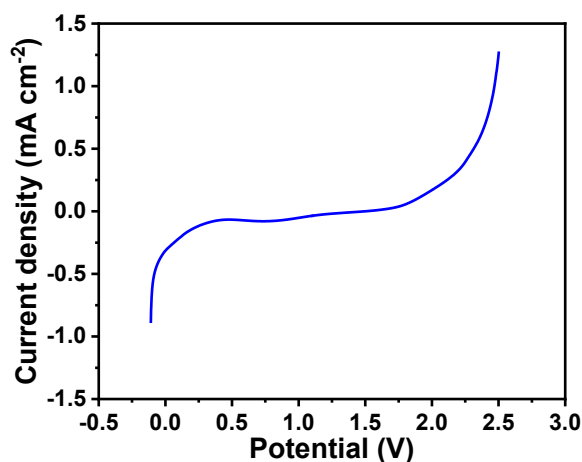


Figure 33. A typical LSV plot for a non-diffusion limited redox system

To find out whether the reaction is diffusion-controlled while quantifying the relationship between the peak current observed in LSV and the properties of the electrochemical system, the Randles-Sevcik Equation is frequently used, which is expressed as follows,

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \nu^{1/2}$$

where I_p is the peak current, n is the number of electrons transferred, A is the effective electrode area (cm^2), D is the diffusion coefficient of the active species ($\text{cm}^2 \text{s}^{-1}$), C is the concentration of the active species (mol L^{-1}), and ν is the scan rate (V s^{-1}) (Bard & Faulkner, 2001). By plotting I_p vs. $\nu^{1/2}$, a linear relationship confirms a diffusion-controlled process. Moreover, the Tafel region can be analyzed to obtain the exchange current density and charge transfer coefficient in the context of reaction kinetics. Here, the BV equation is used.

$$j = j_0 \left[\exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(\frac{-\alpha nF\eta}{RT}\right) \right]$$

In AZIBs, LSV is ubiquitously used to determine the stability window of the electrolyte. LSV identifies the decomposition potential range by detecting where the current increases significantly. LSV can also be used to evaluate the overpotentials of HER or OER in AZIBs. This helps assess electrode corrosion resistance and electrolyte stability. In this research work, LSV measurements were conducted by a Bio-Logic VSP-300 potentiostat using Zn//Ti symmetric cells. The voltage range ranged from -0.5 V to 3.0 V (vs. Zn/Zn²⁺) with a scan rate of 0.1 mV s⁻¹.

4.2.3 Chronoamperometry (CA)

Chronoamperometry (CA) is an electrochemical technique used to study the kinetics and diffusion behavior of electrochemical processes. In a CA experiment, a fixed potential is applied to drive oxidation/reduction reactions. The initial current is high, but as the reactants diffuse to the electrode surface at a slower rate, the current gradually decreases. Under

diffusion-limited conditions, the current-time relationship follows Faraday's laws and is described by diffusion equations (Bard & Faulkner, 2001). The Faraday's Law is given by,

$$Q = nFCV$$

where Q is the total charge passed (C) and V is the volume of the reactive species (cm³). By integrating the current over time, the total charge can be determined, allowing for the calculation of the total amount of active species involved in the reaction. Also, the current response under diffusion control can be described as:

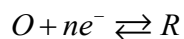
$$i(t) = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}$$

where $i(t)$ is the instantaneous current (A), n is the number of electrons transferred in the reaction, F is the Faraday constant (96485 C mol⁻¹), A is the effective electrode area (cm²), D is the diffusion coefficient, C is the initial concentration of the electroactive species (mol cm⁻³), and t is time (s). In this equation, the current is inversely proportional to the square root of time. By fitting the $i \sim t^{-1/2}$ linear relationship, the diffusion coefficient can be calculated. In AZIBs, CA can be used to investigate the electrochemical kinetics of Zn anodes or cathode materials. By recording the current response at a specific potential, the process can be analyzed to determine whether it is 2D diffusion-controlled, 3D-diffusion controlled, or governed by surface reaction kinetics. In this research work, CA measurements were conducted by a Gamry Interface5000e potentiostat using Zn//Zn symmetric cells in different electrolyte systems at a fixed voltage of -150 mV. The duration of CA measurement was 600 s at a scan rate of 0.1 s per point.

4.2.4 Chronopotentiometry (CP)

Chronopotentiometry is a galvanostatic electrochemical technique in which the current at the working electrode is maintained at a constant value over a defined time interval. During this process, the potential at the working electrode, along with the applied current, is recorded as a function of time. This method is widely used by researchers to investigate chemical reaction mechanisms and assess kinetic parameters. It is also frequently employed in the study of battery behavior and electrodeposition processes. CP is typically conducted in an unstirred electrochemical cell; however, some studies utilize rotating electrodes to enhance the method (Bard & Faulkner, 2001).

In a typical CP setup, a constant current is applied between the working and counter electrodes while the potential is measured at the working electrode with respect to the reference electrode. The redox-active species diffuse towards the surface of the working electrode to sustain the applied current until their diffusion-limited concentration approaches zero at the electrode interface. At this point, the potential shifts to that of the next available redox species in the solution, which could potentially be the solvent. Additionally, CP is commonly utilized in charge/discharge experiments involving batteries to characterize their electrochemical performance and efficiency. Consider a general electrochemical reaction with formal potential $E^{\circ'}$:



Upon applying a constant current to the working electrode, species O undergoes reduction to species R at the surface of the working electrode. Consequently, the potential of the working

electrode shifts progressively to values characteristic of the redox pair, following a time-dependent Nernstian relationship. As the concentration of species O approaches zero at the electrode surface, the potential begins to sharply rise towards more negative values. The resulting potential-time ($E-t$) curve resembles that of a potentiometric titration, featuring a distinct transition time, denoted as τ , analogous to the equivalence point in a titration. Notably, the potential at half of τ corresponds to the formal potential, $E^{\circ'}$. The transition time itself is mathematically related to the concentration and diffusion coefficient of species O , as expressed in the following equation:

$$\tau^{3/2} = \frac{2C_0^* n F A D_0^{1/2}}{3\beta}$$

where C_0^* is the concentration of species O , n is the number of electrons, F is the Faraday constant (96485 C mol⁻¹), A is the working electrode area, D is the diffusion coefficient, and β is the sweep rate. For systems exhibiting fast electrode kinetics, the corresponding Nernstian behavior as a function of time can be described by the following equation:

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \left(\frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \right)$$

where $E_{\tau/4}$ is calculated as:

$$E_{\tau/4} = E^{\circ'} - \frac{RT}{2nF} \ln \frac{D_O}{D_R}$$

A plot of E vs. $\ln[(\tau^{1/2} - t^{1/2}) / t^{1/2}]$ should yield a linear relationship with a slope of RT / nF , indicating a reversible potential-time (E - T) curve. In AZIBs, CP is frequently used to assess the nucleation overpotential (NOP) of Zn anode in different electrolyte systems. In this research work, CP measurements were conducted by a Gamry Interface5000e potentiostat using Zn//Zn symmetric cells in different electrolyte systems at a fixed current of 1 mA. The duration of CP measurement was 3600 s at a scan rate of 0.1 s per point.

4.2.5 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a frequency-domain electrochemical technique. It applies a small amplitude AC signal superimposed on a DC potential or current and measures the system's response. By analyzing the response across different frequencies, the electrochemical properties of the system can be characterized (Bard & Faulkner, 2001). In EIS, the system's response is typically expressed as complex impedance (Z), which consists of a real part and an imaginary part:

$$Z(\omega) = Z'(\omega) + jZ''(\omega)$$

where $Z'(\omega)$ is the real part of impedance related to resistance, $Z''(\omega)$ is the imaginary part of impedance related to capacitance and inductance, and $\omega = 2\pi f$ is the angular frequency. Here, f is the frequency of the AC signal. In EIS, since AC signal is involved, the Ohm's law is written alternatively as follows:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$

where $V(\omega)$ and $I(\omega)$ are the Fourier transforms of the AC voltage and current, respectively.

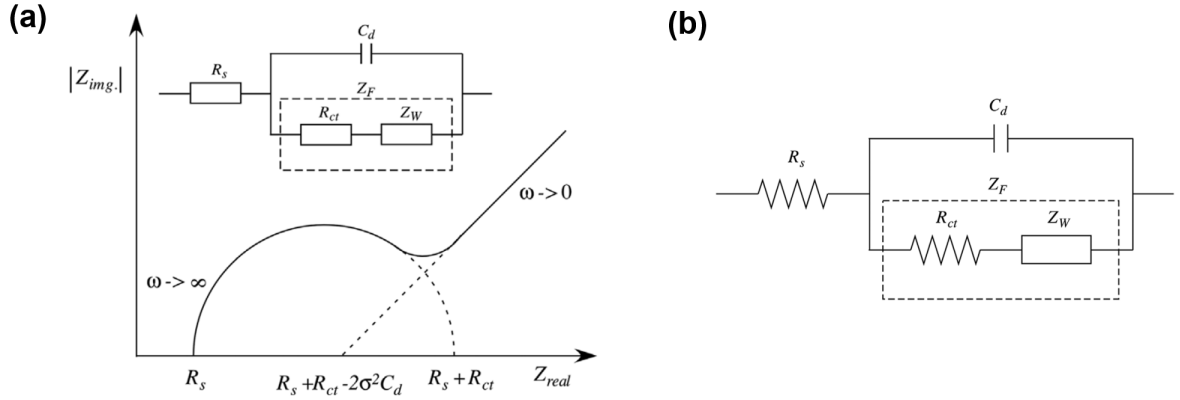
Besides, electrochemical systems are often described using equivalence circuits composed of resistors (R), capacitors (C), inductors (L), and constant phase elements (CPE). In most cases, the simple Randles circuit model is used, which can be described as follows,

$$Z(\omega) = R_s + \frac{1}{\frac{1}{R_{ct}} + j\omega C_{dl}}$$

where R_s is the solution resistance, R_{ct} is the charge transfer resistance, and C_{dl} is the double-layer capacitance. A Nyquist plot is often used where the imaginary part of impedance (Z'') is plotted against the real part (Z'), representing the reaction kinetics. A typical Nyquist plot for an AZIB is shown below (Fushimi et al., 2018).

Figure 34.

(a) The Nyquist plot and **(b)** the corresponding Randles circuit



Note. Adapted from “On the Electropolishing Mechanism of Nickel Titanium in Methanolic Sulfuric acid – An Electrochemical Impedance Study”, by Fushimi et al., 2018, *physica status solidi (a)*, 215(15), 1800011. Copyright 2018 by Wiley-VCH.

As shown in Figure 34, the Nyquist plot generally consists of two regions. The semi-circle region is controlled by charge transfer, whereas the linear region is controlled by diffusion. The intersection of the linear region and the x -axis provides information on the bulk resistance, which can be further used to calculate the ionic conductivity of the electrolyte used via the following equation:

$$\sigma = \frac{L}{RS}$$

where σ is the ionic conductivity (S cm^{-1}), L is the distance between electrodes, R is the bulk resistance of the electrolyte, and S is the contact area of two electrodes. In this experiment, EIS

was recorded by a Bio-Logic VSP-300 potentiostat with frequencies ranging from 100 kHz to 10 mHz and a sinus amplitude of 10.0 mV.

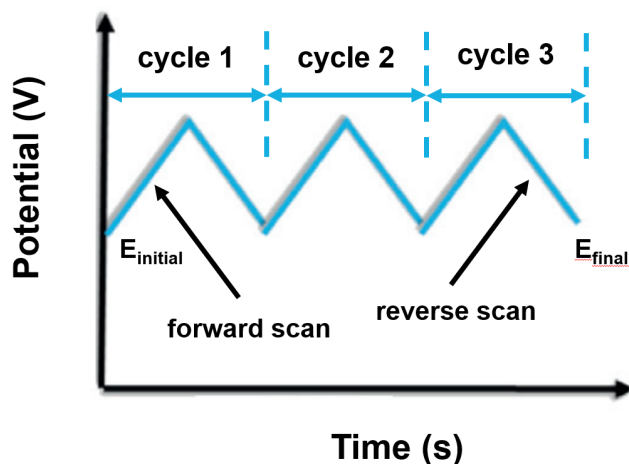
4.2.6 Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) is an electrochemical method that involves measuring the current generated in an electrochemical cell under conditions where the applied voltage exceeds that predicted by the Nernst equation. In this technique, the potential of the working electrode is varied in a cyclic manner while the resulting current response is monitored, allowing for the characterization of redox processes and electrode behavior (Elgrishi et al., 2018).

The potential of the working electrode is measured relative to a reference electrode, which maintains a stable potential, while the resulting applied potential generates an excitation signal similar to that illustrated in Figure 35 (Taherpour & Mousavi, 2018).

Figure 35.

Typical excitation signal for CV with a triangular potential waveform.



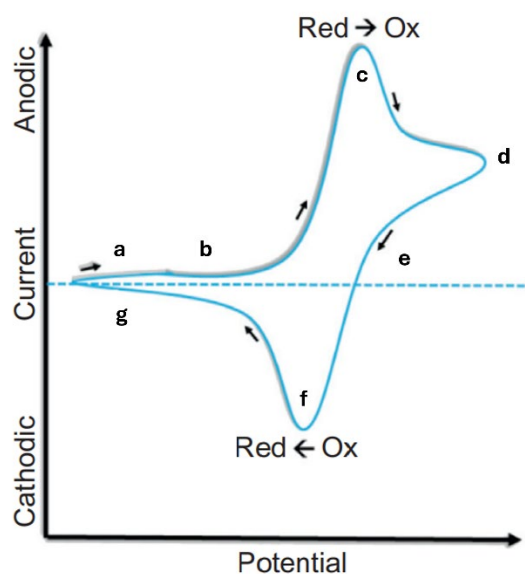
Note. From *Carbon nanomaterials for electroanalysis in pharmaceutical applications*, by Taherpour and Mousavi, 2018, in *Fullerens, Graphenes and Nanotubes* (p. 169-225). Copyright 2018 by Elsevier. Adapted with permission.

During the forward scan depicted in Figure 35, the potential initially sweeps in the negative direction, starting from a higher potential and progressing to a lower potential. The point at which the potential reaches its extremum is referred to as the switching potential, representing the potential sufficient to induce oxidation or reduction of the analyte. The subsequent reverse scan proceeds, during which the potential is swept in the positive direction. It is noteworthy that some analytes undergo oxidation initially, in which case the potential first scans in the positive direction. This cyclic process can be repeated multiple times, and the scan rate may be adjusted as needed. The slope of the excitation signal determines the applied scan rate. A

cyclic voltammogram is generated by recording the current response at the working electrode as the potential is varied during the scans. Figure 36 illustrates a cyclic voltammogram corresponding to a single-electron redox reaction (Taherpour & Mousavi, 2018).

Figure 36.

A cyclic voltammogram for a single-electron redox reaction



Note. From *Carbon nanomaterials for electroanalysis in pharmaceutical applications*, by Taherpour and Mousavi, 2018, in *Fullerens, Graphenes and Nanotubes* (p. 169-225). Copyright 2018 by Elsevier. Adapted with permission.

In Figure 36, the reduction process proceeds from point (a), representing the initial potential, to point (d), which marks the switching potential. In this segment, the potential is scanned in the negative direction to induce reduction, resulting in the generation of cathodic current (i_{pc}). The corresponding peak potential is observed at point (c), termed the cathodic peak potential (E_{pc}), which is achieved when all of the substrate at the electrode surface has been reduced. Once the switching potential (d) is reached, the potential is then scanned in the positive direction, moving from (d) to (g), resulting in anodic current (i_{pa}) and initiating the oxidation process. The peak potential during this anodic process occurs at point (f), referred to as the anodic peak potential (E_{pa}), and is reached once the entire substrate at the electrode surface has been oxidized. CV is essential for studying the redox processes in AZIBs and analyzing the behavior of Zn anode and of various cathode materials. Oxidation and reduction peaks indicate the potential range and mechanisms of the reactions. In this research work, CV measurements were conducted using a three-electrode system with a Bio-Logic multi-channel potentiostat (VSP-300) at voltages from 0.8 V to 1.8 V at a scan rate of 0.2 mV s⁻¹.

4.3 Materials

Super P, polyvinylidene fluoride (PVDF), multi-walled carbon nanotube (CNT), zinc foil (100 μ m, 99.9%), copper foil (20 μ m), stainless steel (SS) foil (20 μ m), and coin cells (type CR-2032) were all purchased from the Saibo company. Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), ethanol (99.5%), and N-methyl-2-pyrrolidine (NMP), manganese (II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%), potassium permanganate (KMnO_4 , 99.0%), sulfuric acid

(99.999%), nitric acid (HNO_3 , 70%), manganese (II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99.99%), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.999%), vanadium (V) oxide (V_2O_5 , 99.9%), sodium hydroxide (NaOH pellets, 97.0%), and poly(ethylene glycol) 4000 (PEG-4000) were all purchased from Sigma Aldrich. The commercial Jell-O powders were purchased from Walmart. Glass fiber separators were purchased from GE Whatman.

4.4 Electrolyte Preparation

To prepare the 2 M ZnSO_4 standard electrolyte (referred to as “ZS electrolyte”), 2.876 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was added in 5 mL deionized water. The resulted solution was ultrasonicated until all $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved. The control electrolytes were prepared by mixing different amount (5.0 wt%, 10.0 wt%, 15.0 wt%, and 20.0 wt%, respectively) of Jell-O powder with 5 mL of 2 M ZS electrolyte at 60 °C overnight. The concentration of 15.0% was optimized based on the Hofmeister effect as well as the tradeoff between mechanical properties and ionic conductivities.

The preparation of the Jell-O QSSE was particularly sensitive to factors such as temperature, concentration of the gelatin, and electrolyte components, and mixing protocols. To address potential sources of error, the preparation process was standardized, and each batch was subjected to physiochemical characterization (e.g., FTIR) to confirm the consistency of experiment. This ensured that any observed variations in electrochemical performance were not due to inconsistencies in the Jell-O QSSE itself.

4.5 Cathode Material Synthesis

4.5.1 Preparation of α -MnO₂ cathode

To prepare the synthesis of α -MnO₂, 0.003 M MnSO₄·H₂O and 2 mL of 0.5 M H₂SO₄ were mixed in 90 mL of deionized water. The solution was magnetically stirred until all chemicals were dissolved and the color became clear. After this, 20 mL of 0.1 M KMnO₄ solution was added to the previously obtained solution, which was then magnetically stirred for 2 hours at room temperature. The above solution was then transferred to a Teflon-lined autoclave and heated for 12 hours at 120 °C via a hydrothermal method. After the reaction had completed, the autoclave was taken out of the oven and cooled completely. The product was collected by centrifugation, washed at least 3 times with water, and dried using a vacuum oven at 80 °C for 8 hours.

4.5.2 Preparation of β -Na_{0.33}V₂O₅ (NVO) cathode

Similarly, the NVO nanowires were prepared using a hydrothermal method. 0.182 g V₂O₅ powders were mixed with 30 mL of deionized water and 0.35 mL of 1 M NaOH in a beaker. 0.1 g of PEG-4000 was then added to the above solution, which was well mixed by magnetic stirring for 15 minutes at room temperature. The obtained solution was then transferred to a Teflon-lined autoclave and heated for 48 h at 180 °C. After the reaction had completed, the autoclave was taken out of the oven and cooled down completely. The obtained product was first washed several times with deionized water and centrifuged. Then the product was further washed with 2-propanol (>99.5%) at least twice and centrifuged again. The finally obtained product was dried at 80 °C for 24 hours.

4.6 Battery Assembly

4.6.1 Preparation of Zn anode

Before use, the purchased Zn foil with 100 μm thickness was polished by sandpaper with 3000, 5000, 7000, and 10000 grits until all passivation layers on the surface were removed. A specific amount of ethanol was sprayed onto the surface of the Zn foil, followed by continuous drying in an oven for 8 hours. The polished Zn foils were then cut into discs with diameters of 13 mm and 12 mm, which were used in the assembly of Zn//Zn symmetric cells, Zn//Cu asymmetric cells, Zn//MnO₂, and Zn//NVO full cells.

4.6.2 Zn//Zn Symmetric Cells and Zn//Cu Asymmetric Cells

The Zn//Zn symmetric cells and Zn//Cu asymmetric cells were assembled using 13-mm Zn anode discs, negative/positive electrode cases, springs, spacers, glass fiber separators (GF/D), and various metallic cathodes (Zn and Cu) with 13-mm diameters. The electrolytes used include 2 M ZS electrolytes and 2 M ZS electrolytes with different amounts of Jell-O QSSE additive. In all cases, the amount of electrolyte used for each coin cell was 150 μL .

4.6.3 Zn//MnO₂ and Zn//NVO Full Cells

The Zn//MnO₂ full cells were assembled using negative/positive electrode cases, springs, spacers, glass fiber separators (GF/D), 12-mm Zn metal discs, and as-prepared MnO₂ cathodes. The Zn//NVO full cells were assembled using negative/positive electrode cases, springs, spacers, glass fiber separators (GF/D), 12-mm Zn metal discs, and as-prepared NVO cathodes.

Chapter 5: Design of an Interfacial Self-Repairing Quasi-Solid-State Electrolyte Enabled by Self-Aggregating Jell-O Jellies

5.1 Introduction

As we mentioned in previous chapters, in replacement of expensive, energy-intensive, and unsafe Li-ion batteries, aqueous Zn-ion batteries (AZIBs) have emerged as a more practical alternative, offering better reversibility and cycling performance. However, numerous bottlenecks have to be tackled before their widespread commercialization. In particular, the notorious dendrite growth and parasitic side reactions form the major roadblock to a stable Zn anode during galvanostatic charging/discharging, jeopardizing the cycle life as well as CE of AZIBs (Dong et al., 2024; Ma et al., 2022; Z. Yang et al., 2024). Learning from the previous literature review, we have concluded that quasi-solid-state electrolytes (QSSEs), especially those based on natural hydrogel electrolytes, can fully enable the practical fabrication of flexible Zn-based devices given their excellent pliability and capability of regulating water uptake due to the internal formation of H-bonds between water molecules and various functional groups (Wang et al., 2024).

Herein, we develop a self-repairing, self-aggregating, and recyclable quasi-solid-state electrolyte consisting of commercially available Jell-O powder, zinc sulfate heptahydrate, and water, which exhibits excellent compatibility with AZIBs with outstanding electrochemical performances. The Zn//Zn symmetric cells can maintain stable cycling for more than 2000 h

under 1 mA cm^{-2} and 1 mAh cm^{-2} , and stably run for more than 120 h under extreme conditions of 50 mA cm^{-2} and 50 mAh cm^{-2} , achieving an ultrahigh depth of discharge (DoD) of 85.5%. The high reversibility achieved is also reflected by the high CE of the Zn//Cu symmetric cells. Remarkably, when coupled with different cathode materials, AZIBs using Jell-O QSSE display an ultralong calendar life of 1000 cycles at 5 C for Zn//MnO₂ full cells, and more than 5000 cycles at 3 A g^{-1} for Zn//NVO full cells with decent capacity retentions and CEs, respectively. Eventually, used Jell-O QSSE is recycled and regenerated in the assembly of new Zn//Zn symmetric cells by suction filtration, which last over 1200 h of cycling without short-circuit. With a combination of characterization and electrochemical testing techniques, we unravel that the superior performance of Jell-O QSSE is achieved by forming a solid-electrolyte interphase (SEI) on the anode surface as well as a 3D triple matrix surrounding water molecules, which synergistically promotes the binding of anions in the Zn²⁺ solvation sheath, reduces the content of free anions, and thus weakens their contribution to the current density. Given the easily recyclable nature, non-toxicity, and outstanding performance of Jell-O QSSE, we believe that it is of great competitiveness in achieving dendrite-free Zn anode towards high-performance AZIBs.

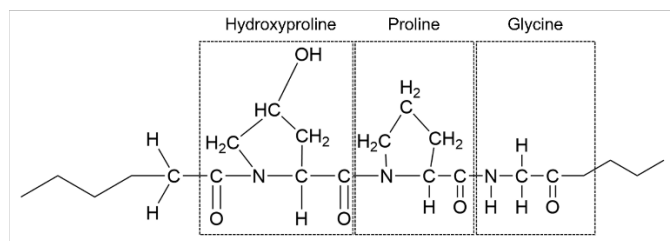
5.2 Results

5.2.1 Physiochemical Properties of Jell-O QSSE

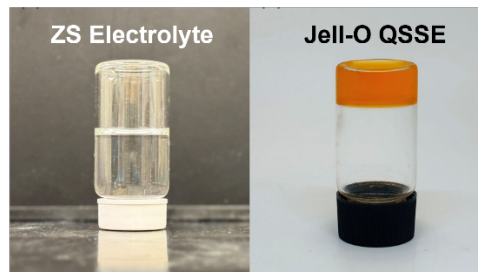
Figure 37.

Physiochemical properties of Jell-O QSSE.

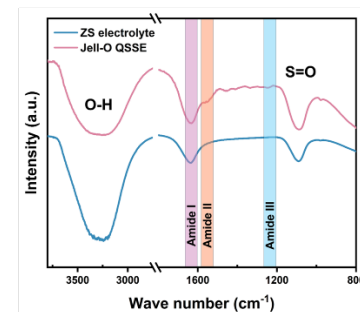
(a)



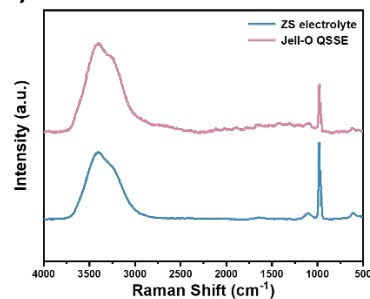
(b)



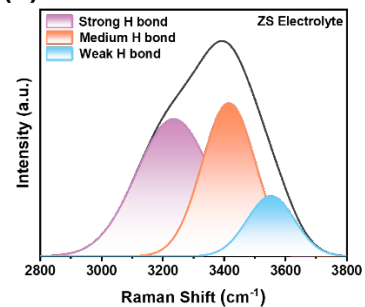
(c)



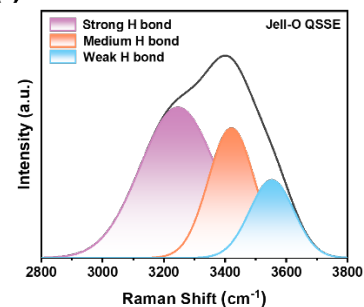
(d)



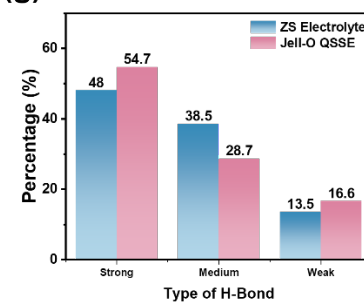
(e)



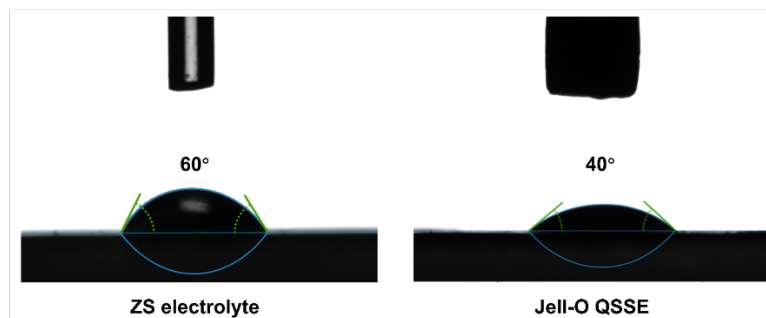
(f)



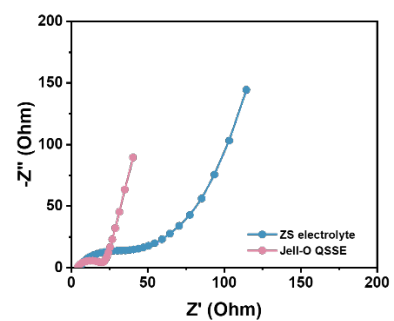
(g)



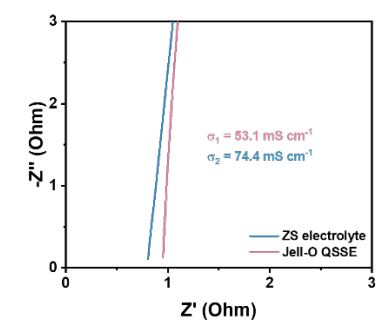
(h)



(i)



(j)



Note. **(a)** Molecular structure of gelatin; **(b)** Photos of liquid ZS electrolyte and gel-form Jell-O QSSE; **(c)** FTIR spectra of ZS electrolyte and Jell-O QSSE; **(d)** Raman spectroscopy of ZS electrolyte and Jell-O QSSE; **(e)** Raman spectroscopy curve fitting results in the range of 2800 – 3800 cm^{-1} for ZS electrolyte; **(f)** Raman spectroscopy curve fitting results in the range of 2800 – 3800 cm^{-1} for Jell-O QSSE; **(g)** Ratios of different types of H-bonds in ZS electrolyte and Jell-O QSSE from Raman spectroscopy curve fitting results; **(h)** Contact angle measurements for ZS electrolyte and Jell-O QSSE with Zn anode; **(i)** Nyquist plot for Zn//Zn symmetric cells with ZS electrolyte and Jell-O QSSE; **(j)** Ionic conductivities of ZS electrolyte and Jell-O QSSE from EIS spectra

The Jell-O QSSE is made up with 2 M zinc sulfate heptahydrate, water, and commercially available Jell-O powder. The Jell-O powder consists mainly of gelatin, along with other flavored or colored food additives. The main ingredient, gelatin, is mainly derived from collagen, which is found in the connective tissues, bones, and skin of animals (T. Huang et al., 2019; Park et al., 2015). **Figure 37a** shows the molecular structure of gelatin that contains glycine, proline, and hydroxyproline, all of which can provide ample bonding sites for H_2O . Thus, it becomes possible to integrate Jell-O powders into numerous commercially available electrolytes. Herein, by introducing a specific amount of Jell-O powders to 2 M ZnSO_4 (ZS) solution, a gel-form, quasi-solid-state electrolyte (QSSE) could be formed upon cooling to room temperature, which is different from the liquid state ZS electrolyte (**Figure 37b**).

The self-aggregation of gelatin molecules is due to the strong hydrogen bonding with water molecules, interconnecting gelatin molecules and creating a 3D matrix (Rao et al., 2022). Similar bonding properties were also observed for other electrolyte systems such as zinc chloride (ZnCl_2) and zinc trifluoromethanesulfonate ($\text{Zn}(\text{OTf})_2$). Various amounts of Jell-O powder (5 wt%, 10 wt%, 15 wt%, and 20 wt%) have been added into a fixed volume of 2 M ZS solution, and the maximum amount allowed was found to be 15% . The electrolyte with maximum concentration (15 wt%) of Jell-O powder is hereby referred to as Jell-O QSSE.

Using both ATR-FTIR and Raman spectroscopy, the molecular structure of electrolytes and bonding environment of water were verified, respectively. As shown by **Figure 37c**, in the FTIR spectra, prominent bands of Amide I, Amide II, and Amide III for gelatin can be observed at around 1635 cm^{-1} , 1559 cm^{-1} , and 1244 cm^{-1} , respectively; additional peaks were also found at around $3200 - 3400\text{ cm}^{-1}$ and 1088 cm^{-1} , corresponding to O-H stretching vibrations in the aqueous solution and S=O stretching vibrations in the sulfate group, respectively. The observation of these peaks was further strengthened using Raman spectroscopy, as shown in **Figure 37d**. To better understand the bonding environment of water molecules in different electrolyte systems, curve-fitting approaches were applied to the Raman spectroscopy. The strong peak at the $2800 - 3800$ Raman shift region, which corresponds to the O-H stretching vibration in water, was then fitted into different types of hydrogen bonds (H-bonds): strong ($\sim 3240\text{ cm}^{-1}$), medium ($\sim 3417\text{ cm}^{-1}$), and weak ($\sim 3552\text{ cm}^{-1}$) H-bonds (Brubach et al., 2001; Y. Dong et al., 2021). The fitting results for the ZS electrolyte and Jell-O QSSE are shown in **Figure 37e** and **f**, respectively. As **Figure 37g** demonstrates, based on the curve-fitting results,

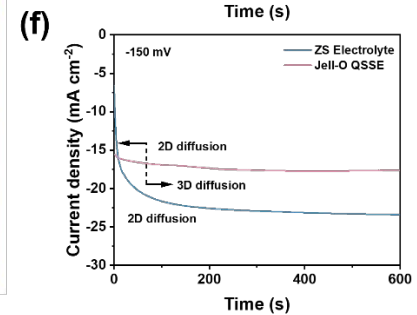
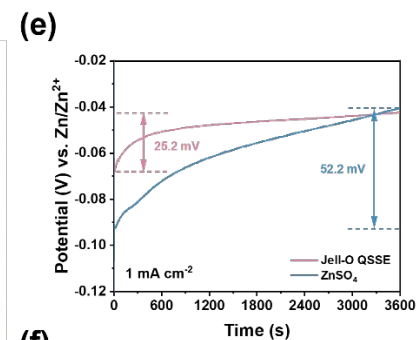
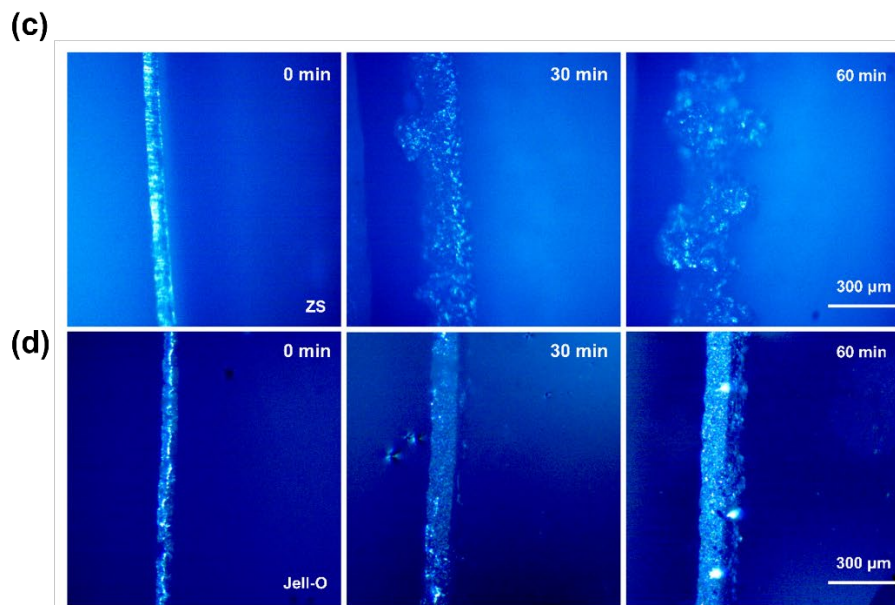
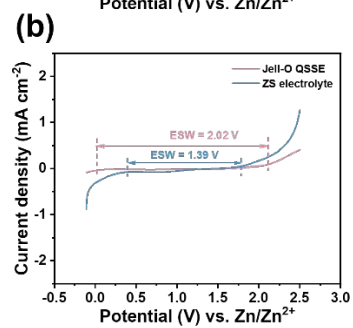
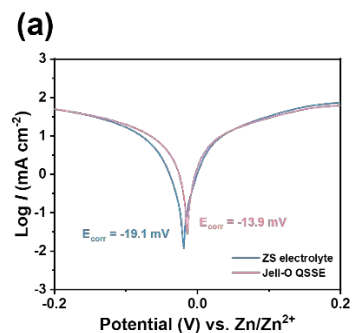
the Jell-O QSSE clearly possesses a higher content of strong H-bonds (54.7%) than the ZS electrolyte (48.0%). This indicates the capability of Jell-O to bind and interact more efficiently with water than zinc sulfate, which reduces the activity of free water in the electrolyte and thus minimizes the potential occurrence of parasitic reactions including HER and water decomposition. It is also critical to determine the wettability of Jell-O QSSE, since good interfacial contact is needed to enable efficient ion transport, uniform Zn deposition, and to prevent uneven current distribution and other side reactions. Hence, contact angle measurements were conducted for both ZS electrolyte and Jell-O electrolyte on Zn anode. The obtained results are shown in **Figure 37h**. The Jell-O QSSE shows smaller contact angle compared to conventional ZS electrolytes, indicating enhanced interfacial wettability of Jell-O QSSE on the metallic Zn anode surface. Consequently, nucleation barriers may be reduced easily due to the high Zn affinity, which promotes ion migration, charge transfer, and uniform Zn growth during repeated cycles (Jia et al., 2020). To compare the ionic conductivities of ZS electrolyte and Jell-O QSSE, Zn//Zn symmetric cells with different electrolytes have been assembled, followed by the collection of EIS spectra. The bulk resistance for each electrolyte was determined from the Nyquist plot (**Figure 37i**), which was then used to calculate the corresponding ionic conductivity. As shown in **Figure 37j**, the calculated ionic conductivity value for the Jell-O QSSE was slightly lower than that of the ZS electrolyte, dropping from 74.4 mS cm^{-1} to 53.1 mS cm^{-1} . However, it still outperforms many other gel electrolytes reported (Cong et al., 2021; Fu et al., 2022; Hao et al., 2022; Lin et al., 2022; Liu et al., 2023; Liu et al., 2022; Quan et al., 2022; Tian et al., 2023; T. Wei et al., 2022; Zhang et al., 2022)

and is sufficient for fast Zn^{2+} ion migration (Yuan Huang, Jiyan Zhang, et al., 2019; Liu et al., 2023).

5.2.2 Dendrite-Free Zn anodes via Jell-O QSSE

Figure 38.

Dendrite-free Zn anodes via Jell-O QSSE.



Note. **(a)** Tafel plot for ZS electrolyte and Jell-O QSSE; **(b)** ESWs of ZS electrolyte and Jell-O QSSE via LSV; **(c)** in-situ optical microscopy for Zn anodes in ZS electrolyte; **(d)** in-situ optical microscopy for Zn anodes in Jell-O QSSE; **(e)** Chronopotentiogram of Zn anodes in both ZS electrolyte and Jell-O QSSE; **(f)** Chronoamperogram of Zn anodes in both ZS electrolyte and Jell-O QSSE

Unlike conventional ZS electrolytes, the Jell-O QSSE can enable dendrite-free anodes, which is demonstrated through numerous characterization and electrochemical techniques. **Figure 38a** shows the potentiodynamic polarization curves of Zn foil in conventional ZS electrolytes and Jell-O QSSE, which suggests that the Jell-O QSSE exhibits a lower corrosion potential of -13.9 mV in contrast to that of ZS electrolytes (-19.1 mV), meaning Jell-O QSSE can favorably inhibit corrosion from either HER or passivation of oxygen. Linear sweep voltammetry (LSV) measurements were also conducted; as indicated in **Figure 38b**, the introduction of Jell-O QSSE broadens the electrochemical stability window (ESW) from 1.39 V to 2.02 V in relative to ZS electrolytes, indicating enhanced resistance to Zn anode corrosion due to side reactions such as HER. In addition, in situ optical microscopy was employed for *operando* observation of Zn dendrite growth in both ZS electrolyte and Jell-O QSSE at a high current density of 5 mA cm⁻². As shown in **Figure 38c**, in the ZS electrolyte, protuberances emerged on the surface of Zn anode within 30 min. As the deposition time increases to 60 min, more protrusions randomly occurred and became enlarged, eventually evolving into Zn dendrites. In

comparison, the Zn anode surface remained smooth and homogeneous Zn deposition could be found throughout the entire testing period of 60 min (**Figure 38d**).

One of the most formidable challenges in long-term cycling of AZIBs is the formation of Zn dendrite, which is primarily associated with the Zn nucleation process. To better understand the morphology of Zn nuclei in different electrolyte systems, the chronopotentiometry (CP) test was conducted on Zn//Zn symmetric coin cells to assess the nucleation overpotential (NOP). As shown in **Figure 38e**, the CP test was conducted at a current density of 1 mA cm^{-1} . Compared to conventional ZS electrolytes (52.2 mV), the Jell-O QSSE demonstrated a significant reduction in NOP (25.2 mV), corresponding to a smaller impetus for preferred desolvation kinetics, smaller grain size, and uniform Zn nucleation. To further characterize the diffusion mechanism and deposition behaviors of Zn^{2+} ions on the Zn surface using conventional ZS electrolytes and Jell-O QSSE, chronoamperometry (CA) was conducted at a constant overpotential of 150 mV. As the chronoamperogram illustrates (**Figure 38f**), in the ZS system, the current densities plummet continuously from -6.6 mA cm^{-2} to -20.9 mA cm^{-2} over the first 68 s, indicating a typical 2D diffusion process of Zn^{2+} ions in the lateral direction of the Zn surface. This rampant 2D diffusion process allows Zn^{2+} to accumulate at high-surface-energy locations and form large nuclei. The rise in current densities still remains in the subsequent 3D diffusion process ($> 68 \text{ s}$), rendering a much lower specific surface energy, which favors inhomogeneous growth of Zn dendrites. Conversely, upon using Jell-O QSSE, the CA curve plateaus at -16.7 mA cm^{-2} after an ephemeral period of constrained nucleation

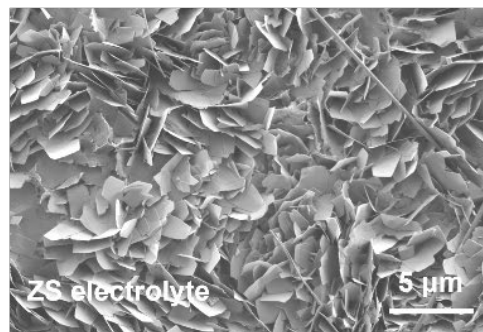
stage, followed by a long-term, imperturbable 3D diffusion process at lower current densities, which is beneficial to uniform Zn deposition.

5.2.3 Morphology on Zn Anode after Cycling

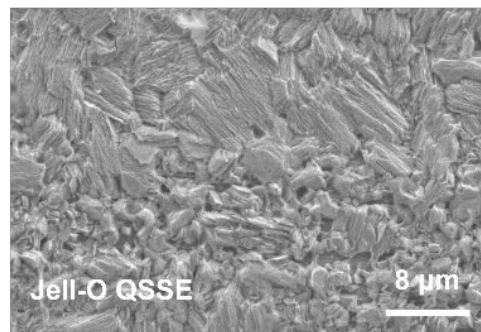
Figure 39.

Morphology of Jell-O QSSE on Zn anode after galvanostatic cycling.

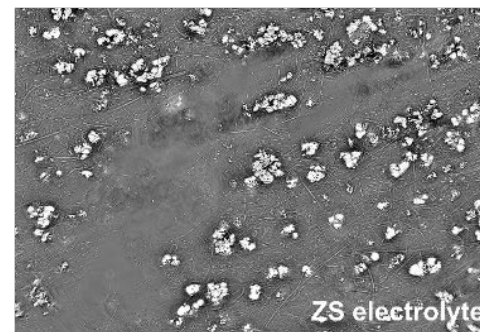
(a)



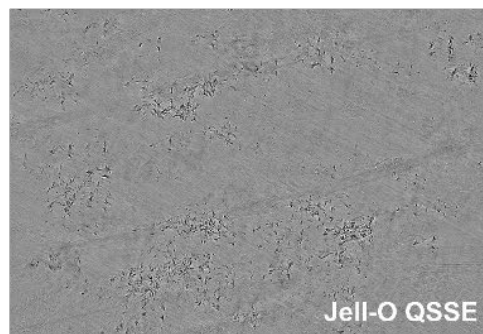
(b)



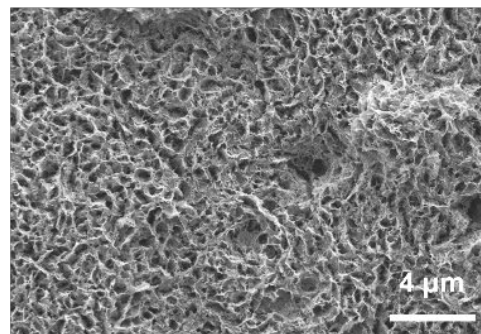
(c)



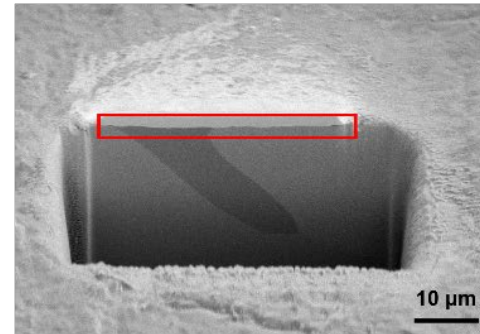
(d)



(e)



(f)



Note. **(a)** SEM image of Zn metal anode after cycling at 5 mA cm^{-2} and 5 mAh cm^{-2} in ZS electrolyte; **(b)** SEM image of Zn metal anode after cycling at 5 mA cm^{-2} and 5 mAh cm^{-2} in Jell-O QSSE; **(c)** SXCL images of Zn anode after cycling at 5 mA cm^{-2} and 5 mAh cm^{-2} in ZS electrolyte; **(d)** SXCL images of Zn anode after cycling at 5 mA cm^{-2} and 5 mAh cm^{-2} in Jell-O QSSE; **(e)** 3D structure of Jell-O QSSE upon freeze-drying; **(f)** FIB-SEM image of Zn anode after cycling in Jell-O QSSE.

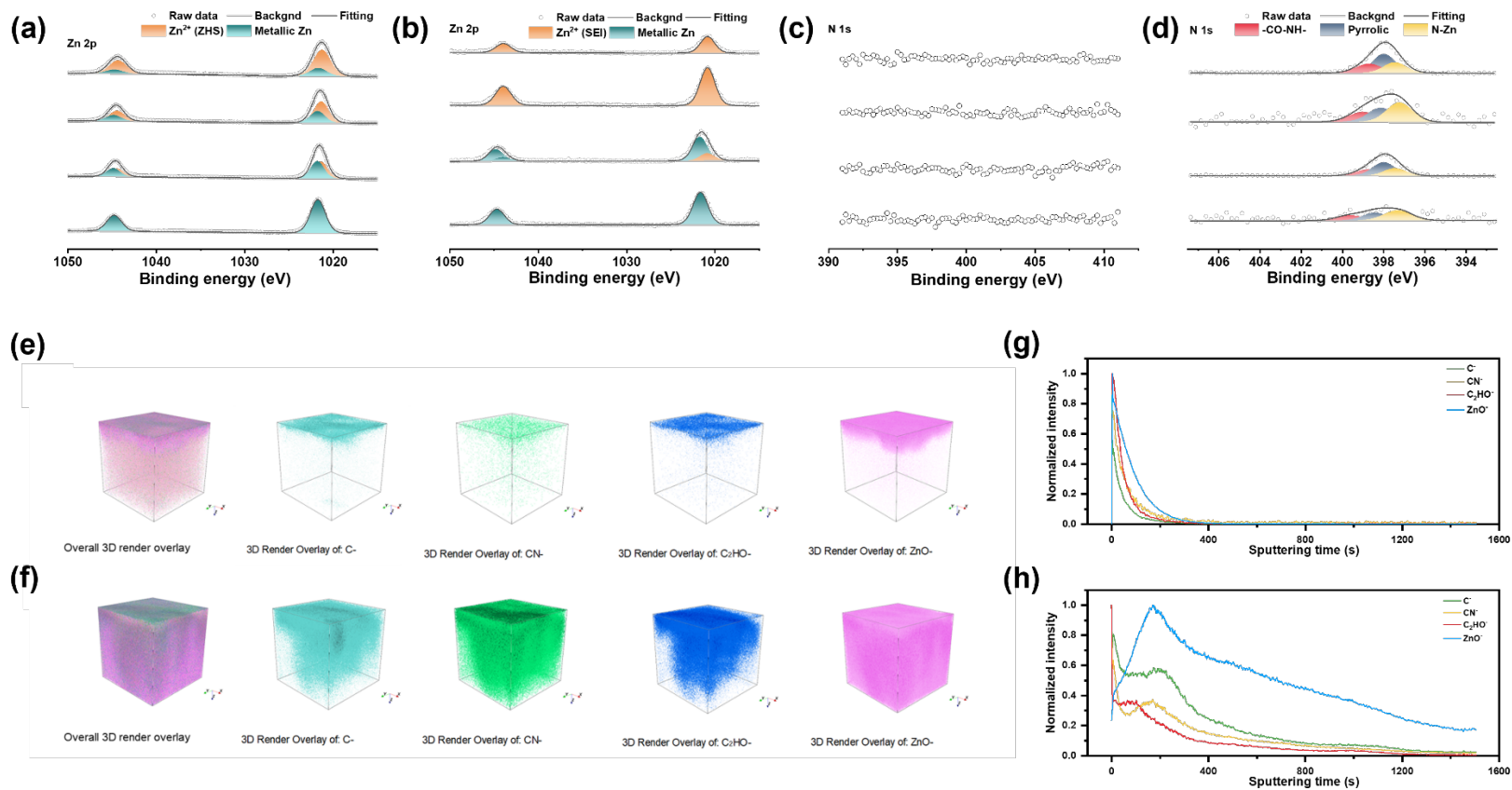
Moreover, the surface and cross-sectional Zn deposition morphology after cycling was observed using scanning electron microscopy (SEM), focused ion beam scanning electron microscopy (FIB-SEM), and synchronous X-ray computed laminography (SXCL). After 50 cycles of plating/stripping at 5 mA cm^{-2} and 5 mAh cm^{-2} , Zn//Zn symmetric cells using different electrolyte systems were disassembled and the Zn anodes were washed and dried. As shown in **Figure 39a**, loose and random Zn flakes were observed on Zn anode with conventional ZS electrolyte due to the severe corrosion; on the other hand, a dense and smooth surface can be observed on Zn anode using Jell-O QSSE (**Figure 39b**). The above results were also supported by the results of synchronous X-ray computed laminography (SXCL), where sharp, inhomogeneous Zn dendrites were only observed on Zn anode using ZS electrolyte after cycling (**Figure 39c**). On the contrary, the Zn anode surface cycled in Jell-O QSSE remains smooth and dense, indicating no side reactions (**Figure 39d**). To further elucidate the observed phenomena, the Jell-O QSSE was also freeze-dried and grinded before it had been sent for

SEM observation. As illustrated by **Figure 39e**, upon freeze-drying, the porous, sponge-like 3D matrix formed by gelatin chains inside Jell-O QSSE could be viewed directly using SEM. As we previously mentioned, this porous 3D matrix is formed via self-aggregation of gelatin molecules. Compared to single molecules, it helps facilitate Zn^{2+} transfer and the binding of anions in the Zn^{2+} solvation sheath, so that the concentration of free anions could be largely reduced. In sharp contrast, in conventional ZS electrolytes, over 50% of the current is carried by anions. The concentration polarization would quickly build up, aggravating side reactions degrade the Zn anode, thus resulting in dendrite formation and deteriorated electrochemical performance. The cross-section of Zn deposition morphology in Jell-O QSSE was also observed using FIB-SEM, shown in **Figure 39f**. As illustrated, a homogeneous solid-electrolyte interphase (SEI) is observed on the surface of the Zn anode cycled in Jell-O QSSE.

5.2.4 Surface Composition and Elemental Valence State Analysis

Figure 40.

Surface composition and elemental valence state analysis.



Note. **(a)** Zn_{2p} XPS spectra of Zn anode after 50 cycles with different etching time (0, 300, 600, 900s) in ZS electrolyte; **(b)** Zn_{2p} XPS spectra of Zn anode after 50 cycles with different etching time (0, 300, 600, 900s) in Jell-O QSSE; **(c)** N_{1s} XPS spectra of Zn anode after 50 cycles with different etching time (0, 300, 600, 900s) in ZS electrolyte; **(d)** N_{1s} XPS spectra of Zn anode after 50 cycles with different etching time (0, 300, 600, 900s) in Jell-O QSSE; **(e)** 3D render overlay for ToF-SIMS of SEI components in ZS electrolyte **(f)** 3D render overlay for ToF-SIMS of SEI components in Jell-O QSSE **(g)** elemental distribution of ToF-SIMS at different sputtering time (0, 300, 600, 900s) for Zn anode cycled in conventional ZS electrolyte; **(h)** elemental distribution of ToF-SIMS at different sputtering time (0, 300, 600, 900s) for Zn anode cycled in Jell-O QSSE

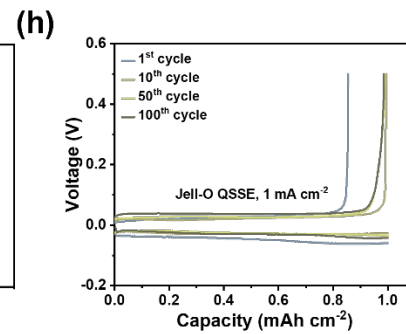
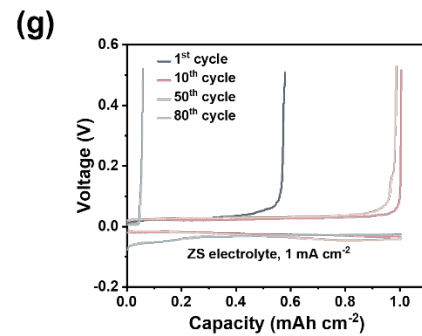
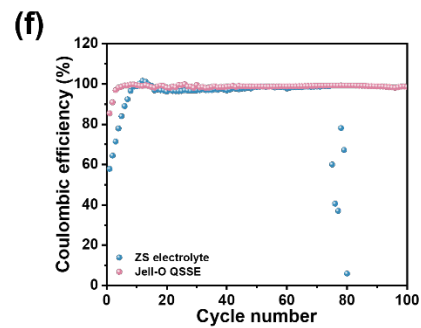
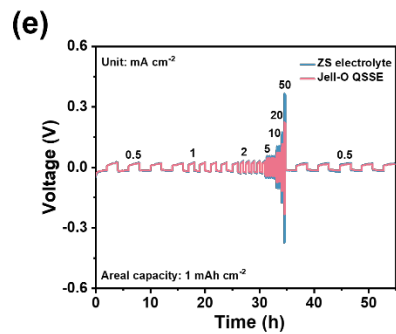
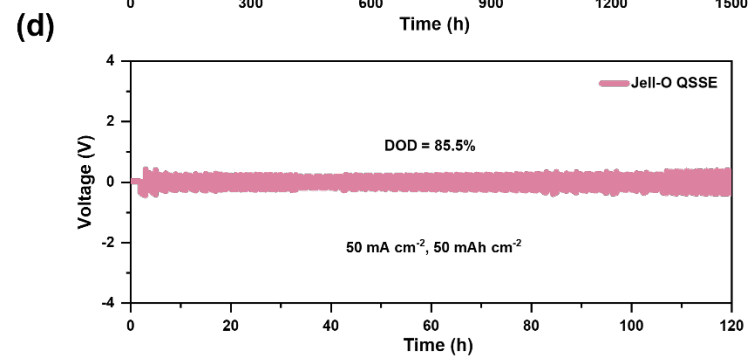
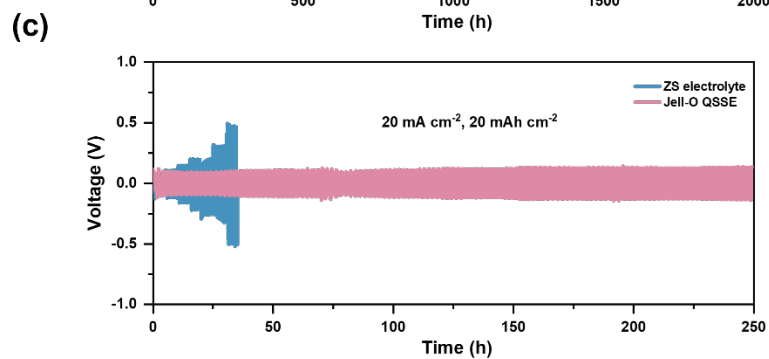
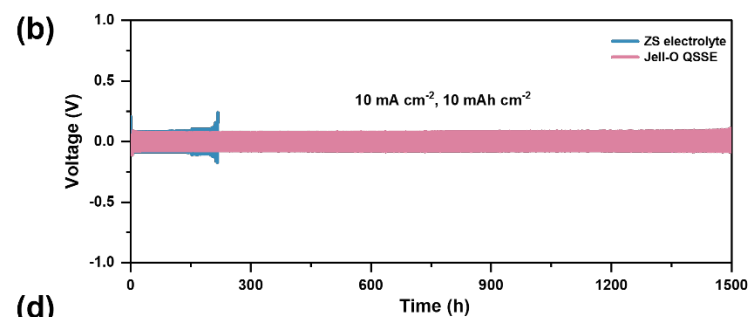
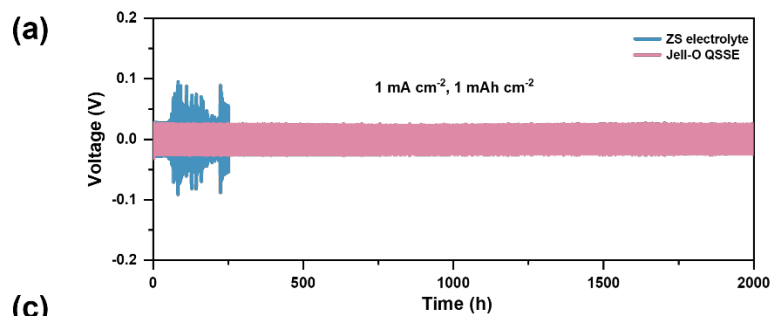
To gain a better understanding of the surface composition and elemental valence state of the SEI, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) at different etching time (0, 300, 600, 900 s) were used. As shown in **Figure 40a**, Zn^{2+} is the dominant component until 300 s of etching, which corresponds to the formation of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ byproduct. The Zn^{2+} peak is almost completely replaced by metallic Zn peak by 600 s of etching time. When etching time reached 900 s, only metallic Zn exists. This is indicative of the gradual disappearance of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ as X-ray penetrates deeper and deeper. On the other hand, in Jell-O QSSE (**Figure 40b**), the Zn_{2p} spectra shows that Zn^{2+} is the dominant component until 600 s of etching. The increased sputtering time to each content increase in metallic Zn corresponds to the formation of SEI that contains Zn^{2+} . In the N_{1s} spectra, despite the progress in etching time, no peaks were observed for Zn anodes in conventional ZS electrolytes (**Figure 40c**). In **Figure 40d**, however, the N_{1s} spectra

of Zn anode cycled in Jell-O show the -CO-NH-, pyrrolic N, and N-Zn peaks, where pyrrolic N and N-Zn always have higher content than the organic -CO-NH- component, which is indicative of the formation of a organic-inorganic hybrid SEI layer. To further view the distribution of SEI components of cycled Zn anode, TOF-SIMS was also utilized at each corresponding etching time. The overall 3D render overlay results and those for each component of the SEI are shown in **Figure 40e** and **f**. The results show that by using Jell-O QSSE, a much denser and thicker SEI is formed on the Zn anode. The elemental distributions of C⁻, CN⁻, C₂HO⁻, and ZnO⁻ for ZS electrolyte and Jell-O QSSE are also shown in **Figure 40g** and **h**, respectively, which are in accordance with the previous XPS results.

5.2.5 Long-term Cycling Performance of Zn//Zn Symmetric Cells

Figure 41.

Electrochemical performance of Zn//Zn symmetric cells and Coulombic efficiency (CE) test.



Note. **(a)** Cycling performance of Zn//Zn symmetric cells at 1 mAh cm⁻² and 1 mA cm⁻²; **(b)** Cycling performance of Zn//Zn symmetric cells at 10 mAh cm⁻² and 10 mA cm⁻²; **(c)** Cycling performance of Zn//Zn symmetric cells at 20 mAh cm⁻² and 20 mA cm⁻²; **(d)** Cycling performance of Zn//Zn symmetric cells at 50 mAh cm⁻² and 50 mA cm⁻²; **(e)** Rate capability of Zn//Zn symmetric cells in ZS electrolyte and Jell-O QSSE; **(f)** CE measurements of Zn//Cu cells using ZS electrolyte and Jell-O QSSE; **(g)** voltage profiles at different cycle numbers for ZS electrolyte; **(h)** voltage profiles at different cycle numbers for Jell-O QSSE

The long-term cycling stability of Zn anodes in Jell-O QSSE was further investigated using Zn//Zn symmetric cell. As **Figure 41a** illustrates, with an areal capacity of 1 mAh cm⁻² and current density of 1 mA cm⁻², the Zn//Zn symmetric cell using Jell-O delivered an ultralong cycle life of over 2000 h with a low overpotential of about 25 mV. In comparison, cells with conventional ZS electrolytes encountered an acute jump in overpotential after only 80 h, potentially due to the formation of Zn dendrites. Furthermore, even at an elevated galvanostatic condition of 10 mA cm⁻² and 10 mAh cm⁻² (**Figure 41b**), 20 mA cm⁻² and 20 mAh cm⁻² (**Figure 41c**), or an extreme condition of 50 mA cm⁻² and 50 mAh cm⁻² (**Figure 41d**), Zn//Zn symmetric cells in Jell-O QSSE could still provide stable plating and stripping behaviors for more than 1500 h, 250 h, and 120 h, respectively. As shown in **Figure 41e**, not only was the rate performance of Zn//Zn symmetric cells using Jell-O QSSE comparable to that using conventional ZS electrolytes at lower current densities (< 5 mA cm⁻²), but at higher current densities (10, 20, and 50 mA cm⁻²), cells using Jell-O QSSE showed significantly lower overpotentials, indicating the excellent stability of Zn anodes. More importantly, the Zn//Zn

symmetric cell could sustain 120 h of cycling at an extreme galvanostatic condition of 50 mA cm⁻² and 50 mAh cm⁻², and a high DoD of 85.5% was achieved. To establish the robustness of the electrolyte, each experimental condition was repeated at least three times with independently prepared zinc electrodes and fresh batches of the Jell-O QSSE. These repeated experiments consistently demonstrated excellent cycling stability and performance, providing strong evidence for the reproducibility of the results. Across all repetitions, the voltage hysteresis profiles remained stable across cycles, indicating uniform zinc-ion transport and deposition without signs of dendrite-induced degradation. The repeatability demonstrated in Zn//Zn symmetric cell tests has significant implications for practical applications of the Jell-O QSSE in zinc-ion battery systems. The robust performance under varying current densities highlights the versatility of the electrolyte, making it suitable for diverse energy storage scenarios, including low-power devices and high-power grid-scale applications. Furthermore, the stability observed in symmetric cells is a direct indicator of the electrolyte's capability to suppress dendrite growth and enable long-term cycling, both critical for commercial adoption.

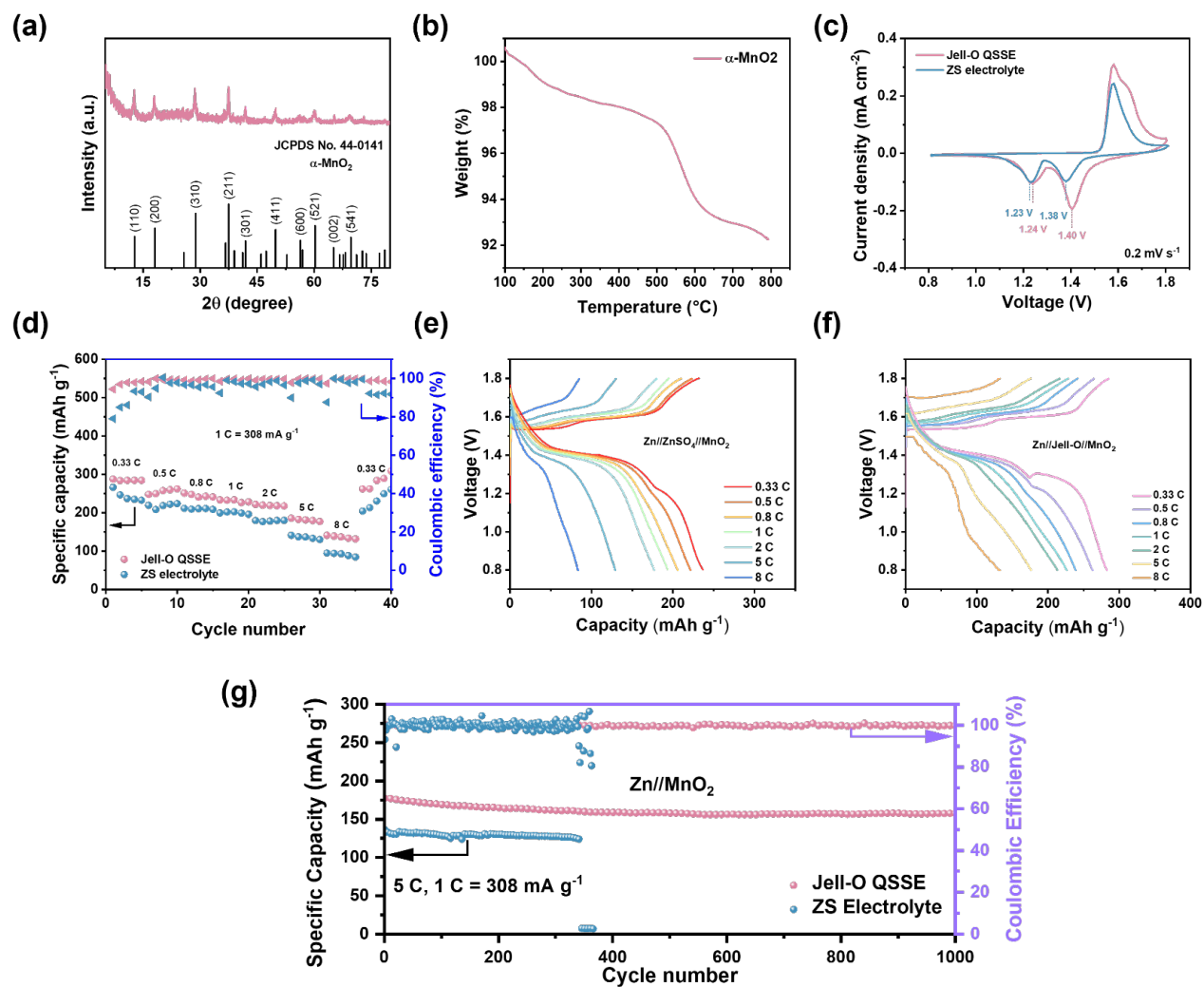
To investigate the reversibility and stability of Zn anode using Jell-O QSSE, Zn//Cu cells were further assembled. As presented in **Figure 41f**, in the first few cycles (cycle 1 to 7), the Coulombic efficiency (CE) remained relatively low, since the plating/stripping of Zn on Cu foil came into a lattice fitting stage (or reshaped Zn coordination). After that, Zn//Cu half cells using conventional ZS electrolytes did not fail to provide stable cycling/stripping (CE > 95%) until the 75th cycle at 1.0 mA cm⁻² and 1.0 mAh cm⁻², where CE started to drop briskly to less than 60% (**Figure 41g**). In sharp contrast, upon cyclic plating/stripping at the same

galvanostatic condition, Zn//Cu cells using Jell-O QSSE realized a high average CE for over 100 cycles, demonstrating excellent cycling stability using Jell-O QSSE (**Figure 41h**). To further ensure the reliability of the results, rigorous statistical analysis was conducted. For instance, the average CE for symmetric cells remained above 98% across all repeated tests, with minimal deviations, even under the more aggressive cycling conditions at higher current densities. The small standard deviations observed in key metrics confirm that the variations between repeats were negligible, reinforcing the robustness and repeatability of the experimental outcomes.

5.2.6 Performance of Zn//MnO₂ and Zn//NVO Full Cells

Figure 42.

Electrochemical performance of Zn//MnO₂ full cells.



Note. **(a)** XRD pattern of as-prepared MnO₂ cathode material; **(b)** TGA pattern of as-prepared MnO₂ cathode material; **(c)** CV profile of Zn//MnO₂ cells using Jell-O QSSE and ZS electrolytes; **(d)** Rate capabilities of Zn//MnO₂ full cells using ZS electrolyte and Jell-O QSSE; **(e)** The galvanostatic charge-discharge curves of Zn//MnO₂ full cells using ZS electrolyte; **(f)** The galvanostatic charge-discharge curves of Zn//MnO₂ full cells using Jell-O QSSE; **(g)** Cycling stability of Zn//MnO₂ full cells using ZS electrolyte and Jell-O QSSE

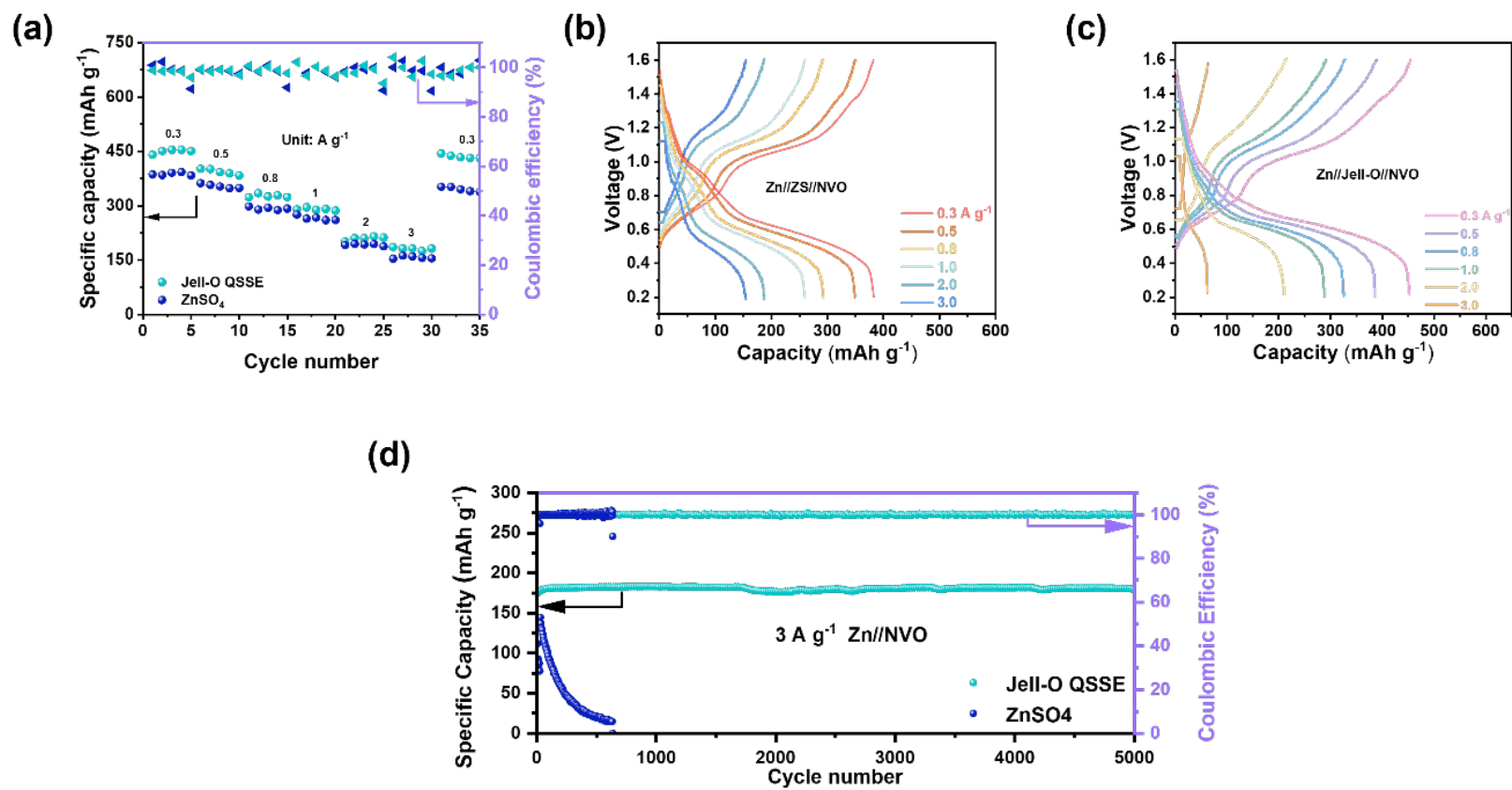
The feasibility of Jell-O QSSE was also examined by further assembling Zn//MnO₂ full cells and Zn//NVO full cells. For Zn//MnO₂ full cells, α -MnO₂ was chosen as the cathode material. As shown in **Figure 42a**, the XRD pattern shows diffraction peaks at 12.8°, 18.1°, 28.8°, 37.5°, 42.0°, 49.9°, 56.4°, 60.3°, 65.1°, and 69.7°, which can be well indexed to (110), (200), (310), (211), (301), (411), (600), (521), (002), and (541) of α -MnO₂ (JCPDS No. 44-0141). Furthermore, the thermogravimetric analysis (TGA) of the as-prepared product is in agreement with that reported previously, which further confirms the composition of the synthesized cathode material (**Figure 42b**). **Figure 42c** shows the CV profiles of Zn//MnO₂ cells using Jell-O QSSE and ZS electrolytes at a scan rate of 0.2 mV s⁻¹. The two CV profiles have a similar shape, and pairs of redox peaks can be clearly identified in both cells, manifesting that Jell-O does not change the mechanism of Zn²⁺ and H⁺ insertion/extraction in MnO₂. However, Jell-O QSSE leads to more intensive redox peaks and positive shifts of cathodic peaks due to the accelerated Zn²⁺/Zn kinetics and enhanced electrochemical activity.

Figure 42d compares the rate capabilities of Zn//MnO₂ full cells using ZS electrolyte and Jell-O QSSE, and the corresponding charge/discharge profiles are shown in **Figure 42e** and **Figure**

42f. Over a wide range of current densities from 0.33 to 8 C, the specific capacities of the cells using Jell-O are much higher than those using ZS. Eventually, a capacity of 261.70 mAh g⁻¹ was retained when the current density was recovered to 0.33 C, demonstrating good reversibility of the full cells using Jell-O QSSE. Conversely, cells using ZS electrolyte show rapid decay in capacity at larger current densities (5 C and 8 C). Moreover, as **Figure 42g** illustrates, at a large current density of 5 C, an impressive capacity retention of 88.7% was obtained after 1000 cycles with a high average CE of 99.6%, indicating excellent cycling stability and rate performance realized by Jell-O QSSE. For the Zn//MnO₂ full cells, at least three independent tests were performed with separately prepared cathodes and electrolytes. These repeated tests were critical to validating the high cycling stability and capacity retention of the Jell-O QSSE when paired with MnO₂ cathodes. Each test consistently demonstrated a high capacity retention and high average CE averaging to the abovementioned values, which highlights the reproducibility of the experiment.

Figure 43.

Electrochemical performance of Zn//NVO full cells.



Note. **(a)** Rate capabilities of Zn//NVO full cells using Jell-O QSSE and ZS electrolyte; **(b)** The galvanostatic charge-discharge curves of Zn//NVO full cells using ZS electrolyte; **(c)** The galvanostatic charge-discharge curves of Zn//NVO full cells using Jell-O QSSE; **(d)** Cycling stability of Zn//NVO full cells using Jell-O QSSE and ZS electrolyte

The Jell-O QSSE adapts to versatile cathode materials as well. As mentioned earlier, in addition to MnO_2 , sodium vanadate ($\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, NVO) has been synthesized and employed as another cathode material, coupling the Zn anode. The rate performance of Zn//NVO full cells using Jell-O QSSE and ZS was juxtaposed in **Figure 43a**, and the corresponding GCD curves are shown in **Figure 43b** and **Figure 43c**. Likewise, cells using Jell-O QSSE exhibit outstanding rate performance with current densities ranging from 0.3 to 3 A g^{-1} , outperforming those using ZS electrolyte. The discrepancy in specific capacities becomes more noticeable when the current density recovered to 0.3 A g^{-1} . A specific capacity of 430.92 mAh g^{-1} was retained for cells using Jell-O, which was much higher than those using ZS electrolyte (338.08 mAh g^{-1}). Superior cycling performance was also observed from cells using Jell-O QSSE. As shown in **Figure 43d**, under a large current density of 3 A g^{-1} , Zn//NVO full cells using Jell-O QSSE still achieved an exceptionally high capacity retention of 99.2% after 5000 cycles. On the contrary, cells using ZnSO_4 started to lose their capacities continuously from the 30th cycle due to parasitic side reactions and Zn dendrite growth, until they lose all the capacities after 635 cycles. Again, for the Zn//NVO full cells, at least three independent tests were performed

with separately prepared cathodes and electrolytes. Each test consistently demonstrated a high capacity retention and high average CE averaging to 99.2% and almost $\sim 100\%$, respectively, which highlights the reproducibility of the experiment.

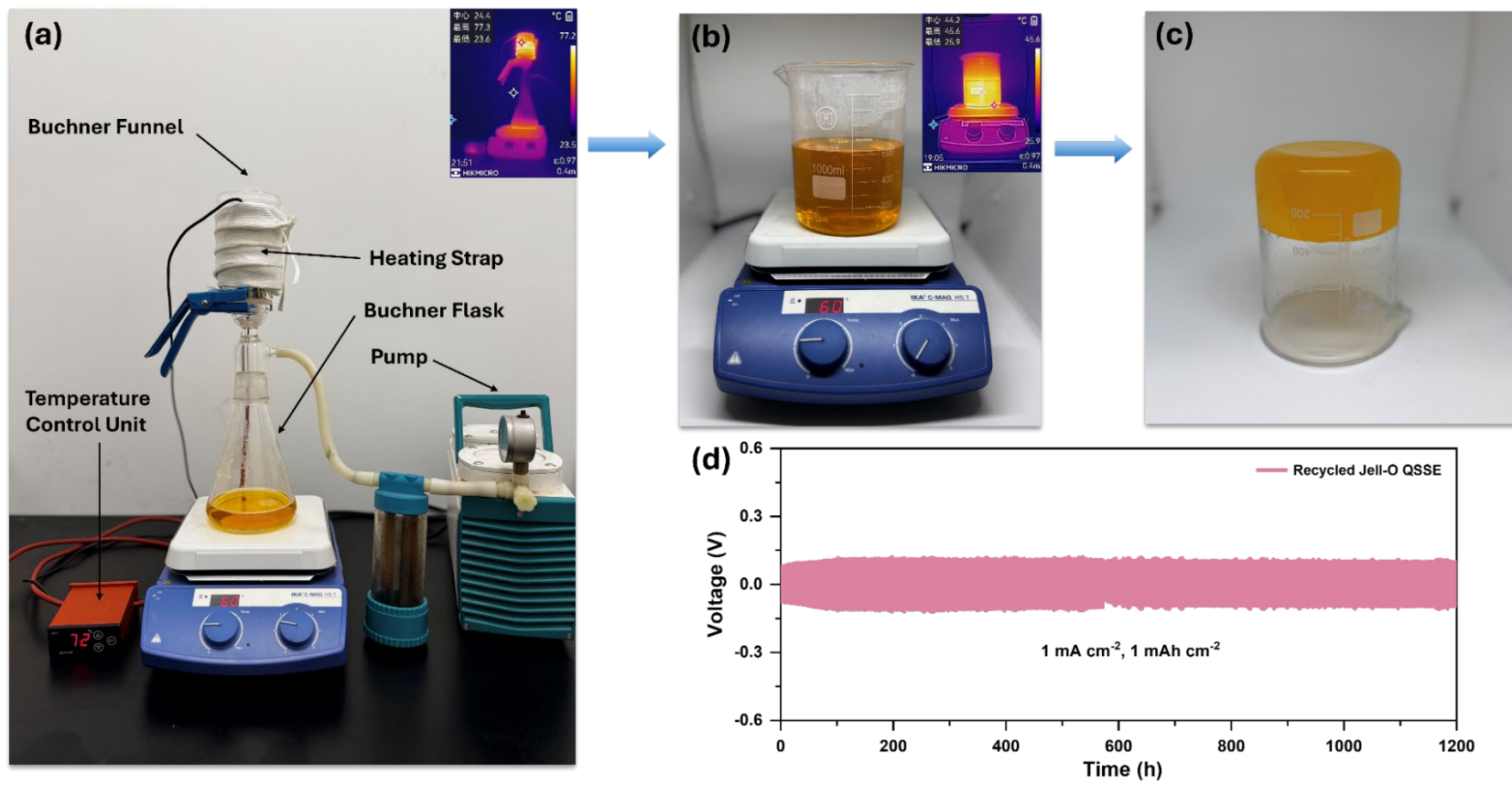
5.2.7 Biocompatibility and Recyclability of Jell-O QSSE

The Jell-O powder is commercially available and generally considered safe for internal use as a food product. Apart from its main ingredient, gelatin, the Jell-O powder consists of plant-derived polysaccharides such as agar-agar and carrageenan, exhibiting a high degree of biocompatibility. Hence, Jell-O presents excellent biocompatibility and is suitable for various biomedical and pharmaceutical applications. The main ingredient, gelatin, is known for its non-toxicity and non-immunogenic properties, which are essential for promoting cell adhesion and proliferation; it is also commonly used as a scaffold in tissue engineering and as a delivery medium for drugs and bioactive compounds due to its biodegradable nature. Similarly, agar-agar and carrageenan, sourced from seaweed, are safe and biocompatible polysaccharides. They are particularly advantageous for their gelation properties, which allows for the creation of stable, three-dimensional matrices that support cellular activities without eliciting significant immune responses.

One of the main advantages of AZIBs over state-of-the-art LIBs is the easy recycling of Zn in comparison to heavy metals such as cobalt. Using the Jell-O QSSE, not only can the Zn anode materials be recycled, but the electrolytes can also be recycled, recovered, and reused in the assembly of new cells. **Figure 44** illustrates a schematic of the recycling process of Jell-O QSSE.

Figure 44.

Recycling of Jell-O QSSE



Note. **(a)** Suction filtration of used Jell-O QSSE **(b)** Reheating of collected, filtered Jell-O QSSE **(c)** Sol-gel transition of collected, filtered Jell-O QSSE at room temperature **(d)** Cycling performance of Zn//Zn symmetric cells at 1 mA cm⁻² and 1 mAh cm⁻².

In **Figure 44a**, used coin cells were completely disassembled and placed on pre-moistened filter paper in the Buchner funnel, which contained used Jell-O QSSE that had transitioned into gel at a cooler temperature in prior. A heating strap was tightly wrapped around the funnel, the temperature of which was maintained at around 60 °C to ensure the flow of Jell-O QSSE through the funnel to the flask. The filtered Jell-O QSSE was then poured into a 1-L beaker with constant heating of 60 °C to avoid sol-gel transition at room temperature, as shown in **Figure 44b**. The corresponding temperature gradients were clearly revealed by infrared camera, as shown in the upper right corner of **Figure 44a** and **Figure 44b**, respectively. Once the temperature of filtered Jell-O became uniform, heat would be turned off and the beaker would be transferred to room temperature until Jell-O QSSE inside the beaker transitioned to gel form, as indicated in **Figure 44c**. Using the regenerated gel-form Jell-O QSSE as an electrolyte additive, Zn//Zn symmetric coin cells were further assembled and tested at 1 mA cm⁻² and 1 mAh cm⁻². As **Figure 44d** illustrates, Zn//Zn cells using recycled Jell-O still demonstrate excellent cycling stability without short-circuit for more than 1200 hours, which reveals the unchanged properties and compatibility of Jell-O QSSE after being recycled.

5.3 Discussion

The use of commercially available Jell-O powders as a key component in the design of QSSEs for AZIBs introduces a number of practical and performance-related advantages. Unlike pure gelatin, which is commonly used in laboratory research, the Jell-O powders are a composite material that includes sugars, stabilizers, and other organic compounds. These additives significantly influence the performance and economic feasibility of the QSSE, making them a promising alternative for large-scale battery production. One of the most notable benefits of using the Jell-O powders is their ability to contribute to the formation of a stable solid-electrolyte interphase (SEI). The sugars and other organic compounds present in the powders participate in interfacial reactions during cycling, facilitating the development of a robust SEI layer on the zinc anode. This SEI layer, as mentioned in earlier sections, plays a crucial role in suppressing parasitic side reactions, such as HER and zinc dendrite formation, thereby enhancing the cycling stability of AZIBs. The enhanced SEI formation demonstrates the potential of Jell-O powders to improve the electrochemical performance of the QSSE. In addition to their electrochemical benefits, the Jell-O powders offer a significant cost advantage over laboratory-grade pure gelatin. At approximately \$12.57 per 100 g compared to \$44.60 per 100 g for pure gelatin, the Jell-O powders provide a more affordable option for electrolyte preparation, especially in the context of large-scale battery manufacturing. The widespread availability of Jell-O powders further supports their practicality as a cost-effective material for commercial applications, aligning with the need for scalable and economically viable energy

storage solutions. Another advantage of Jell-O powders lies in their superior gelation stability compared to pure gelatin. Commercial Jell-O powders are engineered to retain water efficiently, a property that translates into improved gelation behavior in the QSSE matrix. This enhanced gelation stability ensures the formation of a uniform and durable electrolyte network, which is critical for maintaining consistent ionic conductivity and ensuring reliable battery operation. The ability of the QSSE to retain water while maintaining its mechanical and electrochemical properties is particularly beneficial for achieving long-term cycling stability in AZIBs. The combination of improved performance, lower cost, and wide availability positions Jell-O powders as a practical alternative to pure gelatin in the development of QSSEs for AZIBs. The benefits of enhanced SEI formation, superior gelation stability, and improved mechanical properties address critical challenges in electrolyte engineering for zinc-ion batteries. Furthermore, the economic advantages of Jell-O powders align with the growing demand for cost-effective materials in large-scale battery production, making them an attractive option for commercial implementation.

5.4 Conclusion

In summary, a bio-recyclable, self-aggregating Jell-O quasi-solid-state electrolyte has been developed, which can effectively suppress inhomogeneous Zn dendrite growth and is thus crucial for the development of high-performance, cost-effective AZIBs. Various characterization techniques and electrochemical tests have been conducted, revealing that the Jell-O QSSE can synergistically form a stable organic-inorganic hybrid SEI and facilitate the binding of anions in the Zn^{2+} solvation sheath upon cooling at room temperature. As a result,

Zn//Zn symmetric cells using Jell-O QSSE can deliver improved calendar life of over 2000 h at 1 mAh cm^{-2} and 1 mA cm^{-2} , and maintain stable plating/stripping behaviors for over 120 h under extreme conditions of 50 mAh cm^{-2} and 50 mA cm^{-2} with a high DOD of 85.5%. Furthermore, using Jell-O QSSE, Zn//NVO and Zn//MnO₂ full cells were able to operate stably for over 1000 cycles and 5000 cycles, respectively with excellent capacity retentions and CEs. Finally, Jell-O QSSE has been recycled, regenerated, and reused in the assembly of Zn//Zn symmetric cells by applying a suction filtration method. The new symmetric cells can still provide stable, prolonged cycling of over 1200 h, which confirms the bio-recyclability of Jell-O QSSE. These results confirm the feasibility of Jell-O QSSE, which is promising in the application of AZIBs in the future.

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Publication: Journal of the American Chemical Society
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Title	Design of Self-Aggregating and Recyclable Quasi-Solid-State Electrolyte towards Dendrite-Free Zn Anode	Institution Name	University of Waterloo
Instructor Name	Yu, Aiping; Fowler, Michael	Expected Presentation Date	2025-01-01

Figure 12:

TW

Cellulose-based hydrogels: Present status and application prospects

Author: Chunyu Chang,Lina Zhang

Publication: Carbohydrate Polymers

Publisher: Elsevier

Date: 11 February 2011

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Licensed Content Author	Chunyu Chang,Lina Zhang
Licensed Content Date	Feb 11, 2011
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Quasi-Solid-State Zinc Ion Rechargeable Batteries for Subzero Temperature Applications

Author: Yehong Chen, Jianqing Zhao, Ying Wang
 Publication: ACS Applied Energy Materials
 Publisher: American Chemical Society
 Date: Sep 1, 2020
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Quasi-Solid-State Zinc Ion Rechargeable Batteries for Subzero Temperature Applications

Author: Yehong Chen, Jianqing Zhao, Ying Wang
 Publication: ACS Applied Energy Materials
 Publisher: American Chemical Society
 Date: Sep 1, 2020
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Figure 16:

A flexible zinc-ion battery based on the optimized concentrated hydrogel electrolyte for enhanced performance at subzero temperature
 Author: Ying Wang, Yehong Chen
 Publication: Electrochimica Acta
 Publisher: Elsevier
 Date: 1 November 2021
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Figure 17 – 18:

Gelatin/Zn(CF3SO3)2 Polymer Electrolytes for Electrochromic Devices
 Author: Maria Manuela Silva, Verónica de Zea Bermudez, Elvira Fortunato, et al
 Publication: Electroanalysis
 Publisher: John Wiley and Sons
 Date: May 9, 2013
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Syneresis in agar hydrogels
 Author: Shipri Boral, Anita Saxena, H.B. Bohidar
 Publication: International Journal of Biological Macromolecules
 Publisher: Elsevier
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Zn-dominated interphase inhibits the anodic parasitic reactions for Al-air batteries using Zn2+@Agar hydrogel membrane
 Author: Manhui Wei, Kelang Wang, Lingling Kang, Yuyu Zuo, Liping Zhong, Pengfei Zhang, Songmao Zhang, Pucheng Pei, Junfeng Chen
 Publication: Journal of Power Sources
 Publisher: Elsevier
 Date: 15 October 2022
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Figure 21:

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Fourier Transform Infrared Spectroscopy for Molecular Analysis of Microbial Cells
 Author: Jesús J. Ojeda, Maria Ditzlich
 Publication: Springer eBook
 Publisher: Springer Nature
 Date: Jan 1, 2012
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Raman Spectroscopy for Detecting Neurological Disorders: Progress and Prospects
 Author: Mithun N. Megha Sunil, Meri Charles et al
 Publication: Springer eBook
 Publisher: Springer Nature
 Date: Jan 1, 2023
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Applications of Raman Spectroscopy in Agricultural Products and Food Analysis: A Review

Author: Yibin Ying, Danting Yang, Yang Danting, et al
Publication: Applied Spectroscopy Reviews
Publisher: Taylor & Francis
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Figure 24:

The debate on the dependence of apparent contact angles on drop contact area or three-phase contact line: A review

Author: H. Yildirim Erbil
Publication: Surface Science Reports
Publisher: Elsevier
Date: December 2014
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Advancing phosphate ore minerals separation with sustainable flotation reagents: An investigation into highly selective biobased depressants
 Author: Asmae El-bahi,Yassine Taha,Yassine Att-Khoula,Rachid Hakkou,Mostafa Benzaazoua
 Publication: Advances in Colloid and Interface Science
 Publisher: Elsevier
 Date: July 2023
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Figure 26:

Chapter: 18 Advanced micro- and nanoscale characterization techniques for carbonaceous aerosols
 Book: Handbook of Nanomaterials in Analytical Chemistry
 Author: Shahadev Rabha,Binoy K. Sankia
 Publisher: Elsevier
 Date: 2020
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Imaging the inner structure of chromosomes: contribution of focused ion beam/scanning electron microscopy to chromosome research

Author: Astari Dwiranti et al
Publication: Chromosome Research
Publisher: Springer Nature
Date: Feb 15, 2021

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X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)

Author: Richard T. Haasch
Publication: Springer eBook
Publisher: Springer Nature
Date: Jan 1, 2014

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Characteristics of a mixed-gas cluster ion beam for time-of-flight secondary ion mass spectrometry
 Author: Sang Ju Lee, Aram Hong, Jinwan Cho, Chang Min Choi, Ji Young Baek, Jae Yeong Eo, Byeong Jun Cha, Woo Jun Byeon, Jin Young We, Sangwon Hyun, Minwoo Jeon, Choelho Jeon, Dong Jin Ku, Myeung Choul Choi
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Overview of polycapillary X-ray optics
 Author: Paul J. Schields, David M. Gibson, Walter M. Gibson, Ning Gao, Huapeng Huang, Igor Yu. Ponomarev
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 Date: Mar 5, 2012
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Chapter: Thermogravimetric Analysis (TGA)
 Author: Alan Riga, Patrick K. Gallagher, Sergey Vyazovkin, et al
 Publisher: John Wiley and Sons
 Date: Jul 14, 2008
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Author: Achim Walter Hassel, Gunther Eggeler, Lakshman Neelakantan, et al
Publication: physica status solidi (a) applications and materials science
Publisher: John Wiley and Sons
Date: Jul 24, 2018
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Book: Fullerenes, Graphenes and Nanotubes

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