



Bringing real-time observability to practical aqueous zinc-ion batteries

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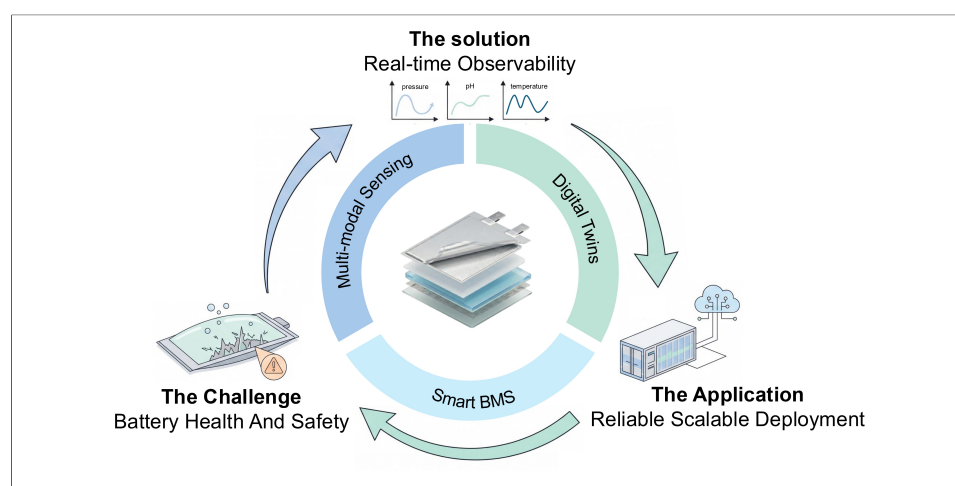
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Abstract

The practical deployment of aqueous zinc-ion batteries (AZIBs) is limited by the lack of observability of internal electrochemical states. Critical failure processes, including hydrogen evolution, zinc dendrite growth, and cathode dissolution, evolve dynamically and remain inaccessible to conventional battery management systems based on external signals. Here, we highlight a sensing-centric approach that enables real-time observability in working AZIBs. By integrating miniaturized *in-situ* sensors, key parameters such as internal pressure, pH, and mechanical stress can be directly monitored during operation, providing continuous access to internal battery state evolution. This transforms AZIBs from black box into observable electrochemical systems, enabling early detection of battery failure and safety risks. Coupling multi-modal sensing with data-driven models and digital twins further enables predictive battery management under realistic conditions, offering a pathway toward reliable and scalable AZIB deployment. It can also be applied for Li metal batteries.



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INTRODUCTION

The global transition toward electrification and carbon neutrality is driving increasing demand for advanced electrochemical energy storage systems, from portable electronics and electric vehicles to grid-scale storage^[1]. Although lithium-ion batteries (LIBs) currently dominate the market, their large-scale deployment is constrained by lithium resource limitations, high costs, and safety concerns associated with flammable organic electrolytes^[2]. Specifically, internal complex reactions in LIBs, such as the reductive attack of hydrogen gas on cathode materials, can lead to severe structural phase transitions and trigger catastrophic thermal runaway. To address these complex safety evaluation challenges, advanced machine learning techniques, such as Artificial Neural Networks (ANN), are being utilized to accurately predict the critical thermal degradation parameters and assess the thermal stability of LIB cathodes^[3]. In parallel, various national energy policies increasingly prioritize safe and sustainable energy storage technologies. For instance, China's *14th Five-Year Plan* emphasizes the diversification of energy storage and the urgent need for intrinsically safe systems to reduce fire risks in storage facilities. Internationally, the EU's *Critical Raw Materials Act* classifies lithium and cobalt as strategic shortages and highlights the importance of reducing reliance on external supply chains. In the United States, the Department of Energy's (DOE) *Long Duration Storage Shot* sets an ambitious target to lower the cost of grid-scale energy storage by 90% to below 0.05 USD kWh⁻¹ within a decade to facilitate widespread clean energy adoption^[4]. In recent years, AZIBs have emerged as a highly competitive alternative. The utilization of aqueous electrolytes reduces the flammability risks associated with organic systems and offers inherent safety advantages. Moreover, zinc resources are abundant, inexpensive, and compatible with ambient-air processing, which can reduce manufacturing costs^[5,6]. Market analyses indicate that the global zinc-ion battery market could exceed \$12.8 billion by 2028, potentially occupying 10% of the energy storage market by 2030 and up to 25% by 2050^[6]. These features make AZIBs attractive for applications ranging from consumer electronics and medical devices to grid-scale energy storage and safety-critical energy systems^[1]. Moreover, the application scope of AZIBs is expanding toward multifunctional systems; for example, emerging zinc-nitrate batteries utilizing advanced asymmetrically coordinated single-atom catalysts can simultaneously deliver electrical energy and valorize nitrate pollutants into ammonia^[7].

Recently, significant laboratory-scale breakthroughs have been achieved regarding AZIBs electrode material design and electrolyte optimization^[4]. For instance, advanced anode interface engineering, such as the multifunctional zinc silicate polymer (LSO) coating, has been developed to effectively suppress zinc dendrites and interfacial corrosion, enabling ultralong cycling stability (over 800 h) in laboratory-scale symmetric cells^[8], similarly, constructing a zincophilic-hydrophobic interfacial layer, such as a sulfonated cellulose acetate nanofiber membrane, can effectively reduce water activity to suppress parasitic reactions while simultaneously promoting Zn²⁺ desolvation for uniform dendrite-free deposition^[9]. Furthermore, drawing inspiration from advanced solid-state electrolyte designs, utilizing electrochemically active materials (EAMs) to construct a self-limiting, mixed conductive interface offers a novel pathway. Such dynamic interfaces can effectively redistribute ion concentrations, provide affine nucleation sites, and alleviate local polarization to fundamentally suppress dendrite growth^[10]. As summarized in [Figure 1](#), these advancements in electrode materials and electrolytes are accelerating the deployment of AZIBs across diverse practical applications. Pioneering enterprises have already launched commercial products for specific applications, indicating early steps toward commercialization. A detailed summary of these pioneering enterprises, their key technologies, and commercial applications is presented in [Table 1](#). For example, *Eos Energy Enterprises* developed the Z3™ Cube containerized system based on zinc hybrid cathode technology for grid and microgrid energy storage^[11]. *Urban Electric Power* and *Salient Energy* have introduced zinc-based systems targeting residential and backup power markets^[6]. In the consumer electronics sector, *Bohai Chemical* has successfully mass-produced laminated pouch AZIBs for devices such as smart locks and IoT terminals and software^[12]. Despite these developments, the overall AZIBs technology remains in the early stages of industrialization, with a

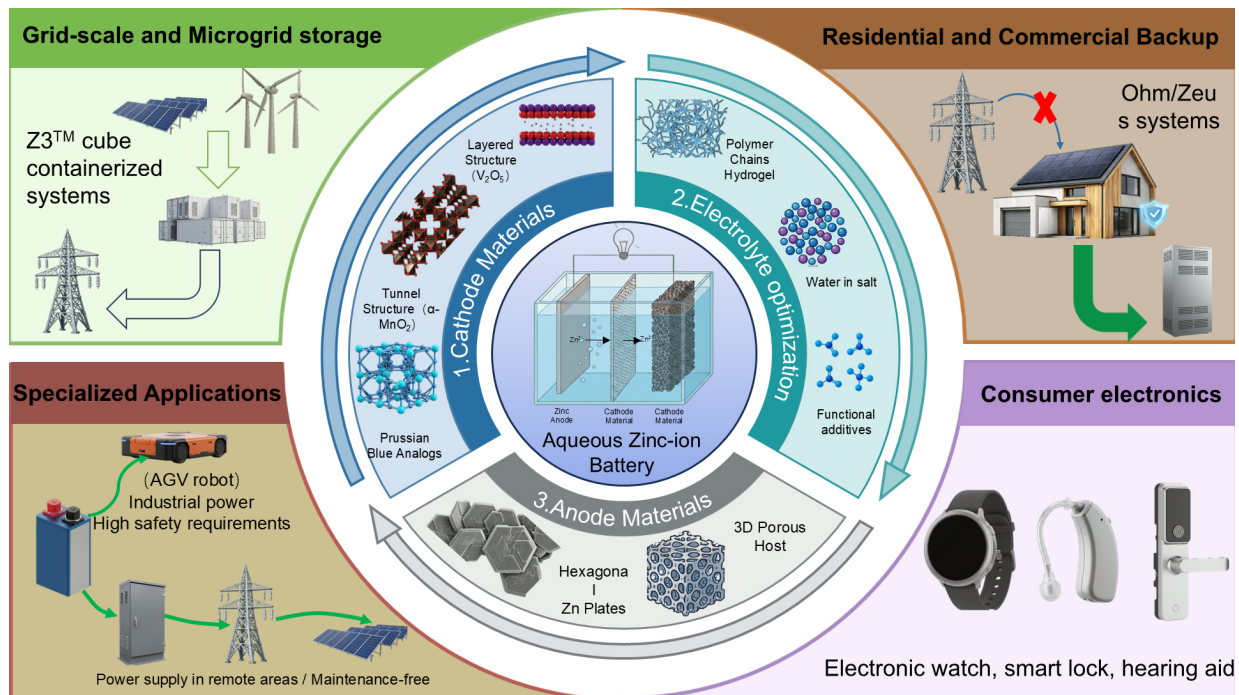


Figure 1. Commercialization applications of aqueous zinc-ion batteries in various scenarios.

Technology Readiness Level (TRL) estimated at around 5–7^[4]. Critical manufacturing challenges remain to be addressed before AZIBs can be widely deployed at scale. Performance achieved in laboratory coin cells is often difficult to reproduce in practical pouch or prismatic formats^[1,4]. Large-scale production can suffer from issues such as non-uniform slurry coating, rapid performance degradation under lean-electrolyte conditions, and gas generation leading to cell swelling due to interfacial side reactions^[4]. Additionally, the existing supply chain lacks standardized manufacturing equipment tailored for zinc-based batteries. System-level energy density and cycle life require further enhancement to meet the growing demands of low-cost, long-duration energy storage^[4].

As AZIBs transition into large-scale applications, their system reliability and life-time cost under complex operating conditions become critical considerations for commercialization. Addressing these challenges requires effective Battery Management System (BMS) capable of precise estimation of battery status including State of Charge (SOC) and State of Health (SOH), as well as reliable Remaining Useful Life (RUL) prediction^[13–15]. Existing BMS architectures were originally developed for LIBs and rely primarily on external measurements such as voltage, current, and temperature^[16]. Taking temperature as an example, heat inside the battery comes from Joule heating, polarization, and side reactions. However, this heat does not spread evenly. Instead, it creates large temperature differences across the surface and deep inside the cell. Traditional monitoring methods usually assume the battery heats up evenly. Because of this, they often miss dangerous internal hot spots^[17]. These hidden hot spots cause the battery to age faster in certain areas. They damage the electrodes unevenly and greatly increase the risk of severe failures, such as thermal runaway (TR). These approaches provide limited insight into internal electrochemical processes and are often insufficient for predicting sudden failure events^[14]. Directly applying such strategies to AZIBs is problematic because aqueous electrolytes introduce distinct electrochemical behaviours and degradation pathways compared with organic systems^[1].

For example, the hydrogen evolution reaction (HER) in aqueous environments can generate gas and increase internal pressure, which may cause pouch cell swelling or mechanical failure^[18]. Traditional BMS architectures rarely monitor parameters related to internal pressure evolution or localized pH fluctuations^[19].

Table 1. Summary of pioneering enterprises, key technologies, and commercial applications of AZIBs

Company	Key technology	Commercial product/Application fields		Reference
Eos Energy Enterprises	Zinc Hybrid Cathode (Znyth™ Technology)	Grid-scale Storage: Z3™ Cube containerized systems	Utilities and Microgrids	[39]
Urban Electric Power	Rechargeable Zn-MnO ₂ (Alkaline-based)	Ohm/Zeus systems for home storage	Residential Backup	[41]
Salient Energy	Zn-Ion Battery (Non-layered Cathode)	Stationary Storage: Modular residential batteries	Commercial building backup power	[42]
Enzinc	Zinc Microsponge Anode (3D Structure)	"Drop-in" high-performance anodes	E-bikes and microgrids	[43]
Vastech Energy	New adhesive formula, new electrode material	VAS-E-1 Energy-based energy storage solution	large-scale energy storage, railway/urban rail transit power recovery	[44]
Bohai Chemical	Effectively improve the zinc deposition/peeling behaviour and inhibit dendrite growth	High-safety AZIB pouch cells	New energy storage, portable electronic devices	[40]
Chilwee Group	Construction of high-energy and long-life zinc-based systems	Zinc-based power battery	Power supply energy storage field civilian field	[45]
ZincFive	Inherently safe and free from thermal runaway risk nickel-zinc (NiZn) battery chemistry system	BC 2 AI Z5 13-90 Battery Cylindrical Cells	Data Centers Intelligent Transportation Information Technology	[46]
WeView	Zinc-iron redox flow battery energy storage technology	VP series zinc-iron liquid flow battery products	Power supply-side energy storage, grid-side peak shaving, and industrial	[47]
AEsir Technologies	High-capacity and deep-cycle nickel-zinc (NiZn) battery technology	Aesir Group 31 Batteries NiZn Pouch	Data Centers Aerospace Applications Defence Applications	[48]
E-Zinc	Long duration energy storage technology	Hydrogen-based zinc-air long-term energy storage system	Power grid, remote areas (such as mining areas, military bases, etc.) and "renewable energy"	[49]
Amazinc	High-security water-based zinc-based battery	Grid-level zinc-based energy storage system	Energy storage in the industrial and commercial sector	[50]
ZAF energy systems	Proprietary electrolyte and zinc electrode formulation	NiZn Prismatic NiZn Pouch NiZn Air	Aerospace/defence, data centers, marine, medical, trucking	[51]
ViZn Energy	The hybrid flow battery technology	GS200® energy storage Z20® energy storage	C&I, Microgrids, Solar & Wind energy, Military, Utility, Mining	[52]

AZIB: Aqueous zinc-ion battery.

In addition, zinc dendrite growth and anode corrosion occur at the microscale and remain difficult to detect using conventional pack-level monitoring^[20]. The current research on AZIBs still focuses largely on materials and electrolyte optimization, while the development of AZIB-specific management systems has received comparatively limited attention^[21]. This imbalance between materials research and system-level management creates a critical gap in monitoring and control as the technology moves toward practical deployment^[1].

An effective BMS architecture combines real-time sensing with physics-based and data-driven models to infer the internal electrochemical state of the battery^[22]. Current modelling efforts for AZIBs cover multiple dimensions. At the microscale, phase-field and lattice-Boltzmann methods are widely used to simulate zinc ion transport and dendrite growth kinetics, revealing the quantitative relationship between the "tip effect" caused by concentration polarization and deposition morphology^[23,24]. For system-level simulations, researchers mostly use continuum modelling methods, like the pseudo-two-dimensional (P2D) model. They do this work using software packages such as PyBaMM, ANSYS Fluent, and COMSOL Multiphysics. These computer tools can link electrochemical, thermal, and mechanical models together. This allows researchers

to simulate a full cell's overall behaviour in real working conditions. It also helps them predict the cell's performance^[22].

For larger battery pack simulations, Machine Learning shows great promise in industry. Large car makers face complex working conditions. To handle this, they now use ML-powered digital twins. They use this technology to simulate and test how battery packs perform in real, changing environments. This data-driven method acts as an important bridge. It connects basic research on battery materials with real-world battery pack use^[22].

Despite these advances, existing models remain difficult to apply directly in practical battery management. Most models rely on offline simulations under idealized assumptions and cannot capture the dynamic evolution of complex side reactions under realistic operating conditions^[23,25]. Crucially, most models lack real-time sensor data inputs, making it difficult to update model parameters as battery ages. As a result, a gap remains between theoretical simulation and practical system-level management^[20]. Building the future smart BMS requires deeply integrating multidimensional in-situ sensing technologies into the modelling process. Real-time measurement of physicochemical parameters, such as ion concentration fields, internal pressure and temperature, can provide accurate feedback for model calibration and enable more accurate tracking of battery states through the full lifecycle^[22].

ELECTROCHEMISTRY AND DEGRADATION IN AQUEOUS ZINC-ION BATTERIES

Developing effective BMS strategies for AZIBs requires a clear understanding of their complex internal electrochemical behaviours and mechanisms that lead to performance degradations. AZIBs function in aqueous environment where charge storage is often accompanied by competing parasitic side reactions. This section will link microscopic ion transport and interfacial reactions to macroscopic battery performance and failure. Understanding these relationships is essential for identifying key parameters that can be monitored for reliable BMS state estimation.

Electrochemical storage mechanisms in aqueous zinc-ion batteries

Electrochemical processes in AZIBs involve complex reaction pathways at both the cathode and the zinc metal anode. At cathode side, energy storage can occur through several mechanisms, including Zn^{2+} intercalation, proton/ Zn^{2+} co-insertion, conversion reactions, and dissolution-deposition processes. The dominant pathway depends on the crystal structure of the cathode material (e.g., layered, tunnel or open-framework structures), the physicochemical properties of the electrolyte such as pH and salt concentration, and the operating voltage window.

Zn^{2+} intercalation/extraction

The Zn^{2+} intercalation/extraction mechanism occurs in cathode materials with large interlayer spacing or open frameworks, such as vanadium-based oxides and Prussian blue analogues (PBAs). During operation, Zn^{2+} ions migrate through the electrolyte and reversibly intercalate into the lattice tunnels or van der Waals interlayer within the host structure while maintaining overall structural integrity^[26]. First, $\alpha\text{-MnO}_2$ is an excellent manganese-based material. It has a large one-dimensional 2×2 pore structure. This open space makes it easy for zinc ions to move in and out, which gives the battery a high energy storage capacity^[5]. However, it suffers from low electrical conductivity and the dissolution of the cathode material into the electrolyte^[26]. Second, V_2O_5 is a typical vanadium-based material with a layered structure^[5]. The distance between its layers is larger than the size of a zinc ion. This allows the zinc ions to easily enter and leave the layers during charging and discharging processes^[5]. PBAs feature spacious three-dimensional channels that can accommodate partially solvated Zn^{2+} species^[5,26].

Proton/ Zn^{2+} co-insertion

In layered manganese-based oxides, charge reaction often involves the synergistic insertion of protons and Zn^{2+} ions. The protons are generated from the water in the aqueous electrolyte. Specifically, the water molecules dissociate into protons (H^+) and hydroxide ions (OH^-). Because protons have a smaller size and faster kinetics, they insert into the cathode material before the zinc ions^[26]. For example, when protons insert into a MnO_2 cathode, they react with the material to form MnOOH ^[5]. The early insertion of protons helps to promote the subsequent transfer and insertion of zinc ions^[26]. At the same time, as protons are consumed, the remaining hydroxide ions react with zinc ions and the zinc sulfate electrolyte^[5]. This reaction forms a by-product called zinc hydroxide sulfate, which deposits on the cathode to maintain the charge balance^[26].

Conversion and displacement

To overcome capacity bottlenecks of traditional intercalation materials, conversion and displacement reactions have emerged as promising strategies for high-energy-density batteries. Conversion reactions in chalcogenide and iodine-based cathodes can bypass lattice intercalation and instead involve multi-electron redox reaction processes that generate new compounds (e.g., ZnS and ZnTe) to provide high theoretical capacities^[26]. However, achieving stable multi-electron conversion in iodine-based cathodes remains challenging due to intermediate dissolution and severe capacity decay. Recently, a dual-zone chloride engineering strategy was proposed to address this by spatially separating chloride environments: a hydrophobic salt is utilized at the cathode to prevent polyiodide desorption and water-induced decomposition, enabling ultra-stable two-electron zinc-iodine chemistry^[27]. Displacement mechanisms, seen in silver vanadium oxides, involve Zn^{2+} replacing metal ions to form a highly conductive metallic network, followed by conventional intercalation within the newly formed Zn-rich phase significantly enhancing the battery's rate capability^[26].

Dissolution and deposition

The dissolution/deposition mechanism represents a distinct reaction pathway characteristic of manganese-based oxides, particularly MnO_2 . This process functions both as a charge storage mechanism and as a major contributor to cathode degradation. During discharge, the thermodynamically unstable Mn^{3+} undergoes disproportionation into Mn^{4+} and Mn^{2+} ^[26]. If the dissolution of Mn^{2+} is irreversible, it results in the loss of active material (LAM) and continuous capacity fading^[26].

Zinc anode plating and stripping

The zinc anode operates through the physicochemical dissolution and deposition of zinc metal during charge and discharge^[5]. During discharge, zinc metal oxidizes and dissolves into the electrolyte as zinc ions, while during charge these solvated zinc ions are reduced and redeposited onto the anode surface. However, under practical operation conditions, the Zn/electrolyte interface often suffers from severe instability, driven by dendrite growth, HER, corrosion, and surface passivation which deteriorate reversibility and cycling stability^[5,28].

Degradation mechanisms in aqueous zinc-ion batteries

Performance degradation in AZIBs arises from coupled physicochemical processes occurring at the anode, cathode, and electrolyte interfaces. At the zinc anode, thermodynamic instability in aqueous electrolyte leads to parasitic reactions such as chemical corrosion and HER, accompanied by non-uniform zinc deposition and dendrite growth^[6,28]. Meanwhile, cathode materials suffer from structural degradation and active material dissolution during repeated cycling^[4,6]. In practical applications, temperature fluctuations further accelerate these degradation pathways by intensifying parasitic reactions. To elucidate the fundamental origins of AZIBs degradation, this section systematically discusses critical failure mechanisms, as illustrated in [Figure 2](#),

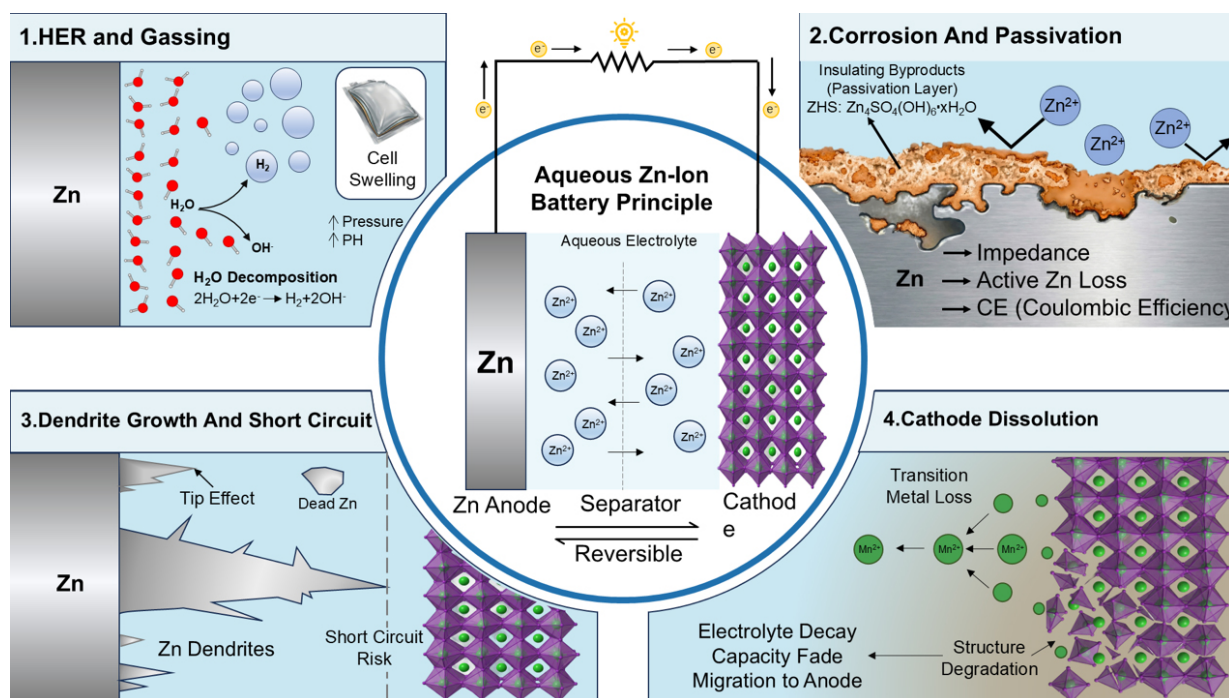


Figure 2. Schematic illustration of the primary degradation mechanisms in AZIBs. AZIB: Aqueous zinc-ion battery.

including HER, corrosion and surface passivation, zinc dendrite formation, and cathode material dissolution, as well as dynamic pH fluctuations and thermal instability^[29].

Hydrogen evolution reaction and gas generation

Owing to the highly negative redox potential of Zn/Zn^{2+} in aqueous electrolytes, the HER can be thermodynamically favoured at the zinc surface^[6,19,28]. During charging or resting conditions, water molecules decompose on the zinc surface, generating hydrogen gas accompanied by the localized accumulation of OH^- ions. The specific reaction^[19] is expressed as:



Continuous hydrogen generation causes gas accumulation within the cell and further results in internal pressure buildup and pouch cell swelling, increased internal resistance, and mechanical failure^[4,28]. Meanwhile, the localized enrichment of OH^- elevates the interfacial pH^[4,19]. More critically, the cascading reactions triggered by HER pose a severe threat to both the long-term cyclic stability and the safety of the battery. On the one hand, continuous electrolyte decomposition coupled with electrode corrosion directly results in irreversible capacity loss, thereby significantly shortening the operational lifespan of the cell^[19]. On the other hand, unvented internal pressure buildup not only compromises mechanical integrity but also frequently precipitates catastrophic safety hazards, such as casing rupture or electrolyte leakage, culminating in complete battery failure^[4,28]. Consequently, the dynamic evolution of internal pressure and localized pH serve as the most direct indicators for monitoring the severity of HER.

Corrosion and surface passivation

The alkaline environment induced by HER promotes the reaction of Zn^{2+} with anions, resulting in the formation of insulating passivating layers such as Zinc Hydroxide Sulfate (ZHS)^[26]. These porous, insulating byproducts hinder Zn^{2+} transport, drastically increasing interfacial impedance and degrading rate

capability^[28]. Meanwhile, continuous corrosion irreversibly consumes active zinc, leading to persistent energy density decay and reduced coulombic efficiency, ultimately restricting both the cyclic stability and operational lifespan of the battery^[30].

Dendrite growth and short-circuit risks

Dictated by the intrinsic crystallographic anisotropy of the hexagonal close-packed (HCP) zinc lattice, coupled with inhomogeneous electric field distributions, Zn^{2+} ions tend to deposit preferentially at surface protrusions with high local electric field intensities or steep ion concentration gradients. This “tip effect” ultimately drives the growth of needle-like or dendritic Zn ^[28]. In addition, dendritic propagation is an inherently self-accelerating process. Once formed, dendrites increase local electric fields and attract more Zn^{2+} . When they penetrate the separator, internal short circuits may occur. Meanwhile, excessive growth causes parts of the active material to detach, forming electrochemically inactive “dead Zn” and resulting in rapid capacity loss^[28].

Cathode dissolution

During prolonged cycling, cathode materials, particularly manganese-based oxides, suffer from the dissolution of transition metal ions (e.g., Mn^{2+}) into the aqueous electrolyte^[6,26]. This continuous dissolution gradually changes the local electrolyte chemistry. Subsequently, these dissolved species can then migrate to the anode and deposit onto its surface, severely disturbing the normal zinc plating kinetics^[26,31]. This crossover leads to the loss of active cathode material, which macroscopically translates into a continuous and irreversible decline in the battery capacity^[6,26,31]. Similarly, in zinc-iodine systems, the severe dissolution and subsequent shuttle effect of polyiodide intermediates constitute a major cathode degradation pathway^[32].

Thermal stability challenges

Although AZIBs are attractive for their intrinsic safety, their practical deployment across diverse conditions requires stable operation across a wide-temperature range to suit varying climates^[30]. For instance, in geological exploration and in the deployment in tropical regions, high-temperature conditions are often encountered. Additionally, during the operation of batteries, heat is inevitably generated due to polarization losses (such as ohmic, electrochemical and concentration polarization), electrochemical reactions, entropy changes of side reactions, and the mixing during relaxation processes^[33]. What is more serious is that if the accumulated heat in a certain area cannot be dissipated, the continuous high temperature may lead to a thermal runaway, which involves a series of chain reactions caused by an internal short circuit. Specifically, elevated temperatures actively accelerate the HER and Zn corrosion, while simultaneously exacerbating the dissolution of cathode active materials, collectively resulting in a rapid decline in cyclic stability^[30,33]. In addition, due to the high volatility of water, high temperatures cause the solvent to evaporate rapidly, which leads to the precipitation of solutes and results in dangerously increased internal pressure of the sealed battery^[30,33,34]. Moreover, when exposed to high temperatures, certain components in the electrolyte may undergo thermal decomposition^[33]. For some advanced electrolyte designs, such as high-concentration “salt-in-water” electrolytes (WISEs) or hydrogels, high temperatures will severely exacerbate problems such as accelerated dehydration and high volatility^[30]. The failure mechanisms of AZIBs under extreme temperatures are still not fully understood, which limits the development of effective mitigation strategies^[33]. Temperature variations also drive key degradation processes, including the formation of insulation byproducts, gas-induced swelling, and structural damage. Therefore, integrating high-precision temperature sensing for real-time monitoring is important for ensuring safety and performance over the full battery lifetime. Despite this, such capability remains largely overlooked in current BMS research.

In summary, the degradation of AZIBs arises from coupled physical and chemical processes, rather than a single mechanism. Accordingly, dynamic parameters such as internal pressure changes, local pH shifts, impedance increase, and coulombic efficiency variation act as key fingerprints for BMS to assess the state of

health.

ADVANCED SENSING TECHNOLOGIES FOR BATTERY MANAGEMENT SYSTEMS

While advanced laboratory characterizations like cryo-electron microscopy (Cryo-EM), Atomic force microscopy (AFM), differential electrochemical mass spectrometry (DEMS) and in-situ Raman spectroscopy have revealed micro-scale failure mechanisms of AZIBs^[29,35], their large size and high costs make them unsuitable for practical deployment in electric vehicle or grid storage. To bridge the gap between mechanistic understanding and real-time management, it is necessary to develop miniaturized, multi-modal sensors that can be integrated into the battery. Current sensing approaches are moving beyond external voltage and temperature measurements toward internal monitoring capable of directly tracking chemical environment shifts.

Optical fiber sensing

To address the severe HER and subsequent gas-induced swelling in AZIBs, optical fiber sensing technology has attracted increasing interest, benefiting from its immunity to electromagnetic interference, robust corrosion resistance, and micron-scale footprint. For instance, Ding et al. developed a hybrid optical fiber sensor by combining a Fabry-Pérot interferometer (FPI) with a Fiber Bragg grating (FBG). When embedded directly within the pouch cell, this sensor enables *operando* monitoring of internal pressure fluctuations driven by HER, with a sensitivity of 137 nm MPa⁻¹, while simultaneously tracking temperature. By converting the HER-related process into real-time optical signals readable by the BMS, this approach allows direct readout by the BMS and avoids the slow response and limited accuracy of conventional external pressure sensors^[18].

Despite exhibiting rapid response times and high sensitivity, the sensing mechanism of this technology is constrained by the inherent cross-sensitivity between pressure and temperature. Mitigating this interference requires the integration of a FBG to perform complex signal decoupling and compensation. Furthermore, the susceptibility of optical sensors to internal mechanical stress and strain can lead to signal distortion under the complex deformation profiles encountered within a battery^[18]. In terms of practical deployment, while the ultra-slim 140 µm diameter enables excellent non-invasive integration, the associated back-end infrastructure entails significant costs. The dependence on bulky and complex external equipment, including interrogators, laser sources, and spectral readout systems - substantially limits its cost-effective and widespread application in portable electronics or large-scale energy storage facilities^[16]. Consequently, future practical implementations must achieve a strategic balance between sensing precision, system complexity, and the preservation of battery performance.

Extended gate field-effect transistors for pH

To probe the chemical drivers of anodic corrosion and dendrite growth, namely electrolyte pH changes and local ion gradients, extended-gate field-effect transistors (EGFETs) and functionalized optical fibers offer practical solutions. For example, Luo et al. developed a miniaturized EGFET-based dual sensor for pH and dissolved oxygen (DO), designed for direct integration into the battery. With a sensitivity of 46 mV pH⁻¹, the device tracks pH changes at the electrode/electrolyte interface during cycling. This enables early detection of conditions that may trigger the formation of insulating byproducts such as ZHS under local pH increase^[19].

However, since its working mechanism relies on the conversion of potential differences, a stable reference fiber electrode must be introduced inside the battery as a reference. This also takes up more space inside the battery. At the same time, the implantation of the fiber electrodes of the EGFET sensor requires an additional diaphragm layer for mechanical protection and electrical isolation^[17]. This inevitably increases the internal resistance of the battery and may cause subtle interference to the local ion transmission path.

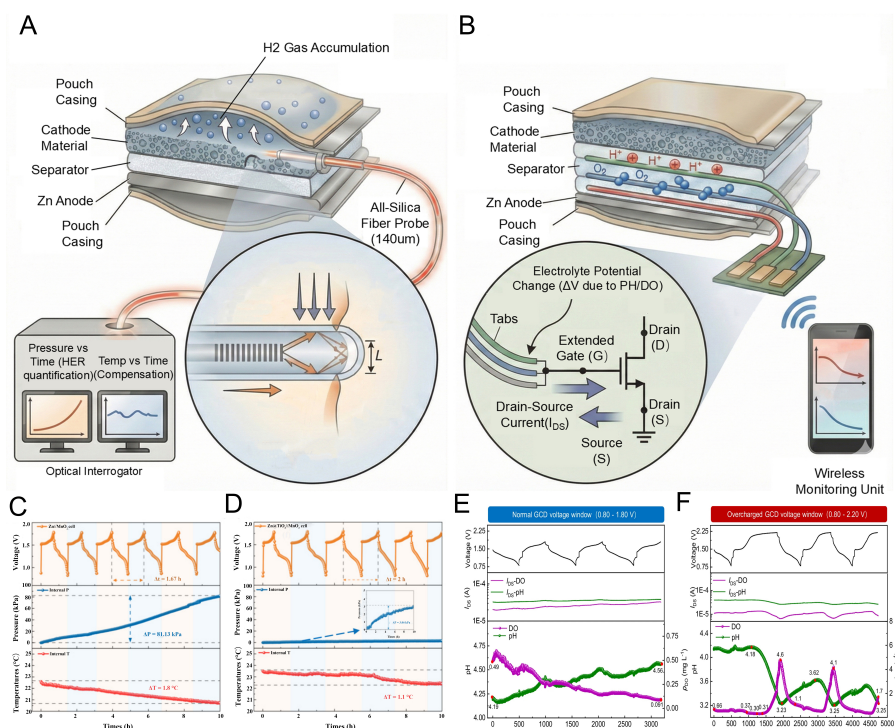


Figure 3. (A) Operando optical fiber monitoring (physical parameters); (B) *In-situ* electrochemical transistor detection (chemical composition); (C) and (D) The *in-situ* monitoring of battery pressure and temperature during the hydrogen evolution process of the Zn-MnO₂ pouch cell and Zn-TiO₂/MnO₂ cell. (C and D) Reproduced with permission from Ref.^[16] copyright © 2025, American Chemical Society; (E) and (F) The resolution voltages, I_{DS}-pH and I_{DS}-DO of the EGFET-pH and DO sensors when detecting aqueous zinc-ion batteries within the normal charging voltage and the overcharging voltage; (E and F) Reproduced with permission from Ref.^[17] copyright © 2025, Springer Nature. HER: Hydrogen evolution reaction; I_{DS}: source-drain current; EGFET: extended-gate field-effect transistor.

The architectures and working principles of the HER and pH sensing systems are illustrated in Figure 3A and B. Operando measurements in Figure 3C and D reveal the pressure and temperature responses of Zn-MnO₂ and Zn-TiO₂/MnO₂ pouch cells, respectively, highlighting differences in gas evolution behaviour during HER. The EGFET sensor responses (I_{DS}-pH and I_{DS}-DO), together with the corresponding real-time evolution of pH and dissolved oxygen (DO), are shown in Figure 3E under galvanostatic cycling at 2C within 0.80-1.80 V, indicating relatively stable interfacial conditions. When the voltage window is extended to 0.80-2.20 V [Figure 3F], pronounced shifts in pH and DO are observed, suggesting intensified side reactions and electrolyte imbalance. Selected data points are highlighted to mark key stages of these processes.

Plasmonic fiber-optic and acoustic emission and strain sensing

Zinc dendrite growth remains a major limitation for AZIBs performance. To probe its early-stage dynamics, plasmonic fiber-optic sensors have been employed to monitor ion activity at the electrode interface^[38]. By detecting localized refractive index changes, this method could track the depletion and accumulation of Zn²⁺ in real time, providing direct insight into interfacial ion transport and enabling non-destructive predict potential dendrite growth. Consequently, this real-time monitoring capability facilitates the dynamic optimization of fast-charging protocols, ensures active safety by mitigating catastrophic failures prior to irreversible physical damage, and significantly reduces operation and maintenance costs in large-scale energy storage systems through targeted predictive maintenance. In parallel, acoustic and strain sensing offer complementary routes to capture the mechanical signals associated with dendrite growth and structural evolution. As summarized by Espinoza Ramos et al., acoustic emission (AE) techniques can detect transient elastic waves generated by processes such as gas bubble formation, electrode cracking, and dendrite

penetration of the separator^[37]. Analysis of these signals in terms of frequency and amplitude allows early identification of internal failure events, often before measurable changes appear in conventional electrochemical outputs such as voltage. In the specific context of AZIBs, this real-time observability is highly valuable for mitigating dominant failure mechanisms. For instance, AE sensors can acutely capture the acoustic signatures of parasitic HER and localized gas accumulation long before macroscopic cell swelling occurs. Furthermore, the technique provides direct evidence of micro-mechanical degradation, monitoring the structural cracking of cathode materials that accompanies continuous dissolution, as well as the critical moments of separator puncture by growing zinc dendrites. By translating these hidden physical and chemical degradation processes into quantifiable acoustic data, AE sensing effectively transforms the AZIB from a “black box” into a highly observable electrochemical system, paving the way for intrinsically safe battery management and predictive diagnostics.

Although advanced sensing technologies, such as AE and plasmonic fiber-optic sensors, show remarkable non-invasive and high-resolution advantages for operando battery monitoring, they still have inherent limitations regarding their sensing mechanisms and practical deployment. In terms of sensing orientation, the simultaneous occurrence of multiple physicochemical degradation processes and the complex wave propagation paths within the battery make it highly challenging to accurately decouple AE events and pinpoint specific degradation mechanisms^[37]. For the plasmonic fiber-optic sensor, the broad spectral bandwidth of the sensor envelope restricts the accuracy of tracking wavelength shifts, and its inherent cross-sensitivity to mechanical strain, local temperature changes, and light power fluctuations necessitates complex signal calibration and decoupling through core mode referencing^[36]. Regarding practical deployment, both technologies face distinct difficulties: AE sensing currently lacks standardized data acquisition settings, leading to scattered and poorly reproducible results; meanwhile, although the plasmonic fiber-optic sensor probe is miniaturized, its “back-end” operation heavily relies on bulky and expensive benchtop equipment like full-scale optical spectrum analysers, which severely limits its cost-effective and widespread application in routine electric vehicle diagnostics or large-scale energy storage systems. Consequently, future practical implementations must achieve a strategic balance between sensing precision, system complexity, and the preservation of battery performance.

The configurations and operating principles of two sensing strategies for dendrite growth are shown in Figure 4A and B. The operando response of sensor a [Figure 4C] exhibits synchronous changes with the galvanostatic charge-discharge profile, directly reflecting the dynamic evolution of interfacial ion activity during battery operation. In contrast, sensor b captures transient mechanical events: distinct waveforms are detected during bubble rupture [Figure 4D] and during graphite structural failure [Figure 4E], highlighting its sensitivity to localized physical processes. Together, these sensing approaches enable the detection of internal gas pressure, pH variation, ion activity, and acoustic or stress signals. By converting otherwise inaccessible chemical and mechanical processes into real-time, quantifiable outputs, they provide critical inputs for BMS to improve state estimation and safety control.

SENSOR DESIGN REQUIREMENTS AND SYSTEM INTEGRATION

Hardware design requirements for *in-situ* sensors

Significant progress has been made in sensing and monitoring AZIBs. Early approaches relied on external voltage and temperature measurements. Recent work enables operando tracking of internal states, including gas pressure, pH changes, and micro-mechanical signals, using optical fibers, EGFETs, and acoustic emission techniques. Despite these advances, key challenges remain for practical deployment in applications such as grid storage and electric vehicles. Many high-precision sensing approaches still depend on bulky laboratory equipment and lack scalable, low-cost integration. At the same time, existing sensors often show limited response speed and poor signal decoupling. For example, conventional pressure sensors can exhibit

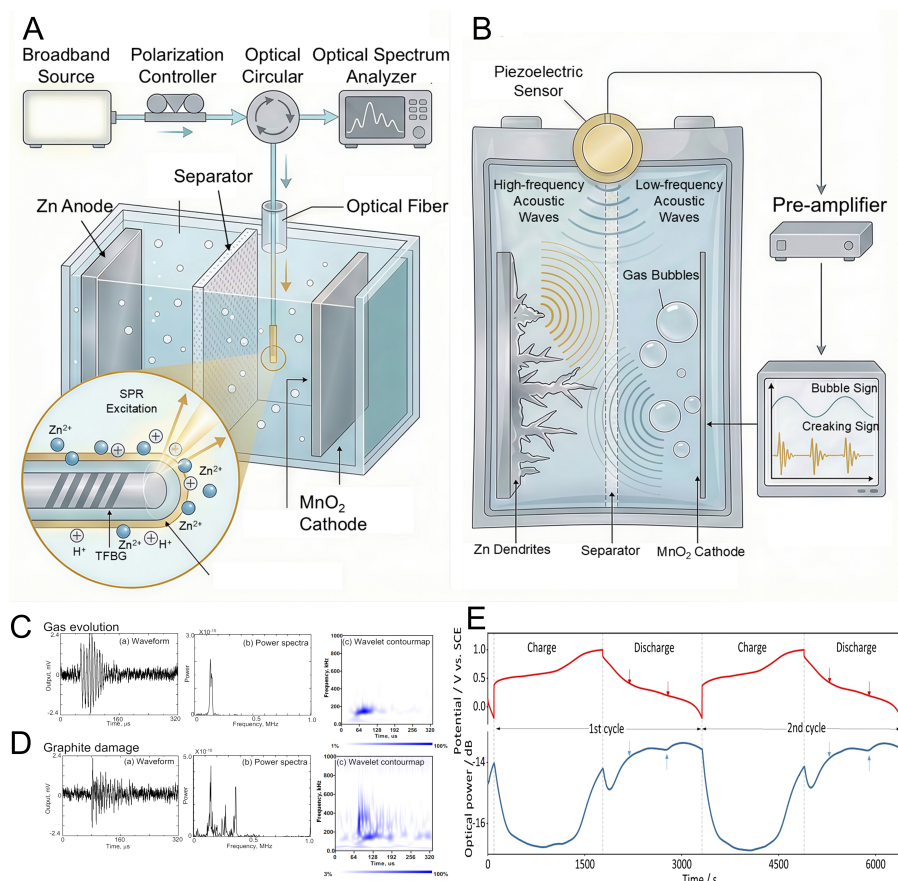


Figure 4. (A) The setup and principle of *in-situ* monitoring of Zn anode interface; (B) The setup and principle of Acoustic emission sensor; (C and D) The waveform detected when the bubble bursts of sensor b and the destruction of graphite of sensor b. (C and D) Reprinted from Ref. [35] under the CC BY 4.0 license; (E) *In-situ* experimental demonstration of sensor a. (E) Reprinted from Ref. [34] under the CC BY 4.0 license. TFBG: Tilted fiber Bragg grating; SPR: surface plasmon resonance; SCE: saturated calomel electrode.

hysteresis during HER monitoring, which restricts their use for real-time safety warnings in BMS. To bridge the gap between fundamental understanding and system-level control, next-generation AZIB sensors should address several critical requirements, which, along with their system-level integration pathways, are comprehensively outlined in Figure 5.

Corrosion resistance and chemical stability

The internal environment of AZIBs is highly dynamic. While the bulk electrolyte is mildly acidic, the local interface can rapidly shift to alkaline conditions during HER. These fluctuations place strict demands on sensor materials and device design. Sensors should therefore use chemically stable materials or adopt architectures that isolate the sensing elements from the circuitry. This is essential to ensure long-term operation over repeated cycling, prevent corrosion, and avoid the release of impurity species that could degrade battery performance [36].

Multi-physics decoupling

Given the complex physicochemical environment inside AZIBs, next-generation sensors must distinguish overlapping signals from different sources. Thermal drift, pressure variation, and mechanical stress often occur simultaneously and can interfere with each other, leading to misinterpretation. Effective signal separation is therefore essential for reliable diagnostics. Established approaches in lithium-ion batteries provide useful guidance. For example, analysing signals across different timescales can help separate

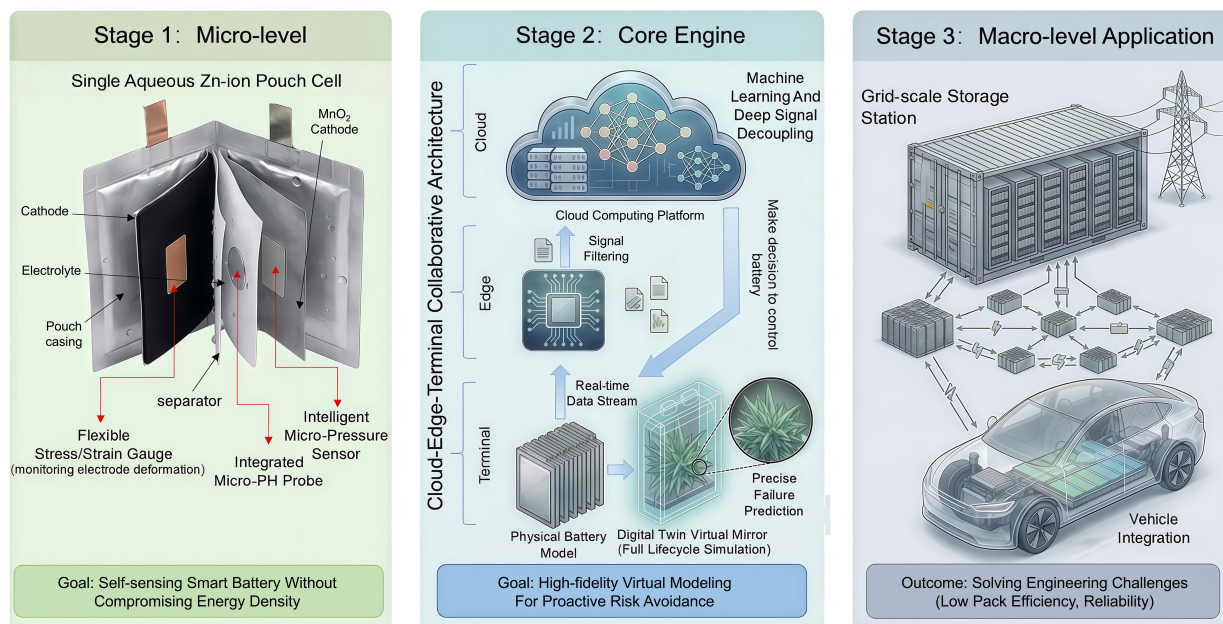


Figure 5. Multi-scale development roadmap and perspective for smart AZIBs management systems. AZIB: Aqueous zinc-ion battery.

corrosion-driven Zn loss from electrochemically induced degradation. The ability to extract independent physical parameters from coupled data streams is fundamental for accurate state estimation in BMS^[38].

Miniaturization and low invasiveness

High sensing accuracy must not come at the expense of altering battery behaviour. Large sensors can occupy internal space, block ion transport, and create local current hotspots, which may even promote dendrite growth^[34]. Future designs should therefore focus on micro-scale devices, such as optical fibers and thin-film sensors, or adopt non-invasive approaches including acoustic and optical methods. These strategies enable high-resolution detection of transient events, such as gas evolution and crack formation, while minimizing disturbance to the system. This is critical for early warning of failure before thermal runaway or internal short circuits occur^[37,39].

From smart sensing to system-level integration

Apart from having high-precision hardware sensors, it is crucial that the large amount of in-situ data generated by the sensors be combined with the upper-level algorithms to achieve the maximum value. At the sensing level, future devices will move toward miniaturized, flexible, and distributed architectures. Sensors for key parameters, such as pH, strain, and gas pressure, can be integrated directly onto electrodes or separators, enabling real-time mapping of internal states without compromising energy density. These large-scale operando datasets will support the development of AI-driven analysis and digital twin models. By combining data processing at the device level with cloud-based computation, BMS platforms can interpret complex signals and predict failure modes such as dendrite growth and thermal runaway^[13,22,40]. At the system level, such approaches will support the transition from single-cell studies to large-scale applications. Improved monitoring, consistency management, and dynamic balancing across battery packs can enhance efficiency and reliability, helping to address key challenges in the practical deployment of AZIBs^[1,40].

CONCLUSIONS

This review summarizes the electrochemical failure mechanisms of AZIBs. It also focuses on how in-situ sensing technologies play a key role in solving this problem. By integrating highly accurate and tiny sensors, key dynamic parameters like internal pressure, pH, and mechanical stress can be captured in real time. This

successfully turns the battery from a “black box” into a clear, measurable electrochemical system.

Looking ahead, the smart management of AZIBs will move beyond basic hardware monitoring. It will focus more on separating different physical signals (multi-physics decoupling) and system-level integration. The key to building the next-generation smart BMS is to combine large amounts of sensor data with data-driven models and digital twin technology. This cloud-edge system architecture can provide accurate early fault warnings at the micro-level. At the macro-level, it can also solve problems for large battery packs in complex environments, such as state estimation, consistency management, and dynamic balancing. In summary, combining multi-modal sensing with advanced software will fundamentally improve system reliability. This will pave the way for the large-scale real-world deployment of AZIBs.

DECLARATIONS

Authors' contributions

Conceptualization: Xu, A.; Zhang, W.; Yang, K.

Data curation: Xu, A.; Wang, Y.; Zhang, G.; Yang, Y.; Tan, R.

Writing - original draft: Xu, A.

Writing - review & editing: Xu, A.; Wang, Y.; Zhang, G.; Yang, Y.; Tan, R.; Zhang, W.; Yang, K.

Supervision: Zhang, W.; Yang, K.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

During the preparation of this manuscript, the AI tool Gemini (version 3.1 pro) was used solely for language editing. Figures 1, 2, 3A and B, 4A and B, and 5 were plotted using PowerPoint, where AI-assisted tools were utilized strictly for assisting in the generation, formatting, and visual enhancement of the graphics. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

Conflicts of interest

Yang, K. is an Associate Editor of the journal *Energy Z*. Yang, Y. is affiliated with Leaf-Tech Ltd., but was not involved in any steps of editorial processing, notably including reviewer selection, manuscript handling, and decision making, while the other authors have declared that they have no conflicts of interest.

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Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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