Proceedings of CONF-FMCE 2025 Symposium: Semantic Communication for Media Compression and Transmission
DOI: 10.54254/2755-2721/2025.GL25783

Design of Next-Generation Dendrite-Free Eco-Electrolytes for High-Voltage Aqueous Zn-Metal Batteries

Ginny Ke

Dana Hall School, Wellesley, MA, USA
ginnykeca@gmail.com

Abstract. As a sustainable alternative to lithium-ion batteries, aqueous zinc-ion batteries (AZIBs) are promising for grid-scale and portable energy storage due to their inherent safety, low cost, and environmental friendliness. However, their widespread practical application is hindered by dendrite formation and side reactions caused by free water molecules in the electrolyte. These issues lead to poor cycling stability, reduced coulombic efficiency, and limited lifespan. In this study, we present an environmentally-friendly alternative - lithium acetate (LiAc) with additives - that improve its hydrophilicity, widen the electrochemical stability window, and promote the formation of a uniform solid electrolyte interphase (SEI) on the zinc anode. We systematically compare the effect of LiAc, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and potassium hydroxide (KOH) in Zn-based electrolytes. Through various characterization techniques, including cyclic charge–discharge tests, linear sweep voltammetry (LSV), X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, viscosity, and contact angle measurements, we found that the optimized Zn:Li molar ratio of 1:4, particularly with LiAc-based systems, exhibits enhanced cycle stability, minimize dendrite formation, and enhanced capacity retention, overall improving the long-term cycling performance. This work provides valuable insights into electrolyte design for high-performance, sustainable AZIBs.

Keywords: Aqueous zinc-ion batteries, Electrolyte additives, Dendrite suppression, Electrochemical stability, Multi-functional electrolyte.

1. Introduction

The global transition toward renewable energy sources, such as solar and wind, has created an urgent and unprecedented demand for reliable, safe, and cost-effective energy storage systems. The intermittent nature of these renewables necessitates the development of large-scale batteries capable of stabilizing the power grid and ensuring a continuous supply of electricity. In this context, aqueous zinc-ion batteries (AZIBs) have emerged as exceptionally promising candidates. Their inherent advantages—including the natural abundance and low cost of zinc, the non-flammable nature of aqueous electrolytes, and their overall environmental friendliness—position them as an ideal technology for grid-scale applications where safety and economic viability are paramount [1].

Despite this great promise, the widespread commercialization of AZIBs is severely impeded by fundamental challenges rooted in the complex interfacial chemistry of the zinc metal anode in

© 2025 The Authors. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).

DOI: 10.54254/2755-2721/2025.GL25783

aqueous environments. The high reactivity of zinc with water triggers a cascade of detrimental phenomena. Firstly, uneven electrochemical deposition leads to the formation of sharp, needle-like zinc dendrites [2]. These structures can grow uncontrollably during battery charging, eventually piercing the separator and causing internal short circuits, which can lead to thermal runaway and catastrophic cell failure. Secondly, the electrochemical potential of zinc is below the reduction potential of water, leading to a parasitic hydrogen evolution reaction (HER) [3]. This side reaction not only consumes water from the electrolyte but also generates hydrogen gas, leading to pressure buildup within the cell and creating a passivating layer on the anode surface that impedes ion flow. Lastly, the anode is susceptible to continuous corrosion, forming electrochemically inert byproducts like zinc oxide (ZnO) or zinc hydroxide ($Zn(OH)_2$), which irreversibly consume the active material and increase the battery's internal resistance [4]. Collectively, these issues result in low Coulombic efficiency, rapid capacity decay, and a severely limited operational lifespan [5].

To mitigate these limitations, one promising approach involves the use of water-in-salt electrolytes (WiSEs), [6] which reduce free water activity to suppress parasitic reactions at the electrode–electrolyte interface. Furthermore, the development of dual-ion zinc batteries (DIZBs), [7] which utilize both cation and anion redox chemistry, offers additional benefits such as high operating voltage and enhanced energy density [8]. Despite these innovations, the challenge of maintaining cost-effectiveness while improving electrochemical performance remains [9].

Recent research has also highlighted the potential of environmentally friendly electrolyte additives and novel zinc salts. Additives like sodium dodecyl benzene sulfonate (SDBS), [10] Tween surfactants, and phosphonate-based compounds have demonstrated improved zinc plating/stripping efficiency, corrosion resistance, and interfacial stability. Meanwhile, greener alternatives to traditional salts, such as Zn(CH3SO3)2, sodium citrate, and Zn(BBI)2, offer pathways to safer and more sustainable electrolyte systems [11].

Collectively, these advancements underscore the importance of a comprehensive electrolyte design strategy that balances safety, performance, and environmental impact. This work aims to explore the synergistic effects of high-concentration salt formulations and multifunctional additives in advancing the practical viability of aqueous dual-ion zinc batteries [12].

This work seeks to bridge the gap between high performance and sustainability by designing a novel electrolyte system based on low-cost and environmentally benign acetate salts. We move beyond conventional additives and alternative salt by proposing a multi-functional electrolyte that combines the benefits of the WiSE concept with a dual-ion chemistry using a synergistic mixture of zinc acetate [$Zn(CH_3COO)_2$] and lithium acetate (LiAc). We hypothesize that this high-concentration acetate formulation will not only create a robust WiSE environment to mitigate anode degradation but also leverage the acetate anion's unique ability to modulate the solvation environment and contribute to a stable solid-electrolyte interphase (SEI).

By introducing LiAc, we aim to enable a high-voltage dual-ion mechanism while simultaneously suppressing dendrite formation and expanding the battery's electrochemical stability window. This study systematically investigates this novel electrolyte, comparing its performance directly against the established high-performance LiTFSI system and the conventional alkaline KOH system. Through detailed electrochemical analysis and material characterization, we aim to elucidate the underlying mechanisms and demonstrate that an eco-friendly, acetate-based electrolyte can provide a viable, cost-effective, and high-performance pathway for the next generation of safe and durable aqueous batteries.

DOI: 10.54254/2755-2721/2025.GL25783

2. Experiments and materials

2.1. Materials and cell assembly

Coin-type cells (CR2032) were assembled in a dry glove box to prevent atmospheric contamination. High-purity zinc foil (50 μm thickness) was used as the anode, and carbon-coated lithium iron phosphate (LFP) deposited on stainless steel foil (10 μm) served as the cathode. A glass fiber separator was placed between the electrodes to prevent short-circuiting and was subsequently soaked with the designated aqueous electrolyte. For this study, various electrolyte systems were prepared and evaluated, including those based on lithium acetate (LiAc), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and potassium hydroxide (KOH), with specific concentrations detailed in the results. Once assembled, the coin cells were hermetically sealed using a crimping tool. All cells were rested for 24 hours at room temperature to ensure complete wetting of the electrodes and separator before electrochemical testing.

2.2. Materials

As seen in Fig. 1,the AZIB cells were assembled in a coin-cell configuration in a dry glove box to prevent moisture or oxygen contamination. The zinc foil (50 μm) served as the anode, while carbon-coated lithium iron phosphate (LFP) on stainless steel foil (10μm) was used as the cathode material. A glass fiber separator was placed between the anode and the cathode to prevent short-circuiting and ensure efficient ion conduction. The separator was soaked with the aqueous electrolyte. Various electrolytes were used based on the experimental configuration, such as lithium acetate (LiAc), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and potassium hydroxide (KOH). The coin cell was then sealed with a crimping tool, ensuring that there were no leaks. The assembled cells were allowed to rest for 24 hours at room temperature to ensure complete wetting of the electrodes and separator before testing.

2.3. Electrochemical measurements

All electrochemical evaluations were performed on the assembled coin-type cells. The electrochemical stability window (ESW) of each electrolyte was determined using linear sweep voltammetry (LSV) at a scan rate of 10 mV/s. This test identifies the operating voltage range within which the electrolyte remains stable without significant decomposition (i.e., hydrogen and oxygen evolution). Galvanostatic charge-discharge cycling was conducted at [Specify C-rate and voltage window, e.g., 0.5 C between 1.0 and 2.4 V] to evaluate key performance metrics, including specific capacity, cycling stability, and capacity retention over extended cycles.

2.4. Characterizations

To further understand the structural integrity, phase transitions, and material degradation mechanism in the AZIB, we used scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. The surface morphology and microstructure of the zinc anode were analyzed using a JEOL-JSM-IT800. SEM imaging was performed at an operating voltage of 10–15 kV to observe changes in the surface topography before and after electrochemical cycling. Corrosion formed on the zinc anode during cycling was also studied to understand the impact on capacity retention and efficiency. To study the crystallinity and phase transitions of the anode before and after cycling, X-ray diffraction (XRD was performed using a Bruker D8 Advance, with Cu Kα radiation (λ = 1.5405

DOI: 10.54254/2755-2721/2025.GL25783

Å). Raman spectroscopy was used to find any potential changes occuring during cycling through vibrational characteristics. A UniRam Raman Spectrometer with a 532 nm laser was used to study the composition of the electrolyte and potentially detect excess water content.

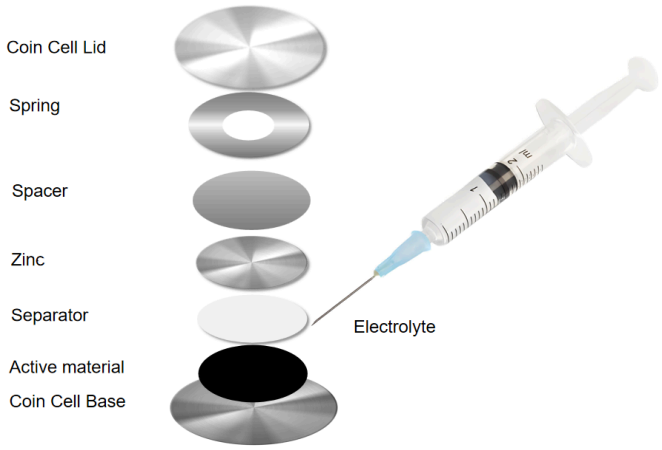


Figure 1. Schematic representation of the coin cell used in the experiments

3. Results

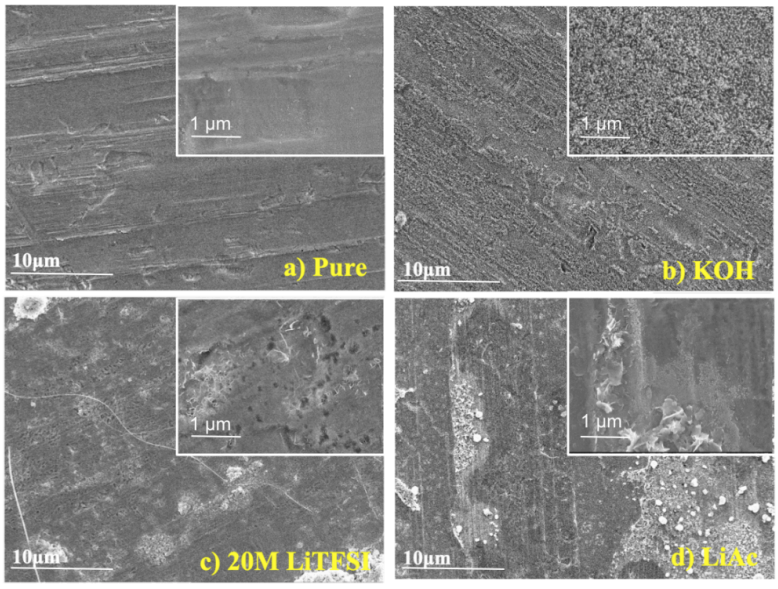


Figure 2. Post-cycling SEM images of Zn anodes from cells using different electrolytes, highlighting the dendrite-free morphology in the LiAc system compared to the corroded surface in the KOH system

3.1. Surface morphology of zinc anodes

SEM imaging of the zinc anodes after prolonged cycling provides direct visual evidence of the electrolyte's impact on interfacial stability. As shown in Figure 2, the anodes cycled in the 20M LiTFSI and the optimized LiAc electrolytes exhibit remarkably smooth, dense, and homogeneous surfaces. This morphology, which closely resembles that of pristine zinc, indicates uniform zinc

DOI: 10.54254/2755-2721/2025.GL25783

deposition and minimal side reactions. In stark contrast, the anode cycled in the KOH-based electrolyte displays a rough, porous surface covered with needle-like dendrites and corrosion byproducts. This detrimental morphology suggests that the alkaline KOH electrolyte promotes parasitic reactions and non-uniform current distribution, leading to rapid degradation. These findings establish the LiAc-based electrolyte as a highly effective system for stabilizing the zinc anode.

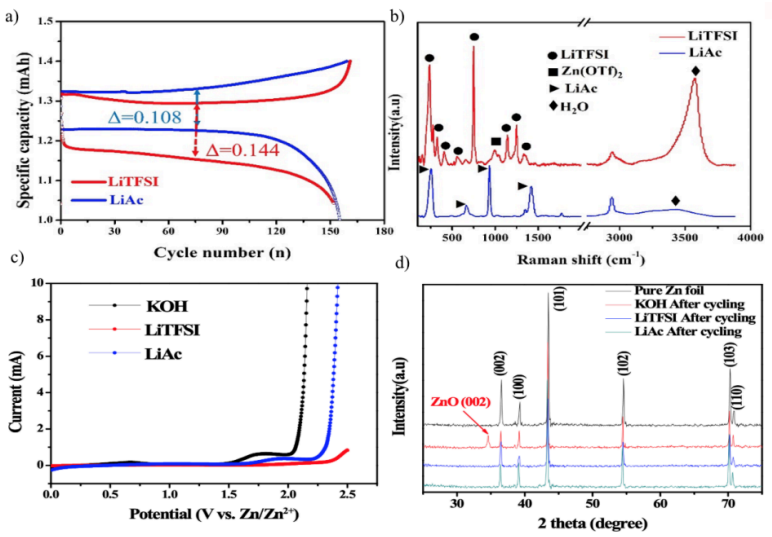


Figure 3. (a) Cycling performance of cells with LiTFSI and LiAc electrolytes. (b) Raman spectra comparing the water content in LiTFSI and LiAc electrolytes. (c) Linear sweep voltammetry showing the electrochemical stability windows of KOH, LiTFSI, and LiAc. (d) XRD patterns of cycled Zn anodes, revealing ZnO formation in the KOH system

In Fig. 3 (a), the data clearly indicated that LiAC outperforms LiTFSI in terms of capacity retention, with a significantly lower capacity loss per cycle. The LiAC-based cells exhibited a capacity loss of only 0.108mAh per cycle, while the LiTFSI-based cell showed a higher loss of 0.144mAh per cycle. Although the differences are seemingly small on a per-cycle basis, it accumulates over time, leading to a noticeable gap in overall capacity retention. This could also indicate that LiAC has more stable electrochemical reactions and less degradation of the zinc anode with less side reactions. In Fig. 3 (b), the Raman spectroscopy analysis of the LiTFSI and LiAC electrolytes, revealing significant differences in their water content and the corresponding impact on electrochemical stability. This data showed that the LiAc electrolyte exhibited a lower intensity in the water-related peaks, when compared to LiTFSI. Lower water content is beneficial because water activity plays a key role in the formation of corrosion products and zinc dendrites during cycling. In Fig. 3 (c), the Linear sweep voltammetry data compares the electrochemical stability windows of LiTFSI, LiAc, and KOH electrolytes. The LSV data shows that both LiTFSI and LiAC exhibited significantly wider electrochemical stability windows compared to KOH, suggesting that the LiTFSI and LiAC systems show a clear suppression of H_2 and O_2 evolution. On the other hand, the data on the KOH-based electrolyte indicated a potential instability under high-voltage cycling conditions. In Fig. 3 (d), the X-ray diffraction (XRD) analysis of the zinc anode cycled in KOH, LiTFSI, and LiAC electrolytes revealed significant differences in the corrosion behaviors of the three systems. The KOH-based electrolyte exhibits clear signs of corrosion, as evidenced by the presence of distinct diffraction peaks corresponding to zinc oxide (ZnO), a byproduct commonly formed in alkaline environments. This would later cause capacity loss, side reactions, and eventual battery degradation.

DOI: 10.54254/2755-2721/2025.GL25783

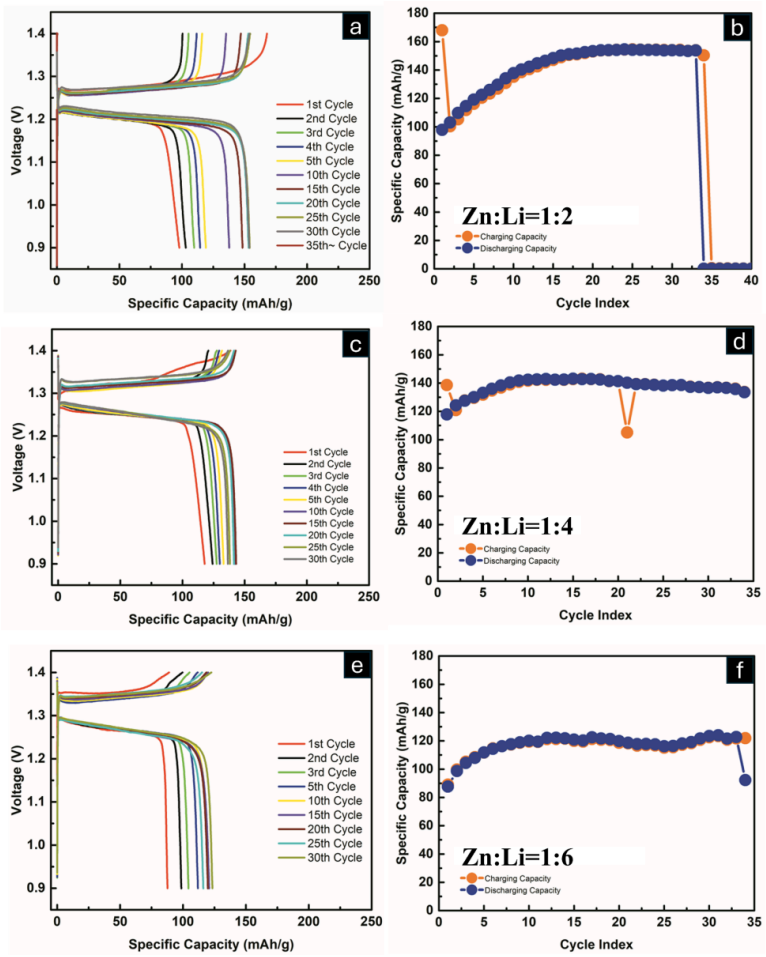


Figure 4. (a - f): Cycling performance of Zn:Li in ratio of 1:2, 1:4, 1:6

3.2. Optimization of zinc acetate to lithium acetate ratio

To maximize performance, the molar ratio of $Zn(Ac)_2$ to LiAc was systematically optimized. Figures 4(a-f) present the cycling performance for Zn:Li ratios of 1:2, 1:4, and 1:6. A clear trend emerges: increasing the lithium concentration raises the operating voltage plateau (Fig. 4a, c, e). However, this benefit comes with trade-offs. The 1:2 ratio cell delivered insufficient capacity, likely due to a limited number of charge carriers. Conversely, while the 1:6 ratio offered a high voltage, its stability was compromised over cycling.

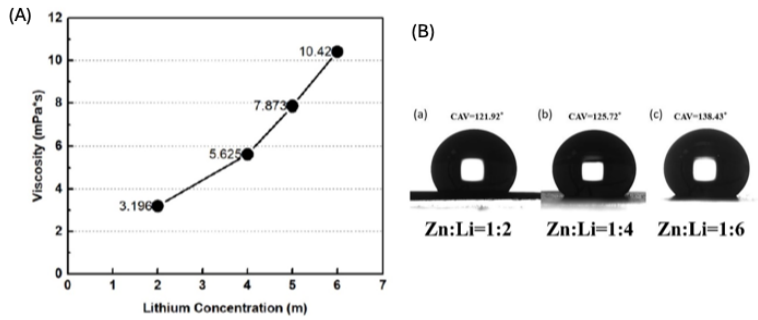


Figure 5. (A) Electrolyte viscosity as a function of Li-ion concentration. (B) Contact angle measurements of electrolytes with different Zn:Li ratios on the zinc anode surface

DOI: 10.54254/2755-2721/2025.GL25783

The interplay between electrolyte composition, viscosity, and wettability, shown in Figure 5, explains these observations. As seen in Fig. 5(a), electrolyte viscosity increases sharply with higher Li-ion concentration. Excessive viscosity can impede ion mobility, increasing internal resistance and harming battery performance. The contact angle measurements (Fig. 5b) indicate how well the electrolyte wets the anode surface, which is crucial for uniform zinc deposition. The 1:4 Zn:Li ratio emerged as the optimal formulation, representing a balance between high ionic concentration for a stable voltage and an acceptable viscosity (η) for efficient ion transport. This ratio ensures good wettability and high ionic conductivity, leading to the most stable and high-performing cell.

4. Discussion and conclusion

Conventional aqueous zinc-ion batteries (AZIBs) face significant hurdles for large-scale energy storage due to high water activity in the electrolyte, which causes dendrite growth, hydrogen evolution, and anode corrosion, ultimately limiting battery lifespan and safety.

To address these issues, this study introduces an innovative, eco-friendly electrolyte using a high-concentration blend of zinc acetate and lithium acetate (LiAc). This "water-in-salt" formulation effectively reduces free, reactive water by 50% (verified by Raman spectroscopy) and enables dendrite-free zinc plating. The optimized electrolyte, with a Zn:Li ratio of 1:4, successfully expands the battery's electrochemical stability window to a high 2.4 V while minimizing side reactions. As a result, the battery demonstrates excellent cycling stability, achieving a stable capacity of 140 mAh/g over 35 cycles.

The superior performance of this acetate-based system is rooted in a fundamental re-engineering of the electrolyte's solvation chemistry. As confirmed by Raman spectroscopy, the high concentration of Zn^{2+} and Li^{+} ions, along with the acetate (Ac^{-}) anions, drastically reduces the quantity of free, bulk-like water molecules. Instead, water is sequestered within the primary solvation sheaths of the cations. This configuration fundamentally limits water's availability to participate in detrimental side reactions. The direct consequence, observed in our material characterization, is the complete suppression of ZnO corrosion byproducts (confirmed by XRD) and the promotion of a smooth, dendrite-free zinc deposition morphology (visualized by SEM). Furthermore, we propose that the acetate anion participates in the formation of a robust, organic-inorganic solid-electrolyte interphase (SEI) on the zinc anode. This interfacial layer acts as a physical shield, preventing direct contact between the anode and reactive species while ensuring uniform ionic flux, thereby contributing to the exceptional cycling stability. The high operating voltage is a direct result of the successful dual-ion mechanism, which couples the Zn^{2+}/Zn redox reaction at the anode with the Li^{+} intercalation/de-intercalation at the LFP cathode.

The significance of these findings extends beyond the immediate performance metrics. This work presents a paradigm shift away from expensive and environmentally problematic electrolytes. Fluorinated salts like LiTFSI, while effective, are costly and can generate toxic hydrofluoric acid upon decomposition, posing safety and disposal challenges. Similarly, alkaline electrolytes like KOH are highly corrosive and promote irreversible degradation of the zinc anode. In stark contrast, our zinc/lithium acetate system is formulated from inexpensive, readily available, and non-toxic materials, presenting a truly sustainable and scalable pathway for energy storage. The achievement of a 2.4 V electrochemical stability window in a safe, low-cost aqueous medium is a critical step, bridging the performance gap between conventional aqueous batteries and higher-voltage non-aqueous systems without compromising the intrinsic safety advantages of a water-based electrolyte.

Looking forward, while this study establishes a strong proof-of-concept, several avenues exist for further advancement. The immediate next step is to prolong cycling beyond 1000 cycles to

DOI: 10.54254/2755-2721/2025.GL25783

rigorously validate the long-term stability and quantify the Coulombic efficiency with high precision. To further probe the underlying mechanisms, advanced operando characterization techniques, such as in-situ SEM or cryo-EM, could be employed to visualize the evolution of the SEI and the zinc deposition process in real time. Future research should also explore the rational design of functional electrolyte additives—such as leveling agents or film-forming precursors—to further refine the SEI's properties and enhance plating uniformity. Finally, scaling this technology from coin cells to practical pouch cell configurations is essential. This will allow for the evaluation of performance under realistic conditions and for addressing engineering challenges such as gas management and thermal stability, ultimately paving the way for the commercial viability of these safe, sustainable, and high-performance aqueous dual-ion batteries.

References

[1] Ji, B.; Yao, W.; Tang, Y. High-Performance Rechargeable Zinc-Based Dual-Ion Batteries. Sustain. Energy Fuels 2020, 4 (1), 101–107. https: //doi.org/10.1039/C9SE00744J.

[2] Yang, Q.; Li, Q.; Liu, Z.; Wang, D.; Guo, Y.; Li, X.; Tang, Y.; Li, H.; Dong, B.; Zhi, C. Dendrites in Zn-Based Batteries. Adv. Mater. 2020, 32 (48), 2001854. https: //doi.org/10.1002/adma.202001854.

[3] Bayaguud, A.; Fu, Y.; Zhu, C. Interfacial Parasitic Reactions of Zinc Anodes in Zinc Ion Batteries: Underestimated Corrosion and Hydrogen Evolution Reactions and Their Suppression Strategies. J. Energy Chem. 2022, 64, 246–262. https: //doi.org/10.1016/j.jechem.2021.04.016.

[4] Xie, D.; Sang, Y.; Wang, D.-H.; Diao, W.-Y.; Tao, F.-Y.; Liu, C.; Wang, J.-W.; Sun, H.-Z.; Zhang, J.-P.; Wu, X.-L. ZnF2-Riched Inorganic/Organic Hybrid SEI: In Situ-Chemical Construction and Performance-Improving Mechanism for Aqueous Zinc-Ion Batteries. Angew. Chem. Int. Ed. 2023, 62 (7), e202216934. https: //doi.org/10.1002/anie.202216934.

[5] Bai, S.; Huang, Z.; Liang, G.; Yang, R.; Liu, D.; Wen, W.; Jin, X.; Zhi, C.; Wang, X. Electrolyte Additives for Stable Zn Anodes. Adv. Sci. 2024, 11 (4), 2304549. https: //doi.org/10.1002/advs.202304549.

[6] Salt particle suspension electrolyte with trace-water for improving ionic concentrations at interfaces in zinc-based dual-ion batteries - Journal of Materials Chemistry A (RSC Publishing) DOI: 10.1039/D5TA00256G. https: //pubs.rsc.org/en/content/articlehtml/2025/ta/d5ta00256g (accessed 2025-06-21).

[7] Multi-electron bipolar-type organic molecules for high-capacity dual-ion zinc batteries - Journal of Materials Chemistry A (RSC Publishing) DOI: 10.1039/D4TA00476K. https: //pubs.rsc.org/en/content/articlehtml/2024/ta/d4ta00476k (accessed 2025-06-21).

[8] Cao, C.; Kingan, A.; Hill, R. C.; Kuang, J.; Wang, L.; Zhang, C.; Carbone, M. R.; van Dam, H.; Yoo, S.; Yan, S.; Takeuchi, E. S.; Takeuchi, K. J.; Wu, X.; Abeykoon, A. M.; Marschilok, A. C.; Lu, D. Resolving the Solvation Structure and Transport Properties of Aqueous Zinc Electrolytes from Salt-in-Water to Water-in-Salt Using Neural Network Potential. PRX Energy 2025, 4 (2), 023004. https: //doi.org/10.1103/PRXEnergy.4.023004.

[9] Li, G.; Sun, L.; Zhang, S.; Zhang, C.; Jin, H.; Davey, K.; Liang, G.; Liu, S.; Mao, J.; Guo, Z. Developing Cathode Materials for Aqueous Zinc Ion Batteries: Challenges and Practical Prospects. Adv. Funct. Mater. 2024, 34 (5), 2301291. https: //doi.org/10.1002/adfm.202301291.

[10] Bao, Q.; Tang, P.; Gong, Z.; Wang, P.; Shi, F.; Zhu, M. High Concentrations of Sodium Dodecylbenzene Sulfonate Electrolyte Additives Improve the Performance of Aqueous Zinc Ion Batteries. Solid State Ion. 2025, 422, 116817. https: //doi.org/10.1016/j.ssi.2025.116817.

[11] Sun, C.; Miao, R.; Li, J.; Sun, Y.; Chen, Y.; Pan, J.; Tang, Y.; Wan, P. Green Environmentally Friendly “Zn(CH3SO3)2” Electrolyte for Aqueous Zinc-Ion Batteries. ACS Appl. Mater. Interfaces 2023, 15 (16), 20089–20099. https: //doi.org/10.1021/acsami.3c00521.

[12] Yang, J.; Yin, B.; Sun, Y.; Pan, H.; Sun, W.; Jia, B.; Zhang, S.; Ma, T. Zinc Anode for Mild Aqueous Zinc-Ion Batteries: Challenges, Strategies, and Perspectives. Nano-Micro Lett. 2022, 14 (1), 42. https: //doi.org/10.1007/s40820-021-00782-5.