Boosting Zn-ion Battery Performance with Electrolyte Innovation

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Abstract

Aqueous Zn-ion batteries are a promising candidate for safe, low-cost, and sustainable energy storage. In this work, we investigate $ZnSO_4$ electrolytes with and without targeted additives for Zn‖V_2O_3 cells. A baseline $ZnSO_4$ system provides stable performance but shows moderate impedance growth during extended cycling. The addition of $MnSO_4$ improves interfacial stability by supplying Mn^{2+} to buffer cathode dissolution and reduce polarization. Incorporating Na_2SO_4 alongside $MnSO_4$ further enhances ionic transport and stabilizes Zn diffusion, resulting in a hybrid electrolyte that significantly lowers charge-transfer resistance and suppresses interfacial degradation. Electrochemical characterization, including cyclic voltammetry, galvanostatic cycling, and impedance spectroscopy, reveals sharper and more reversible redox peaks, reduced impedance evolution, and improved rate performance. The optimized $ZnSO_4$ + Na_2SO_4 + $MnSO_4$ electrolyte achieves the highest capacity retention and cycling stability, demonstrating the effectiveness of simple additive strategies to advance aqueous Zn-ion battery technologies.

Aqueous zinc-ion batteries (ZIBs) have emerged as one of the most promising next-generation energy storage systems owing to their intrinsic safety, low cost, and use of earth-abundant materials. However, conventional $ZnSO_4$ electrolytes often face challenges such as parasitic side reactions, hydrogen evolution, electrode surface corrosion, and progressive impedance growth, which collectively limit their long-term performance. In this study, we systematically investigate $ZnSO_4$ electrolytes with and without targeted additives in Zn‖V_2O_3 cells to address these limitations. The baseline $ZnSO_4$ electrolyte provides reasonable cycling stability, but gradual resistance buildup and polarization are observed during extended operation. Introducing $MnSO_4$ as an additive markedly improves interfacial stability by continuously supplying Mn^{2+} ions that act as a buffer to mitigate cathode dissolution and strengthen the electrode–electrolyte interface. To further enhance ion transport and electrolyte balance, Na_2SO_4 is incorporated alongside $MnSO_4$, creating a synergistic hybrid electrolyte. This combination increases ionic conductivity, promotes smoother Zn^{2+} diffusion pathways, and effectively suppresses interfacial degradation. Electrochemical analyses—including cyclic voltammetry, galvanostatic cycling, rate performance testing, and electrochemical impedance spectroscopy—demonstrate sharper and more reversible redox peaks, reduced charge-transfer resistance, slower impedance evolution, and improved rate tolerance in the hybrid system. The optimized $ZnSO_4$ + Na_2SO_4 + $MnSO_4$ electrolyte ultimately delivers superior cycling stability, higher capacity retention, and enhanced reversibility compared to the baseline electrolyte, highlighting the effectiveness of simple additive engineering as a practical route to advancing aqueous Zn-ion battery technologies

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1 Introduction

As part of this project, my contribution focused on defining the motivation, framing the problem, and setting the objectives for electrolyte design in aqueous Zn-ion batteries. I highlighted the real-world significance of this work, emphasizing that aqueous Zn-ion systems are attractive for large-scale energy storage due to their high safety, low cost, and based on abundant materials. However, the practical use of $ZnSO_4$ electrolytes is limited by interfacial instability, parasitic side reactions, hydrogen evolution, electrode corrosion, and impedance growth.

In developing the study framework, I established key assumptions, $ZnSO_4$ was chosen as the baseline electrolyte due to its solubility and compatibility with Zn anodes, and V_2O_3 was selected as a representative cathode material, while focusing on the electrolyte as the main variable. I also acknowledged limitations such as the restricted temperature range for testing, the synthesis procedures for the electrolyte and cathode, and the need for long-term validation in practical cells.

I defined the project objectives to explore electrolyte modifications that could extend cycle life, enhance capacity, and improve interfacial stability. This included comparing baseline $ZnSO_4$ against additive and hybrid electrolyte systems to determine the effects of $MnSO_4$ and Na_2SO_4. The central problem addressed was that $ZnSO_4$ alone cannot prevent interfacial degradation or capacity fading, necessitating additive and hybrid strategies for practical performance.

Finally, I proposed and validated a hybrid $ZnSO_4$ electrolyte system modified with $MnSO_4$ and Na_2SO_4. Electrochemical testing demonstrated that this hybrid-additive system reduces impedance, stabilizes Zn^{2+} transport, and significantly improves long-term cycling stability in Zn‖V_2O_3 cells, offering a practical pathway to enhance aqueous Zn-ion battery performance.

2 System Overview



Fig.1 Battery test machine



Fig.2 Coin battery

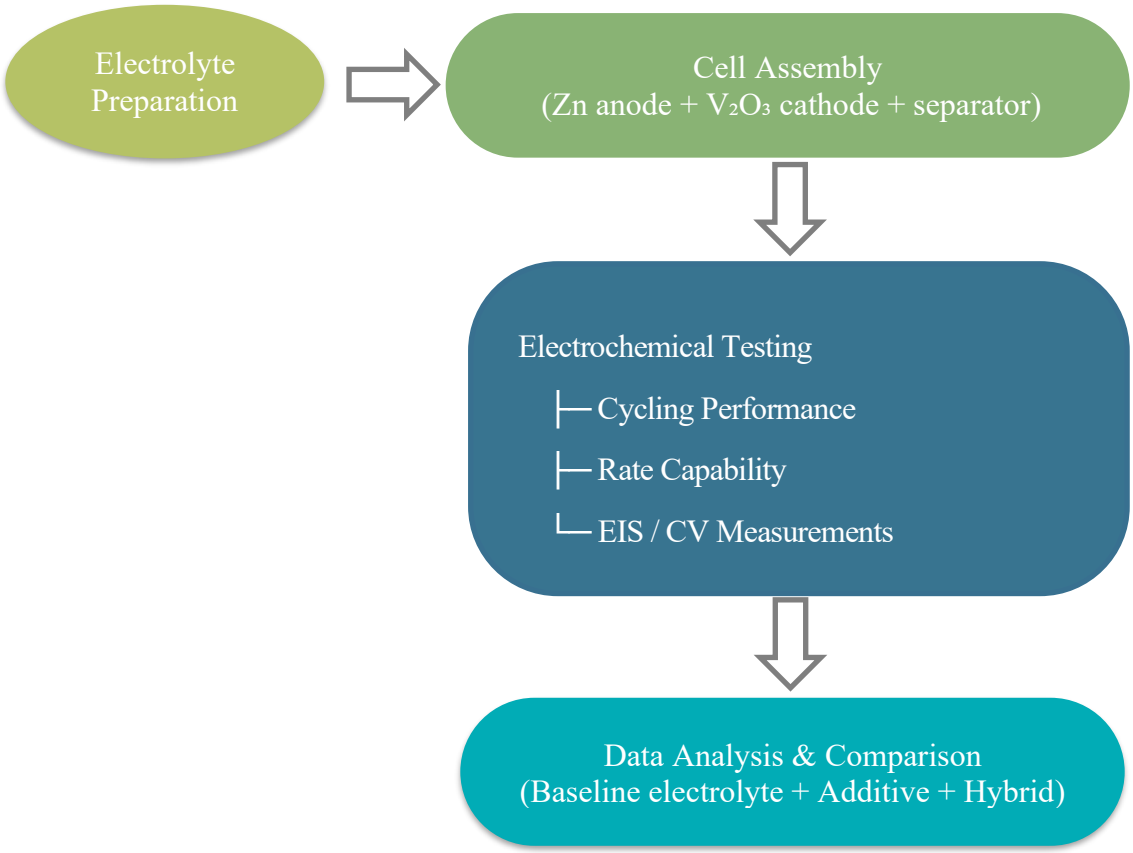


Fig.3 Flow chart of the battery system

3 Methodology

3.1 Resources and Tools

The study was conducted using standard laboratory equipment and carefully selected materials to ensure reliability and reproducibility. Electrochemical testing was performed on a Battery test machin, which enabled cyclic voltammetry, galvanostatic charge–discharge, and impedance spectroscopy measurements (EIS). A CR2032 battery coin cell type, crimping machine, separators, spacer, spring were also utilized during cell assembly. For electrolyte preparation we utilized , magnetic stirrer, analytical balance for the making of electrolyte. The active materials consisted of zinc foil as the anode, V_2O_3 as the cathode, and $ZnSO_4$ as the baseline electrolyte. Additives including $MnSO_4$ and Na_2SO_4 were introduced to form modified and hybrid electrolyte systems. The Neware Lab software was employed for data recording and analysis.

3.2 Evaluation Procedure

The evaluation process began with the preparation of the electrolyte systems: a baseline $ZnSO_4$ electrolyte with different concentration, an additive electrolyte with $MnSO_4$, a hybrid system of $MgSO_4$ and lastly a hybrid system containing both $MnSO_4$ and Na_2SO_4. Each electrolyte was prepared by dissolving the salts in distilled water with magnetic stirrer for mixing under continuous stirring until fully homogeneous. CR2032 coin cells were then assembled with zinc foil as the anode, V_2O_3 as the cathode, and the prepared electrolytes as the ionic medium. Electrochemical characterization was performed through cyclic voltammetry to study the reversibility of Zn-ion redox reactions, galvanostatic cycling to evaluate capacity retention and cycle number that reach around 1000 cycle to define the long-term stability of each battery cell, and electrochemical impedance spectroscopy to assess interfacial resistance and ion transport properties. Results from these electrolyte systems were compared systematically to highlight the influence of $MnSO_4$ and Na_2SO_4 on performance.

3.3 Others & Safety

In addition to the main procedures, several supporting considerations were integrated into the methodology. All experiments were carried out at room temperature, except one experiment which we used battery test amchine unfer hightempreture to test battery behavior such as capacity retention, reversibility of Zn-ion and interfacial resistance. Safety precautions were strictly followed during electrolyte preparation and cell assembly to ensure proper handling of chemicals and to avoid contamination. To confirm the consistency of results, multiple cells were fabricated and tested under identical conditions, providing reproducibility and minimizing the effect of experimental variation.



Fig.4 battery assembly

4 Results Discussion

The baseline $ZnSO_4$ electrolyte demonstrated stable but limited performance, with moderate impedance growth and gradual capacity fading over repeated cycles. Cyclic voltammetry curves revealed redox peaks that were relatively broad, indicating less reversible Zn^{2+} intercalation into the V_2O_3 cathode. Galvanostatic cycling confirmed this behavior, as the cell retained only moderate capacity after extended cycling, establishing a clear baseline for comparison. Electrochemical impedance spectroscopy further showed higher charge-transfer resistance, confirming that interfacial processes were a bottleneck in the unmodified system.

The addition of $MnSO_4$ to the $ZnSO_4$ electrolyte improved both stability and reversibility. The Mn^{2+} ions acted as a stabilizing agent by buffering cathode dissolution and reducing polarization, which was reflected in sharper redox peaks in the cyclic voltammetry profiles. Impedance spectra also displayed reduced resistance compared to the baseline, while cycling tests demonstrated improved capacity retention and rate capability. However, although performance was enhanced, the $MnSO_4$ additive alone did not fully eliminate interfacial degradation, suggesting further optimization was required.

The hybrid electrolyte, containing both $MnSO_4$ and Na_2SO_4, exhibited the most promising results. Na_2SO_4 facilitated smoother Zn^{2+} diffusion and enhanced ionic conductivity, working synergistically with $MnSO_4$ to stabilize the cathode–electrolyte interface. Quantitatively, the hybrid system delivered the highest specific capacity and the lowest impedance growth over long-term cycling. The redox peaks in cyclic voltammetry were sharp and highly reversible, while charge–discharge tests showed excellent capacity retention even under higher current densities. Compared to the baseline system, the hybrid electrolyte reduced charge-transfer resistance significantly, suppressed side reactions, and demonstrated improved cycling durability.

From a system-level perspective, the main bottlenecks identified were related to electrolyte-induced side reactions, hydrogen evolution, and gradual electrode corrosion. While $MnSO_4$ mitigated some of these effects, the synergistic introduction of Na_2SO_4 addressed ion transport limitations and further stabilized the system. Remaining challenges include optimizing additive concentrations, testing at elevated temperatures, and validating performance in larger cell formats. Future improvements could also focus on integrating additional hybrid salts or pH buffers to further suppress hydrogen evolution and extend cycle life.

Overall, the evaluation confirms that while $ZnSO_4$ alone provides a functional baseline, significant performance gains can be achieved through additive and hybrid modifications. The $ZnSO_4$ + Na_2SO_4 + $MnSO_4$ electrolyte emerged as the most effective strategy, delivering reduced impedance, enhanced cycling stability, and higher overall capacity, demonstrating its potential for advancing aqueous Zn-ion battery technologies.

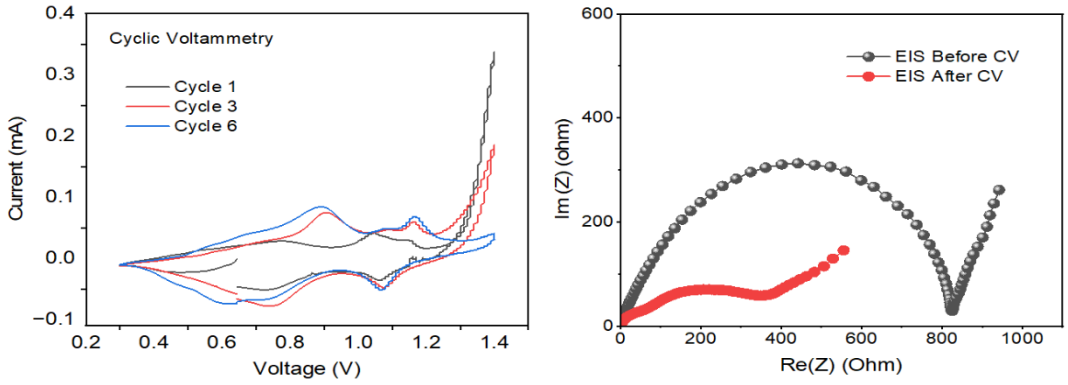


Fig.5(a) Cyclic voltammetry shows defined redox peaks for V_2O_3
Fig.5(b) The Electrochemical Impedance **(EIS)** for **Zn|V_2O_3** demonstrates the variation in resistance observed before and after

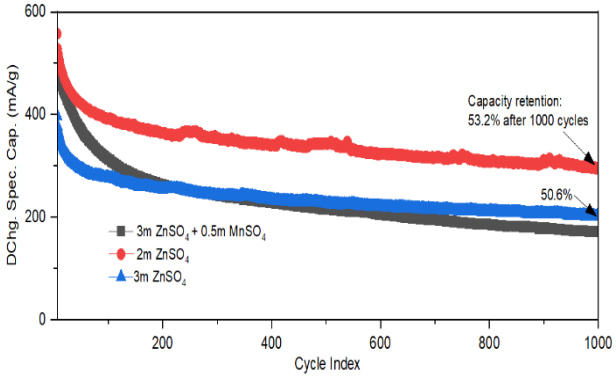


Fig.6 Cycling performance comparison of electrolytes with and without

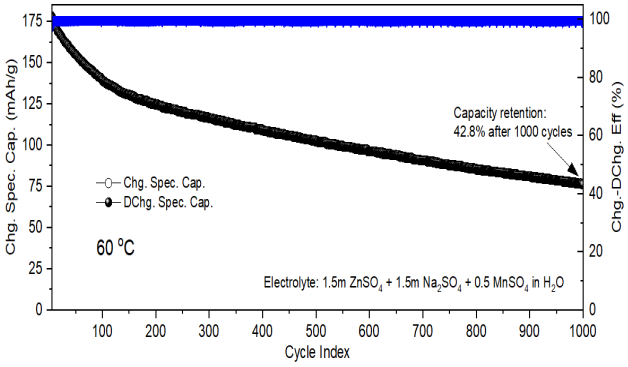


Fig.7 Cycling stability and capacity performance of the battery under high temperature

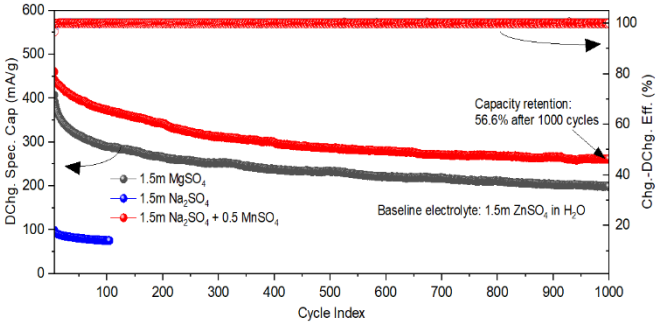


Fig.8 Enhanced capacity performance of hybrid electrolytes through additive incorporation

5 Reflections on Challenges

During this project, several technical and process-related challenges were encountered. On the experimental side, preparing and handling different electrolyte concentrations required precision to avoid inconsistencies in results. Small variations in solubility limits, or inconsistent electrolyte distribution in the separator of the coin cell occasionally led to differences result which affect reproducibility of the measurements. Furthermore, ensuring stable cycling of the Zn‖V_2O_3 cells was sometimes hindered by electrode degradation, which limited long-term testing. unexpected findings also shaped the project outcome. For instance, while $MnSO_4$ was initially expected to provide only moderate improvements, it demonstrated a stronger stabilizing effect than anticipated. Similarly, the hybrid addition of Na_2SO_4 revealed a synergistic benefit, greatly enhancing ion transport and stability beyond what was predicted from literature alone.

6 Conclusion and Future Work

This project demonstrated the effectiveness of electrolyte optimization in enhancing the performance of aqueous Zn-ion batteries. By systematically comparing the main electrolyte $ZnSO_4$ with additive and hybrid formulations, we found that the incorporation of $MnSO_4$ significantly stabilized the cathode interface, while the combination of $MnSO_4$ and Na_2SO_4 further improved Zn2 transport and reduced charge-transfer resistance. Electrochemical analyses—including cyclic voltammetry, impedance spectroscopy, and galvanostatic cycling, revealed sharper and more reversible redox peaks. Overall, the $ZnSO_4$ + Na_2SO_4 + $MnSO_4$ formulation is the most promising, delivering the highest capacity retention and durability.

Despite these promising results, the study also faced limitations. The experiments were conducted under restricted temperature and cycling conditions, which do not fully replicate real-world applications such as grid storage or high-power scenarios. The cathode material (V_2O_3) stability and scalability remain areas that require long-term validation. Additionally, electrolyte optimization was limited to a small amount of additives, leaving space to explore other salts components that may further suppress side reactions. Future work will focus on expanding testing conditions to higher temperatures, longer cycling periods, and practical scale cells. Furthermore, we aim to test additional additives or gel/polymer-based modifications to extend stability. These steps will help refine the electrolyte system and move closer to practical implementation of Zn-ion batteries in large-scale energy storage applications.

7 Reference

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