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Current Opinion in
Electrochemistry

Review Article

Cathode chemistry innovations in anode-free aqueous zinc metal batteries

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The emergence of anode-free aqueous zinc metal batteries (AF-ZMBs) represents a transformative approach that combines intrinsic safety and low cost with maximized energy density. While significant research has focused on electrolyte optimization and interface engineering to enhance zinc reversibility, comprehensive analysis of cathode chemistry specifically tailored for anode-free configurations remains limited. This review systematically examines recent advancements in innovative cathode design strategies, spanning intercalation, hybrid-ion, dual-ion, and conversion mechanisms, and analyzes their respective capabilities in maintaining zinc inventory and structural stability. By critically assessing the current landscape and future potential of these cathode systems, this work aims to establish fundamental design principles for developing practical anode-free zinc battery technologies.

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Current Opinion in Electrochemistry 2026, **55:**101805

This review comes from a themed issue on **Innovative Methods in Electrochemistry (2026)**

Edited by **Antonio Doménech-Carbó**

For a complete overview see the Issue and the Editorial

Available online 13 December 2025

https://doi.org/10.1016/j.coelec.2025.101805

Introduction

Rechargeable aqueous zinc metal batteries (ZMBs) are proposed as a sustainable and cost-effective alternative to lithium-ion systems, valued for zinc's natural abundance, and operational safety, and lower cost associated with the use of aqueous electrolytes [1,2]. However, a critical examination of the material landscape reveals a more nuanced picture [3]. While zinc metal itself is indeed less expensive benefiting from a resilient, mature supply chain and recycling infrastructure, its fundamental electrochemistry presents a unique challenge: a much higher mass is required to store the same amount of charge compared to lithium. This implies that a widespread adoption of conventional zinc batteries, which employ a significant excess of zinc in the anode, could paradoxically drive increased demand and pressure on zinc resources, undermining its cost advantage. Furthermore, state-of-the-art $Zn-MnO_2$ batteries deliver only modest specific energy ($\sim$189 Wh kg^{-1}), constrained by aqueous electrolytes' limited voltage window and the inefficient utilization of the massive zinc anode [4,5]. In a standard configuration, the thick zinc foil acts as a passive reservoir, contributing significant dead mass and volume without full electrochemical utilization. To fully capitalize on zinc's economics and supply-chain advantages while breaking through this energy density ceiling, a fundamental redesign of the cell configuration is essential.

This necessity drives the emerging focus on anode-free ZMB (AF-ZMB) electrochemistry, which represent a paradigm shift in cell design [6]. By eliminating the initial zinc anode and plating zinc directly onto a current collector from Zn^{2+} ions stored in the cathode, AF-ZMBs represent the ultimate form of maximizing energy density and minimizing material use. This configuration directly addresses the mass-efficiency dilemma by ensuring that every gram of zinc in the system is actively involved in energy storage. However, realizing this promise hinges on solving the core issue of zinc reversibility [7]. The successful operation of an anode-free battery demands a Coulombic Efficiency

(CE) of zinc plating and stripping on inert substrates as current collectors that approaches 99.9—100 %, a formidable challenge given the parasitic reactions like hydrogen evolution and corrosion in aqueous environments [8—10]. Indeed, contemporary research efforts are strategically focused on electrolyte innovation and interfacial engineering to address the fundamental challenges associated with zinc metal anodes [11—13].

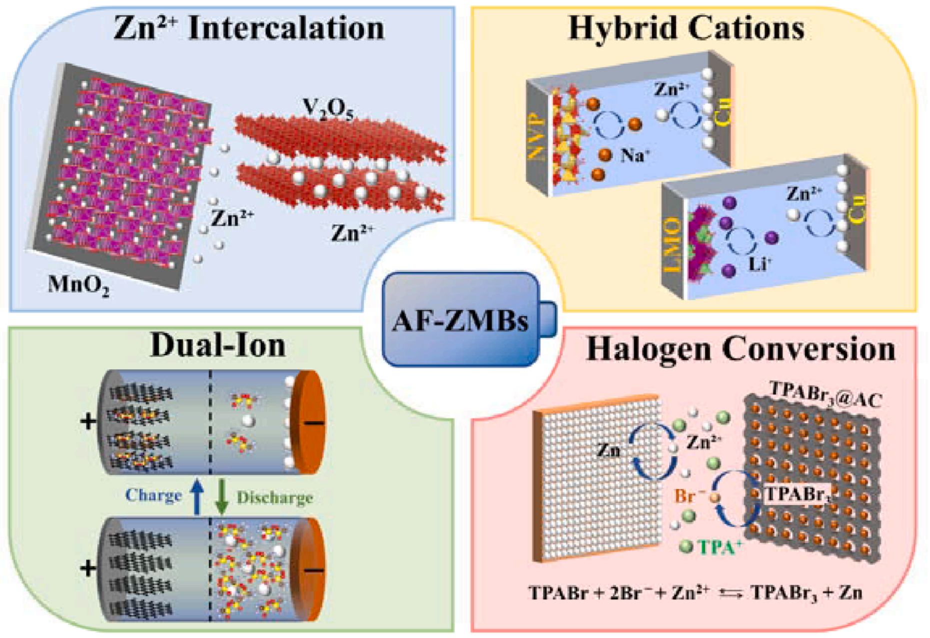
The operational paradigm of AF-ZMBs fundamentally diverges from conventional ZMBs by requiring the cathode to serve a dual function as both the exclusive zinc source and active host material, thereby eliminating the conventional zinc metal anode. This paradigm shift establishes three stringent design requirements that go beyond those for conventional ZMB cathodes: (1) sufficient intrinsic zinc content, typically requiring prezincated structures, to supply the entire cell's zinc inventory; (2) exceptional structural resilience to withstand repeated, deep extraction of Zn^{2+} ions without irreversible phase changes or collapse; and (3) highly reversible redox chemistry to minimize irreversible zinc loss at the cathode, a factor that directly compounds with inefficiencies at the anode. Consequently, the overall efficiency and longevity of an AF-ZMB are not merely dictated by the reversibility of zinc plating/stripping at the anode. They are fundamentally constrained by the cathode's structural integrity, kinetic properties, and thermodynamic stability. The choice of cathode chemistry is therefore the primary determinant in managing the twin challenges of zinc inventory loss and host lattice degradation, making its rational design the cornerstone of viable anode-free systems. This review systematically examines four primary cathode strategies for AF-ZMBs: conventional Zn^{2+} intercalation cathodes, hybrid-ion systems utilizing alternative charge carriers (e.g., Li^+, Na^+), dual-ion configurations based on anion shuttling mechanisms, and conversion-type chemistries exemplified by halogen-based systems, as illustrated in Figure 1, together forming the foundation for viable AF-ZMB.

Conventional Zn^{2+} intercalation

Conventional Zn^{2+} intercalation cathodes undergo a critical transformation in anode-free configurations. This demands exceptional structural stability and electrochemical reversibility, requiring robust host frameworks withstanding repeated Zn^{2+} extraction/reinsertion and contain pre-intercalated Zn^{2+} as the initial zinc inventory. The operational mechanism involves Zn^{2+} extraction from the cathode during charging, accompanied by host metal oxidation (e.g., V^{4+}/V^{5+}), with zinc depositing on the current collector; discharge reverses this process through zinc stripping and Zn^{2+} reinsertion.

Vanadium-based oxides, such as V_2O_5 and VO_2, are attractive for their high theoretical capacities and multielectron redox chemistry. Nevertheless, their practical implementation in AF-ZMBs is severely challenged by

Figure 1



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Cathode chemistries for anode-free zinc metal batteries (AF-ZMBs).

the strong electrostatic interaction of divalent Zn^{2+} ions and the severe dissolution, respectively leading to sluggish ion diffusion kinetics and substantial structural degradation. For AF-ZMBs, the development of pre-zincated compositions (e.g., $Zn_xV_2O_5$) with optimized interfacial chemistry is crucial to creating a robust cathode acting as a reliable zinc reservoir providing Zn^{2+} for high-efficiency plating and stripping at the anode current collector. Improving the interfacial stability is an effective way as demonstrated with the anode-free full cell of $Cu@Al_2((OH)_{0.46}F_{0.54})_6{\cdot}H_2O$ (AOF)||$Zn_{0.5}VO_2$, assembled using pre-zincated VO_2 as the cathode, exhibiting a record−high cycle life (2000 cycles at 1 A g^{-1}) and average CE (99.95 %), as shown in Figure 2a−b [14].

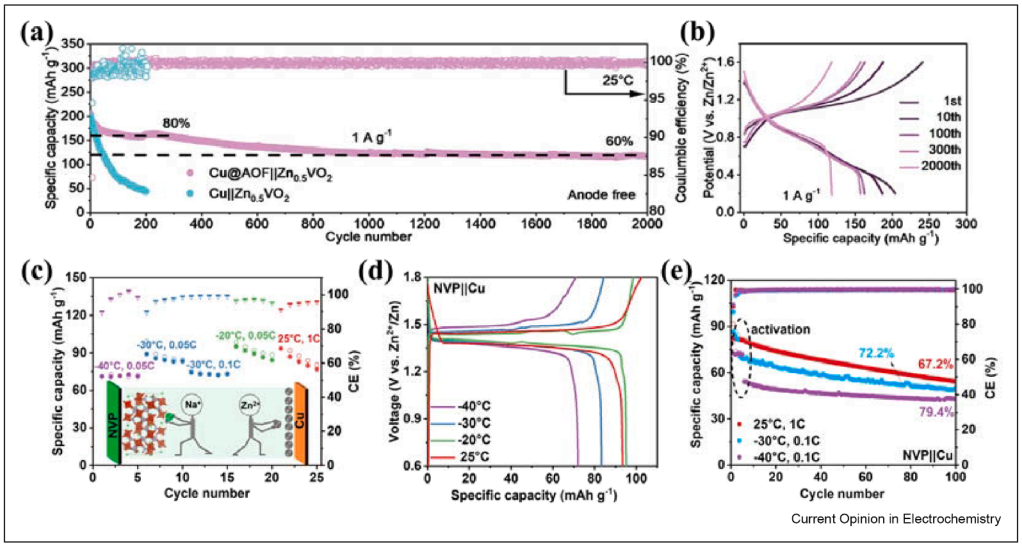
Manganese-based oxides, particularly MnO_2, are promising cathodes for zinc batteries due to their high voltage and low cost. However, their application in anode-free configurations is hindered by structural instability from Jahn-Teller distortion and manganese dissolution, severely compromising cycling efficiency [15]. Electrolyte engineering using concentrated electrolytes and Mn^{2+} additives, alongside material strategies including cationic doping, have shown improved stability. In 2021, an anode-free full cell consisting of a pre-zincated β-MnO_2 cathode, a C/Cu anode and the 3 M $Zn(CF_3SO_3)_2$ electrolyte with 0.1 M $Mn(CF_3SO_3)_2$ additive was demonstrated, yet achieving only 80 cycles [16]. To circumvent the complex pre-zincation process, a subsequent study employed the $ZnMn_2O_4$ cathode. The Cu||$ZnMn_2O_4$ cell exhibited significantly improved cycling stability, retaining 80 % capacity after 275 cycles at 0.5 mA cm^{-2} [17].

While conventional Zn^{2+} intercalation cathodes offer a straightforward route to AF-ZMBs, their practical realization demands coordinated advances in both cathode engineering and electrolyte design. Ongoing efforts to stabilize vanadium oxides through structural pillaring and manganese oxides against dissolution require complementary electrolyte optimization. Specifically, concentrated electrolytes with tailored anions (e.g., $SO_4{}^{2-}$, Cl^-, OTF^-) serve crucial functions in modulating Zn^{2+} solvation structures, suppressing cathode dissolution, and guiding uniform zinc deposition. This integrated strategy, combining robust cathode architectures with advanced electrolyte formulations, proves essential for developing high-performance AF-ZMBs where cathodes must simultaneously serve as stable host structures and reliable zinc reservoirs.

Dual cations and intercalation cathodes

A distinct strategy to circumvent the challenges associated with Zn^{2+} intercalation involves the use of non-Zn ion intercalation cathodes. This innovative approach decouples the redox chemistry at the cathode from the zinc reaction at the anode. Instead of hosting Zn^{2+}, these cathodes are designed to reversibly (de)intercalate a different, typically more mobile monovalent cation such as H^+, Li^+, or Na^+. The charge-compensating reaction for this process occurs at the anode, where Zn^{2+} from the electrolyte is simultaneously plated or stripped. The overall cell's charge

Figure 2



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(a) Cycling performance of Cu||$Zn_{0.5}VO_2$ full cells using bare Cu and Cu@AOF ($Al_2((OH)_{0.46}F_{0.54})_6{\cdot}H_2O$, AOF) at a current density of 1 A g^{-1}. (b) Charge/discharge voltage curves of Cu||$Zn_{0.5}VO_2$ full cells using Cu@AOF after different cycles. Reproduced from Ref. [14] with permission copyright 2023 John Wiley and Sons. (c) Specific capacity of Cu||NVP ($Na_3V_2(PO_4)_3$, NVP) batteries at the temperature range of 40 °C−25 °C. (d) Charge−discharge curves of Cu||NVP batteries at the temperature range of 40 °C−25 °C. (e) Cycling performance of Cu||NVP batteries at the temperature range of 40 °C−25 °C. Reproduced from Ref. [18] with permission copyright 2025 Elsevier.

balance is maintained by the shuttling of these different ions through the electrolyte, creating a unique mixed ion working mechanism [19].

The electrochemical mechanism is best illustrated by specific examples. In a system employing a spinel $LiMn_2O_4$ (LMO) cathode, the charging process involves the de-intercalation of Li^+ from the LMO framework, while Zn^{2+} ions from the electrolyte are reduced and deposited as metallic Zn(0) onto the anode current collector. While its energy density is lower than in non-aqueous Li-ion cells, LMO's stable spinel framework enables exceptionally fast Li^+ diffusion and high cycling stability. Thus, this configuration strategically trades maximum specific energy for superior rate capability and longevity in a safe aqueous AF-ZMB. Upon discharge, the metallic zinc is oxidized (stripped), releasing Zn^{2+} back into the electrolyte, while Li^+ ions re-intercalate into the cathode. Benefiting from the ZnF_2 additive in the electrolyte, an anode-free cell with initial configuration stainless steel||LMO was verified, exhibiting initial charge/discharge capacities of 96/78 mAh g^{-1}, thus providing a high initial CE of 81.25 % [20]. A similar principle applies to NASICON-type $Na_3V_2(PO_4)_3$ (NVP) (Figure 2c–e), where Na^+ acts as the co-charge-carrying species for the cathode, coupled with Zn plating/stripping at the anode. Specifically, the Cu||NVP batteries achieved high discharge voltage of 1.4V, along with remarkable low-temperature performance at −40 °C [18]. Nevertheless, NVP cathodes in aqueous zinc batteries continue to face persistent degradation challenges, including vanadium dissolution, unstable cathode-electrolyte interface formation, and structural degradation from repeated Zn^{2+} insertion/extraction, resulting in progressive capacity loss.

The hybrid ion strategy employs monovalent ions (Li^+, Na^+) instead of Zn^{2+} to decouple cathode and anode reactions, enabling faster diffusion kinetics and enhanced structural stability in established cathode frameworks like LMO and NVP. Although dual-salt electrolytes (e.g., $Zn(OTF)_2$ + LiOTF or NaOTF) facilitate this configuration, they create complete reliance on the electrolyte as the exclusive zinc source. This demands exceptionally high anode Coulombic efficiency to prevent irreversible depletion of the finite zinc inventory—a fundamental trade-off reminiscent of lead-acid systems [21,22]. Consequently, the implementation of highly concentrated electrolytes presents a viable strategy for preserving adequate zinc inventory while optimizing the electrolyte-to-capacity ratio.

Dual-ion batteries and anion storage cathodes

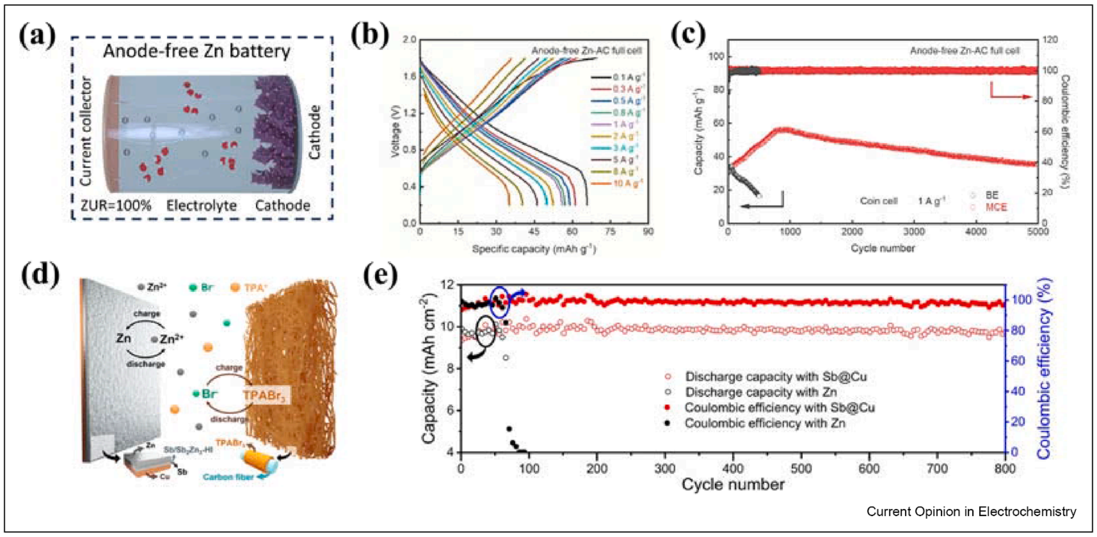
Dual-ion batteries represent a distinct energy storage mechanism based on reversible anion storage in cathodes, contrasting with conventional cation-only-based systems. In this design, energy storage occurs through simultaneous reactions at both electrodes: the anode undergoes zinc deposition/stripping, while the cathode hosts the insertion or adsorption of anions (e.g., SO_4^{2-}, $TFSI^-$) from the electrolyte (Cathode + A^- $\rightleftharpoons$ Cathode-A + e^-). During charging, anions insert into the cathode structure as Zn^{2+} deposits onto the anode, while discharging reverses this process [23]. This creates a unique system where both cationic and anionic species contribute reversibly to energy storage.

The application of dual-ion chemistry in aqueous zinc batteries faces an additional challenge: ensure the stability of graphite against structural degradation during anion intercalation in aqueous environments. Recent advances in electrolyte engineering have effectively addressed these issues. Highly concentrated "water-in-salt" electrolytes have expanded the electrochemical stability window, enabling more durable anion intercalation into graphite while reducing the electrolyte mass and volume [26]. However, the practical implementation of aqueous anode-free configuration utilizing graphite anion-intercalation cathodes has yet to be thoroughly validated and represents a critical area for future investigation. Consequently, parallel efforts have focused on exploring alternative carbonaceous materials, such as activated carbons that rely on capacitive anion adsorption rather than intercalation, offering improved cycling stability in aqueous media. Electrolyte additives such as methylurea have significantly improved zinc reversibility, enabling an anode-free Zn||AC cell to achieve an average CE of 99.93 % and stable cycling for over 5000 cycles (Figure 3a–c) [24]. As reported, the oxidative stability of the electrolyte is the critical factor enabling successful anion intercalation in graphite cathodes [27,28]. This dual-ion mechanism creates an electrolyte-centric design challenge similar to hybrid cation systems: the electrolyte must concurrently provide both the zinc cation source for the anode and sufficient anion concentration for cathode reactions, necessitating highly concentrated formulations that inevitably incur trade-offs in cost, viscosity, and overall energy density [29,30]. Collectively, progress in electrolyte design is paving the way for practical aqueous anode-free dual-ion battery systems that leverage the advantages of zinc metal chemistry while overcoming the inherent limitations of anion hosting in aqueous environments.

Halogen conversion chemistry

The integration of halogen conversion chemistry, particularly the I^-/I_2 redox couple, represents a transformative strategy for AF-ZMBs [31]. Unlike conventional intercalation-based cathodes, the ZnI_2 system operates through a reversible two-electron conversion mechanism ($ZnI_2 \rightleftharpoons Zn + I_2$), offering high theoretical capacity. Remarkably, the typically detrimental

Figure 3



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(a) Structures of anode-free Zn batteries. (b) Rate performance of anode-free Zn||AC (activated carbon, AC) full cell measured in a coin cell. (c) Cycling performance of anode-free Zn||AC full cell at a current density of 1 A g^{-1}. Reproduced from Ref. [24] under a Creative Commons license 2025 Elsevier. (d) A schematic diagram of the anode-free Zn||Br$_2$ battery with an areal capacity of 10 mAh cm^{-2}. (e) Long-term cycling performance at 10 mAh cm^{-2} and 10 mA cm^{-2}. Reproduced from Ref. [25] under a Creative Commons license 2023 Spring Nature.

polyiodide shuttle effect is harnessed advantageously to form a protective SEI that guides uniform zinc deposition. It is worth noting that Zn-halogen chemistry has been extensively studied in redox flow battery configurations, where the active materials are dissolved in liquid electrolytes stored in external tanks [32]. While sharing similar redox chemistry, the static cathode design in AF-ZMBs fundamentally differs by integrating both zinc and halogen sources within the electrode structure, eliminating the need for complex flow systems and external tanks [33]. This integrated approach offers potential advantages in system simplicity and volumetric energy density, though it faces distinct challenges in managing the dissolved halogen species within a confined cell architecture.

Interface design and electrolyte engineering have enabled significant progress in anode-free zinc-halogen batteries. The implementation of interphases and halogenated solvation structures effectively suppresses side reactions while guiding uniform, dendrite-free Zn deposition. For example, I_3-mediated modification transforms Cu surfaces through *in situ* formation of Cu nanoclusters, enabling homogeneous zinc deposition and achieving 162 Wh kg^{-1} in $Cu||ZnI_2$ full cells [34]. Alternatively, CuI conversion electrodes create a hybrid mechanism where the collector simultaneously hosts Zn plating/stripping and CuI conversion reactions ($ZnI_2 + 2Cu \rightleftharpoons 2CuI + Zn$), dynamically compensating Zn loss in anode-free cell to achieve 3000 cycles without capacity decay [35]. Substantial progress in electrolyte engineering and interface design has enabled remarkable performance metrics in anode-free zinc-halogen systems. Through optimized electrolyte engineering employing co-engineered salts and solvents, $Cu||ZnI_2$ cells achieve exceptional performance, maintaining >80 % capacity retention over 1000 cycles at practical mass loadings with energy densities of 82 Wh kg^{-1} [36]. Halogen hybridization with bromine or chlorine further enhances energy density to 113−145 Wh kg^{-1}, though iodine-related degradation persists under lean-electrolyte conditions. By coupling interface engineering (Figure 3d and e), the Zn−Br$_2$ system, leveraging an Sb/Sb$_2$Zn$_3$ heterostructured interface, demonstrates exceptional scalability by achieving a remarkable theoretical energy density of 274 Wh kg^{-1} [25]. This performance translates effectively to a practical pouch cell configuration, which delivers 62 Wh kg^{-1} using a 0.5 M ZnBr$_2$ electrolyte with 0.25 M TPABr additive. More technically, a dry process to fabricate the ZnI$_2$ electrode was introduced, achieving a record areal loading mass of $\sim$100 mg cm^{-2} based on ZnI$_2$ (equivalent to 15.8 mAh cm^{-2}) [37]. This innovative fabrication method demonstrates significant promise for practical high-energy AF-ZMBs, offering both scalable production compatibility and a clear pathway from laboratory research to commercial application. These results confirm the viability of halogen conversion chemistry for practical AF-ZMBs, while the success of this chemistry critically depends on sophisticated electrolyte engineering, where optimized concentration and composition simultaneously regulate polyhalide diffusion kinetics and promote the formation of protective interphases.

Conclusions and perspectives

The development of anode-free zinc metal batteries represents a paradigm shift in aqueous energy storage, offering a pathway to maximize energy density while minimizing material usage and cost. This review has systematically examined the electrochemical mechanisms and material challenges across four distinct cathode chemistries suitable for AFZMBs. While each approach, i.e., conventional Zn^{2+} intercalation, hybrid ion intercalation, dual-ion mechanisms, and ZnI_2 conversion chemistry, presents unique advantages, they all converge on the fundamental requirement of achieving near-perfect CE in zinc plating/stripping. The success of any AFZMB configuration ultimately depends on the delicate interplay between cathode stability, electrolyte formulation, and interface engineering, with the cathode chemistry playing a decisive role in determining the system's viability. For instance, using a $ZnMn_2O_4$ cathode, the anode-free design achieves approximately 2.5 times higher energy density at the active material level compared to a conventional configuration with an N/P ratio of 3 (627.2 vs. 237.6 Wh kg^{-1}) [38]. This improvement highlights the tremendous potential of eliminating excess zinc anode mass.

Looking forward, several critical research directions emerge as priorities for advancing AFZMB technology. First, the development of standardized testing protocols for accurately measuring Coulombic efficiency (CE) under practical conditions is essential for meaningful comparison between different systems, coupled with the assessment of realistic full-cell level energy density that accounts for all inactive components. Second, the utilization of low-cost, lightweight inert current collectors, instead of conventionally reported Cu, represents a crucial research direction, as these substrates can significantly reduce inactive mass and, especially, cost while providing favorable zinc deposition morphology. Third, the strategic design of functional cathodes that serve as both zinc reservoirs and sources of self-regulating protective interphases, exemplified by ZnI_2-derived SEI formation or Zn-rich compounds, is critical for simultaneously ensuring anode stability and cathode efficiency in AF-ZMBs. Additionally, the integration of advanced characterization techniques with computational screening methods will accelerate the discovery of novel cathode materials and redox mechanism specifically tailored for anode-free operation. Finally, scaling considerations must be addressed early, including the development of feasible pre-zincation strategies and the optimization of electrolyte-to-capacity ratios to ensure practical energy density at the pack level. As research in this field matures, the convergence of cathode design, electrolyte engineering, and interface control will undoubtedly unlock the full potential of anode-free zinc batteries as a sustainable and cost-effective energy storage solution.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (52377214), Basic Research Program of Jiangsu (Grants No BK20251305), Startup Research Fund of Southeast University (4003002418), and the Helmholtz Association basic funding.

Data availability

No data was used for the research described in the article.

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