

Electrolyte Chemistry for Zinc Halogen Flow Batteries

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Cite This: <https://doi.org/10.1021/acsenerylett.6c00406>



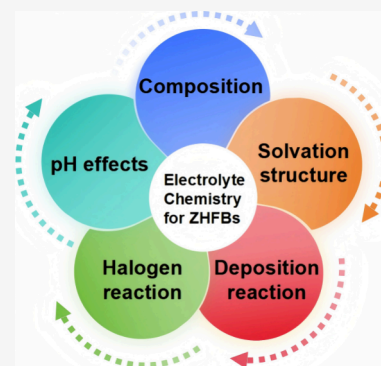
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ABSTRACT: Zinc-halogen flow batteries (ZHFBs) are promising candidates for long-duration energy storage due to their high theoretical energy density, low cost, and material sustainability. However, their practical application is hindered by persistent issues such as Zn dendrite formation and irreversible halogen redox, both of which fundamentally stem from electrolyte chemistry. This Review provides a comprehensive summary of recent progress in the electrolyte chemistry of ZHFBs, focusing on five key aspects: electrolyte composition, solvation structure, Zn deposition electrochemistry, halogen reaction behavior, and pH effects. It systematically analyzes the optimization mechanisms affecting reaction kinetics of active ions (Zn^{2+} and halides), the potentials and interfacial reactions governing Zn deposition, as well as the redox pathways of halogen species. In addition, current challenges are discussed and future research directions for electrolyte development in ZHFBs are proposed. This Review aims to offer valuable guidance for the design, optimization, and practical application of advanced electrolytes for ZHFBs.



The global energy landscape is rapidly shifting toward renewables, primarily wind and solar power.^{1,2} However, the inherent intermittency and volatility of these renewables create a critical mismatch between energy generation and consumption, driving the urgent need for long-duration energy storage (LDES) systems.³ Among various storage technologies, redox flow batteries (RFBs) have emerged as a leading candidate for LDES systems due to their unique architecture that allows independent scaling of energy capacity and output, exceptional cycle life, inherent safety, and rapid response times.^{4,5} Within various RFBs, the all-vanadium RFB has been the most commercialized system. However, their widespread application is constrained by the high and fluctuating cost of vanadium as well as their relatively low energy density.^{6,7} Consequently, there is growing research interest in alternative chemistries based on more abundant and cost-effective elements.

Zinc-based flow batteries, which rely on the Zn/Zn^{2+} plating and stripping reaction (Figure 1a), offer a compelling combination of high theoretical capacity (820 mA h g^{-1} , $5855 \text{ mA h cm}^{-2}$), low cost, natural abundance, and environmental friendliness.^{8,9} Within this family, zinc-halogen flow batteries (ZHFBs), primarily Zn–Br and Zn–I systems, are particularly attractive.^{10,11} The halogen conversion ($\text{X}^-/\text{X}_2/\text{X}_3^-$) provides a highly soluble and reversible redox couple, enabling elevated energy densities.¹² Compared to other aqueous zinc-based FBs, such as zinc–iron (Zn–Fe) and zinc–nickel (Zn–Ni), ZHFBs demonstrate distinct advantages (Figure 1b): (i) High voltage and energy density: The Zn/X redox couple delivers a higher cell voltage—particularly Zn–Br

at approximately 1.8 V, compared to Zn–Fe (~ 1.2 V) and Zn–Ni (~ 1.7 V), which directly translates into increased energy density.¹³ (ii) Abundant and low-cost materials: Both zinc and halogens are earth-abundant and significantly cheaper than elements like nickel.¹⁴ (iii) Simple system design: Unlike Zn–Fe or Zn–Ni systems, which may involve solid-phase transformations or suffer from limited solubility, the halogen catholyte in ZHFBs remains fully soluble. Besides, ZHFBs typically employ straightforward porous membranes, while Zn–Fe and Zn–Ni systems often require more complex ion exchange membranes.^{15,16}

Despite these merits, the practical realization of ZHFBs has been largely hindered by critical challenges such as Zn dendrite formation and polyhalide shuttle, both of which are inherently linked to the electrolyte chemistry.^{17,18} Over the past decades, significant research efforts have been devoted to tackling those issues, highlighting the urgent need for a comprehensive and fundamental understanding of effective optimization strategies. However, existing reviews on zinc-based batteries tend to offer broad overviews covering electrode material modifications, electrolyte and separator improvements, or multiple battery systems, including Zn–Br, Zn–I, Zn–air, Zn-ion batteries.^{19–21} What remains notably lacking is a systematic and

Received: February 8, 2026

Revised: April 20, 2026

Accepted: April 20, 2026

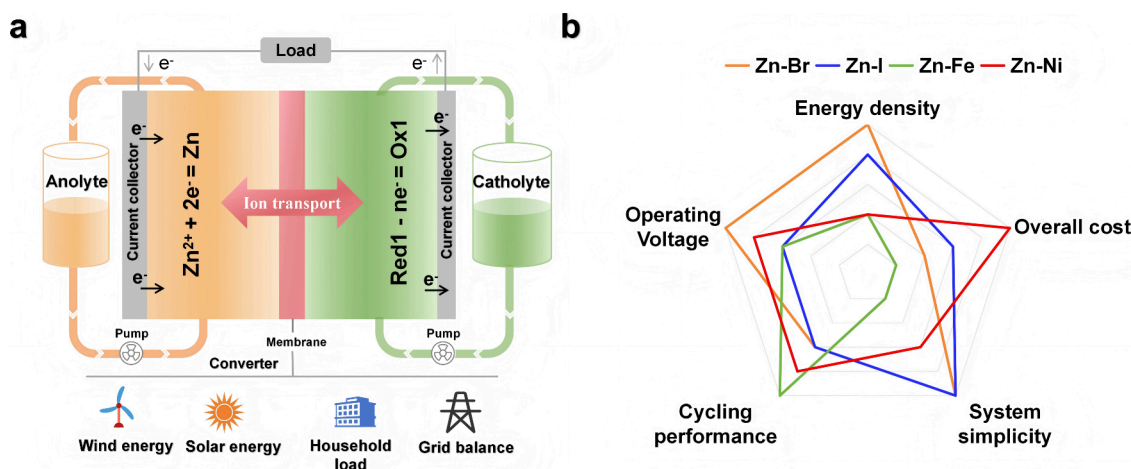


Figure 1. Status of zinc-based flow batteries. (a) Schematic diagram of a zinc-based flow battery. (b) Comparison of various zinc-based flow batteries.

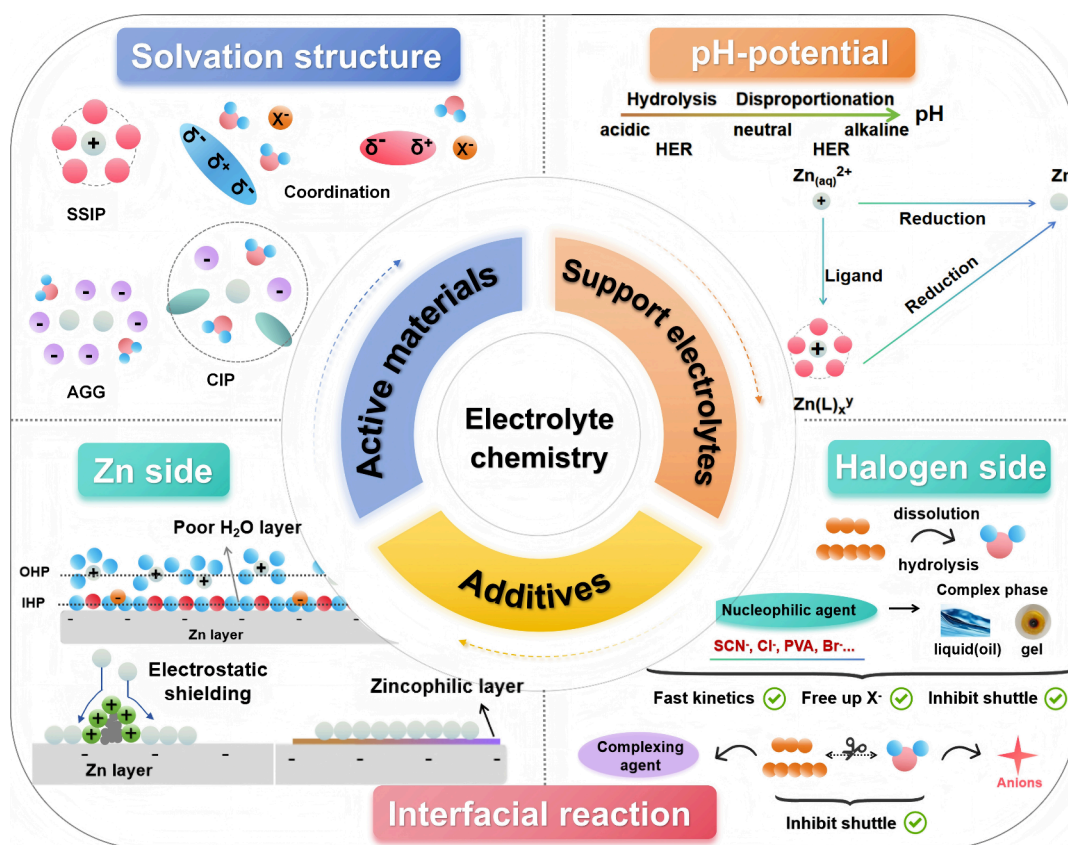


Figure 2. Illustration of electrolyte chemistry for ZHFBs including composition selection, solvation structure design, Zn deposition electrochemistry, halogen reaction behavior, and pH effect.

dedicated analysis of the electrolyte chemistry specific to ZHFBs, particularly in elucidating the complex interplay among electrolyte composition, solvation structure, interfacial electrochemical behaviors, and their collective impact on battery performance.

Herein, this Review provides a focused, in-depth, and mechanistic exploration of aqueous electrolyte chemistry in ZHFBs, covering critical aspects such as electrolyte composition selection, solvation structure design, zinc deposition electrochemistry, halogen reaction behavior, and the pH effect (Figure 2). By systematically analyzing how electrolyte

chemistry directly mitigates core failure modes of zinc dendrite formation at the negative side as well as polyhalide shuttle effect and sluggish kinetics at the positive side, this Review aims to establish a foundational framework for the rational design of advanced electrolytes. Furthermore, it highlights key challenges and future research directions related to electrolyte development in ZHFBs, addressing both fundamental scientific questions and practical industrial considerations, thereby paving the way toward more efficient, durable, and commercially viable ZHFBs.

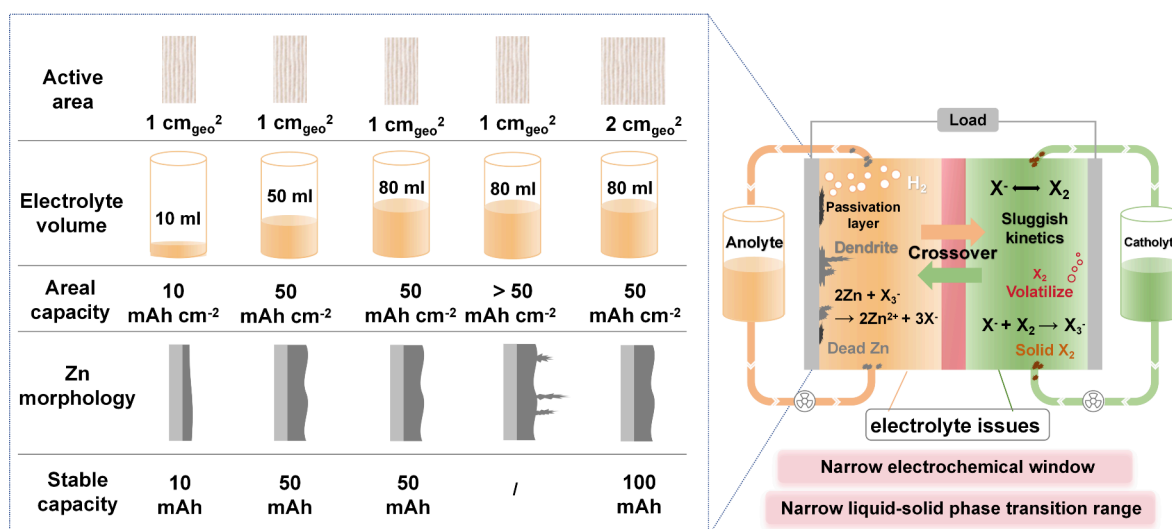


Figure 3. Challenges of ZHFBs in conventional electrolytes.

ELECTROLYTE PROPERTIES IN ZHFBs

The electrolyte in ZHFBs is far more than an ion-conducting medium; it serves as the core of the system, hosting the active species for both the anode and the cathode. Its properties govern essential processes such as charge transfer, mass transport, and interfacial stability.²² Consequently, electrolyte chemistry fundamentally determines critical performance metrics, including Coulombic efficiency (CE), voltage efficiency (VE), energy efficiency (EE), cycle life, and operational flexibility.^{23,24} Moreover, failures at the zinc anode—such as dendrite formation, hydrogen evolution, and corrosion—and at the halogen cathode—such as shuttle effects and sluggish reaction kinetics—can be directly traced to the thermodynamic and kinetic characteristics of the electrolyte system.^{25,26}

Ion Conduction

The primary function of the electrolyte in ZHFBs is to ensure rapid ion transport to maintain the charge balance during operation. Ionic conductivity (κ), which quantifies this transport efficiency, is governed by the concentration (n), charge (z), and mobility (μ) of ions ($\kappa = F \sum n_i z_i \mu_i$).²⁷ This relationship reveals a fundamental trade-off: increasing the concentration of zinc halide salts elevates the number of charge carriers, which tends to enhance the ionic conductivity. However, higher salt concentrations also increase the viscosity of solution due to stronger ion–ion and ion–solvent interactions.²⁸ Once beyond an optimal concentration, the benefit gained from a higher carrier density is overshadowed by the pronounced reduction in ion mobility, leading to a net decline in overall conductivity.²⁹

Ionic conductivity directly dictates the ohmic resistance (R_Ω) of the cell, as described by $R_\Omega = (1/\kappa) \cdot (l/A)$, where l is the distance between the two electrodes and A is the cross-sectional area of the electrodes.³⁰ A high R_Ω contributes significantly to voltage losses ($\eta_\Omega = I \cdot R_\Omega$), increasing charge voltage and reducing discharge voltage, which directly lowers the voltage efficiency ($VE = V_{\text{discharge}}/V_{\text{charge}}$).³¹ Therefore, an electrolyte with a low conductivity (high R_Ω) can reduce the VE of the system. This means that a greater fraction of the input energy is lost as heat during charging, lowering overall energy efficiency.³²

Furthermore, since power density ($P_{\text{max}} = V^2/4R$) is inversely related to total area-specific resistance, low conductivity limits the achievable power output—a constraint that intensifies at higher current densities.³³ Therefore, formulating an electrolyte with high ionic conductivity is not simply an optimization target but an essential requirement for creating high-power, high-efficiency ZHFB stacks. Such electrolytes enable rapid charging and discharging cycles with minimal energy loss, supporting a better overall battery performance.

Redox Reaction Supports

In a zinc halide flow battery (ZHFB), the electrolyte serves not only as the ionic conductor but also as the reservoir for the electroactive species responsible for energy storage. This characteristic distinguishes ZHFBs from batteries with solid-phase electrodes, such as those using Zn foil anodes and halogen element cathodes.³⁴

Notably, unlike the soluble–soluble redox chemistry in liquid–liquid RFBs such as all-vanadium, the capacity of ZHFBs is governed by the amount of Zn that can be reversibly deposited and stripped on the electrode.³⁵ This means that even if there is excess electroactive species dissolved in the electrolyte, the overall capacity can still be limited if the solid Zn deposition process encounters issues such as dendrite formation, surface passivation, or other inhibitive factors (Figure 3).²⁴

Therefore, the volumetric energy density (E_v) of a ZHFB is expressed as

$$E_v = \frac{C \cdot V_{\text{nom}}}{\text{Vol}} = \frac{C_a \cdot A \cdot V_{\text{nom}}}{\text{Vol}}$$

where C is total capacity, V_{nom} denotes the nominal discharge voltage, Vol is the total system volume, C_a is the area capacity, and A is the active area (electrode reaction area).³⁶ This equation highlights three key points: (i) Area capacity: The area capacity quantifies the amount of zinc deposition per unit area. Achieving stable cycling of ZHFBs at high area capacities requires a highly reversible zinc plating-stripping process. (ii) Active area: A larger active area permits more Zn deposition at a fixed current density and plating duration, thereby enhancing the overall capacity. (iii) Cell voltage: Variations in electrolyte composition, particularly the activity of ions and the pH, can

shift these potentials in accordance with the Nernst equation, thereby regulating the energy density of the system.

The power (P) of cell stack ($P = V \cdot I$), is fundamentally dependent on the current (I), which is defined as the amount of electric charge flowing through a circuit per unit time.³⁷ A larger reaction area allows more redox reactions to occur simultaneously, thereby increasing the amount of charge transferred per unit time. Consequently, increasing the total active area of a cell stack can simultaneously enhance its capacity and power.³⁸

■ ELECTROLYTE ISSUES IN ZINC HALOGEN FLOW BATTERIES

The practical deployment of ZHFBs is hindered by limited cycle life, low Coulombic efficiency, and poor stability—issues fundamentally rooted in the intrinsic properties of conventional aqueous electrolytes rather than mere engineering challenges.³⁹ Electrolyte chemistry, including its composition, solvation structure, and thermodynamic and kinetic properties, governs the electrochemical performance and is the primary origin of these failure modes.⁴⁰ This section focuses on elucidating how the intrinsic properties of the electrolyte constitute the primary origin of the key challenges facing ZHFBs (Figure 3).

Electrolyte Attribution for Zn Plating/Stripping Failure

The reduction potential of the Zn^{2+}/Zn couple (-0.76 V vs SHE) lies perilously close to the reduction potentials of water and protons, making the hydrogen evolution reaction (HER) an inevitable parasitic side reaction in aqueous electrolytes.^{41,42}

The HER not only consumes charge, drastically reducing Coulombic efficiency of Zn plating/stripping, but also locally increases the pH. This rise in pH promotes the formation and precipitation of zinc hydroxide and oxide passivation layers on the electrode surface.⁴³ Furthermore, even in the absence of an external current, the deposited zinc layer undergoes continuous chemical corrosion via the reaction ($\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$).⁴⁴ Halide ions can further catalyze this corrosion process, causing the self-discharge of ZHFBs.

The morphology of Zn plating is governed by ion transport and interfacial reaction kinetics. In conventional aqueous electrolytes, Zn^{2+} exists as a hexahydrate complex $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$. The desolvation of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ imposes an energy barrier that promotes uneven nucleation and the tip effect, fostering dendrite growth.⁴⁵ This phenomenon is especially pronounced at high area capacities. As the thickness of zinc deposition grows, the interfacial demand for Zn^{2+} ions surpasses the rate at which ions can diffuse from the bulk electrolyte, leading to severe concentration polarization.^{46,47} Once deposition becomes diffusion-controlled, protrusions experience enhanced ion flux due to shorter diffusion distances, accelerating localized dendritic growth in a self-perpetuating cycle.⁴⁸ These phenomena underscore that electrolyte chemistry is the fundamental origin of the Zn electrode instability.

Electrolyte Attribution for Halogen Conversion Failure

The failure of halogen conversion reactions is primarily attributed to four electrolyte-governed challenges. First, the shuttle effect arises from the diffusion of soluble elemental halogens (X_2) and polyhalides (X_3^-) across the separator, leading to parasitic oxidation of deposited zinc and rapid self-discharge ($\text{Zn} + \text{X}_2 \rightarrow \text{Zn}^{2+} + 2\text{X}^-$ and $\text{Zn} + \text{X}_3^- \rightarrow \text{Zn}^{2+} + 3\text{X}^-$).^{49,50} This crossover is dictated by the permeability of

these species, which is influenced by the efficacy of complexing agents and the physical properties of electrolyte.⁵¹ Second, the electron transfer and phase transformation inherent to the halogen redox couples of $\text{I}^-/\text{I}_2/\text{I}_3^-$ result in sluggish reaction kinetics and high polarization. The reaction rate is controlled by electrolyte factors such as local halide concentration, halogen–halogen bond strength, and mass transport.⁵² Third, the volatility and high corrosivity of generated halogens, particularly Br_2 and Cl_2 , cause active material loss and pose significant safety and component degradation risks. Finally, the reaction pathway and stability of the halogen species are highly pH-dependent. For instance, in alkaline media, elemental bromine can disproportionate into bromide and hypobromites ($3\text{Br}_2 + 6\text{OH}^- \rightarrow 5\text{Br}^- + \text{BrO}_3^- + 3\text{H}_2\text{O}$) leading to irreversible capacity loss. This sensitivity severely restricts the operable pH window for stable battery performance.⁴⁹

Intrinsic Limitations of the Electrolyte

Beyond specific electrode reactions, the overall performance of zinc-halogen flow batteries (ZHFBs) is fundamentally constrained by the intrinsic limitations of conventional aqueous electrolytes. Two universal, system-agnostic challenges are the narrow electrochemical stability window (ESW) and the limited liquid-phase temperature range.

The operational cell voltage is capped by the thermodynamic ESW of water (~ 1.23 V vs. SHE, or ~ 1.99 V vs Zn^{2+}/Zn). This imposes a critical constraint across different halogen couples. The Zn/Cl_2 (~ 2.12 V vs Zn^{2+}/Zn), Zn/Br_2 (~ 1.85 V vs Zn^{2+}/Zn), and Zn/I_2 (~ 1.30 V vs Zn^{2+}/Zn) systems operate at or beyond this practical limit, triggering the oxygen evolution reaction (OER) at the positive electrode during charging.^{53,54} The OER competes with halogen oxidation, reducing Coulombic efficiency, consuming active materials, and causing detrimental electrolyte changes (e.g., pH drift, gas evolution) that threaten long-term stability.⁵⁵ This voltage ceiling therefore represents not merely an energy density limitation but a fundamental barrier to long-term operational stability.⁵⁶

Notably, the challenges of dendrite formation, hydrogen evolution, halogen shuttling, corrosion, and pH sensitivity are common to both static and flow zinc-halogen batteries as they originate from the intrinsic properties of the Zn^{2+}/Zn couple and halogen chemistry. However, their manifestations and mitigation requirements diverge significantly due to the unique flow architecture. Continuous electrolyte circulation and the decoupling of power and energy introduce distinct demands: flow batteries require strictly homogeneous reaction environments—unlike static cells that can tolerate nonuniform polyhalide complexes—because any precipitate or gel would clog electrodes, flow channels, and pumps. They also necessitate active, system-wide pH management rather than local interfacial buffering; broader material compatibility as corrosive electrolyte contacts pumps, tubing, seals, and tanks; and extended cycling stability targeting thousands of cycles instead of hundreds. These distinctions underscore that electrolyte design for ZHFBs must transcend static-battery strategies, integrating chemical functionality with hydrodynamic compatibility, dynamic process control, and multi-component system integration to enable practical, scalable deployment.

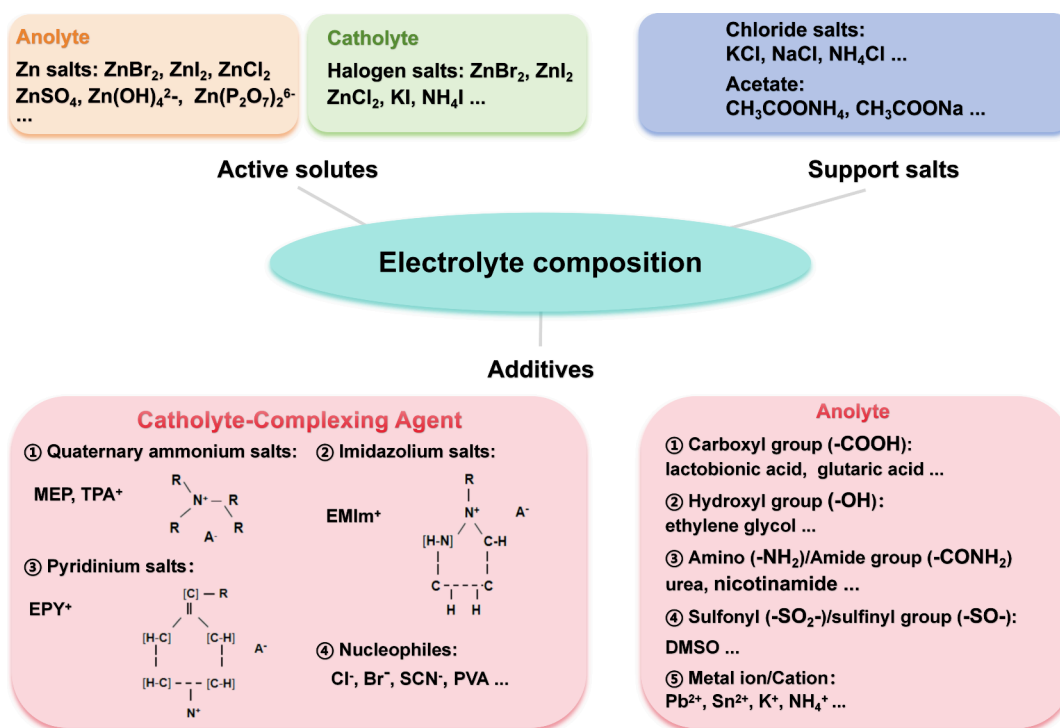


Figure 4. Electrolyte composition of ZHFBs including active solutes, supporting electrolytes, and catholyte additives or anolyte additives.

ELECTROLYTE DESIGN STRATEGIES

To overcome the fundamental challenges of ZHFBs, advanced electrolyte design strategies have emerged as a crucial approach. These strategies mainly focus on molecular-level design to precisely tailor bulk electrolyte properties, including solvation structure, Zn interfacial reactions, halogen redox reaction behavior, and the pH environment. Critically, these four aspects are not independent. The solvation structure of Zn^{2+} directly dictates its interfacial transport and HER activity, thereby governing Zn interfacial reactions, which in turn modulates local pH. Conversely, pH strongly affects halogen speciation and reaction pathways, while halide ions themselves could participate in Zn^{2+} solvation and the solvation structure of halide ions can also affect the kinetics of halide reactions.

Electrolyte Composition

The foundational step in electrolyte regulation is the rational selection of its core components, involving a deliberate choice of active solutes, supporting salts, and functional additives (Figure 4). The choice of composition directly determines the solvation structures, reaction behavior, and pH, which will be discussed subsequently.

Active Solutes. The active solute is the cornerstone of the electrolyte, which supplies the electroactive species for energy storage. For the anolyte, the primary requirement is a source of Zn^{2+} ions. For the catholyte, the active material is a halide ion (X^-). Zn halide salts (e.g., ZnBr_2 , ZnCl_2) are the most common choice, serving as a combined source for both the Zn anolyte and the halogen catholyte.^{57,58} Besides, advanced configurations may employ separate anolytes and catholytes with distinct active solutes to independently optimize the reactions at each electrode. For example, ZnSO_4 is selected as active solute of anolyte, and KI, NH_4I , or KBr is the active solute of catholyte, where ZnSO_4 have been widely studied in static zinc-ion batteries, and K^+ or NH_4^+ cations can influence the solubility of polyiodides and the electrochemical double

layer.⁵⁹ Furthermore, in alkaline electrolytes, Zn source can exist as the complex anion such as $\text{Zn}(\text{OH})_4^{2-}$ or $\text{Zn}(\text{P}_2\text{O}_7)_2^{6-}$, which significantly alters the deposition mechanism, particularly, the Zn deposition potential.⁶⁰

Notably, the concentration of the active solute is a key parameter of ZHFBs. Increasing the concentration of active solutes will increase the number of charge carriers, thereby delivering more capacity of ZHFBs. However, when the concentration exceeds a certain critical point, it will lead to higher electrolyte viscosity due to enhanced ion–ion and ion–solvent interactions.⁶¹ This can decrease the ionic conductivity of the electrolyte, as the benefit of more charge carriers is eventually overshadowed by their reduced mobility. Moreover, high-concentration electrolytes, especially “water-in-salt” electrolytes, can reduce water activity.⁶² However, they can also accelerate corrosion and, if approaching the saturation limit, there is a risk of salt crystallization during operation.⁶³

Supporting Salts. The supporting salts are composed of electrochemically inert cations and anions such as KCl, NaCl, NH_4Cl , $\text{CH}_3\text{COONH}_4$, and CH_3COONa . Their primary function is to enhance ionic conductivity by increasing the total concentration of charge carriers.⁶⁴ Especially in concentrated zinc halide solutions, the supporting ions could provide alternative conduction pathways to mitigate the conductivity loss caused by the viscous zinc halide matrix.⁶⁵ However, excessive concentration of supporting salts can induce ion pairing and increase viscosity.⁶⁶

Beyond affecting the bulk transport properties, the supporting salts can also regulate the interfacial electrochemistry and ion–solvent interactions. The cation species in the supporting salt significantly influences the Zn deposition morphology through interfacial effects.⁶⁷ For example, NH_4^+ cations exhibit unique behavior by adsorbing preferentially onto the Zn deposition layer. This adsorption creates a cationic shielding layer that homogenizes the interfacial electric field,

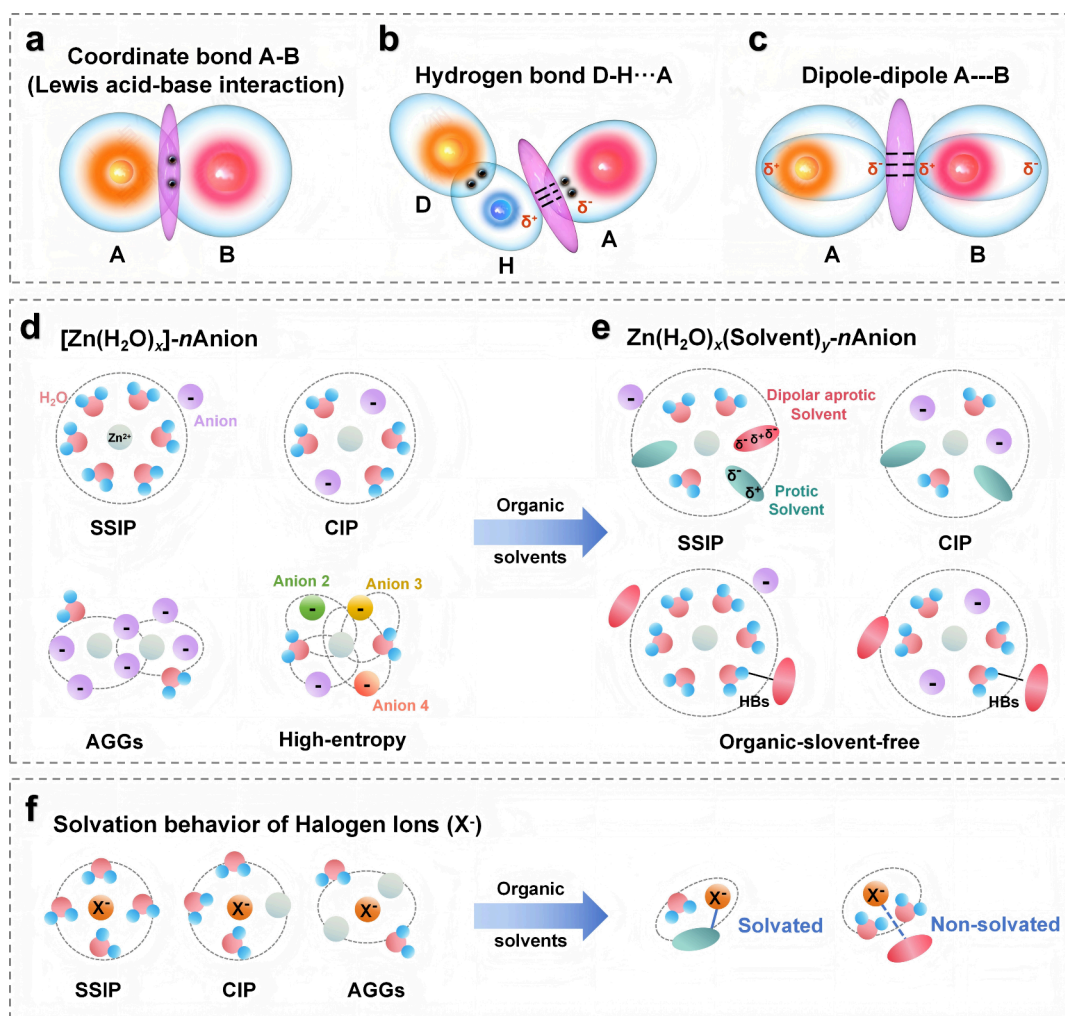


Figure 5. Solvation structure design. The formation mechanisms of (a) coordination bonds, (b) hydrogen bonds, and (c) dipole–dipole interactions. Solvation structure of (d) the $[\text{Zn}(\text{H}_2\text{O})_x]\text{-}n\text{Anion}$ type and (e) $\text{Zn}(\text{H}_2\text{O})_x(\text{Solvent})_y\text{-}n\text{Anion}$ type. (f) Solvation behavior of halogen ions.

promoting lateral Zn growth and suppressing dendrite formation.⁶⁸ Besides, among alkali metal cations of supporting salts, the effectiveness of promoting uniform Zn deposition follows the trend $\text{K}^+ > \text{Na}^+ > \text{Li}^+$, which correlates with their hydrated radii and adsorption energies.⁶⁹ K^+ , with the weakest hydration, readily approaches the electrode interface, compacting the double layer and homogenizing the electric field.⁷⁰ This promotes uniform nucleation and dense Zn plating, whereas the strongly hydrated Li^+ creates a diffuse layer, favoring dendritic growth.⁷¹ The anion component, typically Cl^- , plays a complementary role in modifying the Zn^{2+} solvation structure. Cl^- ions can displace water molecules to enter the primary solvation shell of Zn^{2+} , forming contact ion pairs (ZnCl_x^{2-x}), thereby reducing water activity at the electrode interface and increasing the overpotential for hydrogen evolution. Additionally, this solvation structure modification alters the dehydration kinetics of Zn^{2+} , influencing nucleation behavior.⁷²

Electrolyte Additives. Additives as a functional component can selectively influence interfacial reactions, solvation structures, and mass transport, thereby addressing the core failure modes of dendrite formation and halogen shuttle with high efficiency.

In catholytes, complexing agents are mainly added to suppress halogen shuttle, which can be divided into four classes of quaternary ammonium salts, imidazolium salts, pyridinium salts, and nucleophiles. The common quaternary ammonium salts are MEP (*N*-methyl-*N*-ethylpyrrolidine bromide), TPABr (Tetrapropyl ammonium bromide), the typical imidazolium salts are EMImBr (1-ethyl-3-methylimidazolium bromide), and the familiar pyridinium salts are EPYBr (1-ethylpyridinium bromide).^{73–75} All of them can bind with polyhalide anions, especially tribromide ions (Br_3^-) through electrostatic interactions, subsequently forming a dense, water-immiscible liquid phase due to hydrophobic interactions.^{75,76} Their complexing ability is closely related to their molecular structure, which will be discussed in detail later. The nucleophiles usually shift the equilibrium ($\text{X}^- + \text{X}_2 \rightleftharpoons \text{X}_3^-$) toward the direction of the reactants to suppress shuttle, especially for Zn–I flow batteries. The Cl^- , Br^- , SCN^- , and PVA can bind with I_2 , forming I_2Cl^- , I_2Br^- , I_2SCN^- , and $\text{I}_2\text{-PVA}$ liquid phase or gel complexes, respectively, to inhibit the formation of I_3^- shuttle.^{77–80}

In anolyte, the additives aim to achieve uniform Zn deposition by modifying the electrode–electrolyte interface, which can be divided into the following five categories according to functional groups: (i) Carboxyl Group

($-\text{COOH}$). Molecules like lactobionic and glutaric acids strongly adsorb onto the Zn deposition layer, promoting a larger number of nucleation sites and a finer-grained deposit. Additionally, they can weakly coordinate with Zn^{2+} in the bulk electrolyte, subtly altering the solvation structure.^{81,82} (ii) Hydroxyl Group ($-\text{OH}$). The type of additives such as ethylene glycol can form hydrogen bonds with water molecules to disrupts the water network, increasing the overpotential for HER.⁸³ (iii) Amino ($-\text{NH}_2$)/Amide Group ($-\text{CONH}_2$). Urea and nicotinamide are prominent examples. These groups can adsorb on the Zn surface and participate in the solvation shell of Zn^{2+} , modifying deposition kinetics.⁸⁴ (IV) Sulfonyl ($-\text{SO}_2-$)/Sulfinyl Group ($-\text{SO}-$). Compounds like 3,3'-bipyridinesulfonate and dimethyl sulfoxide (DMSO) are potent water-molecule regulators. Their strong polarity allows them to effectively compete with water molecules for coordination sites around Zn^{2+} , creating a water-poor inner solvation shell suppressing HER.⁸⁵ (V) Metal ions/Cations. The inorganic additives can function through preferential deposition or adsorption. For example, Pb^{2+} and Sn^{2+} have high hydrogen evolution overpotentials and can preferentially deposit in comparison to Zn^{2+} deposition, forming a protective layer.^{86,87} K^+ and NH_4^+ , as discussed previously, modulate the electric double layer and exhibit a strong cationic shielding effect to promote dense deposition.^{88,89}

SOLVATION STRUCTURE DESIGN

Building upon a given electrolyte composition, the solvation structure design represents the first critical step in translating bulk properties into desired interfacial behavior. Solvation structure, the spatial arrangement and interaction between solute ions and solvent molecules, governs key processes such as ion transport kinetics, interfacial stability, and parasitic reactions (e.g., HER or shuttle effect). Rational design of the solvation structure can significantly enhance the cycling life, energy efficiency, and capacity of ZHFBs. In this section, the formation mechanisms of solvation structures are dissected. In addition, the limitations of solvation structure in conventional electrolytes are analyzed and the advanced strategies for optimizing Zn^{2+} and halide ion (X^-) solvation environments are outlined.

Formation Mechanisms of Solvation Structures

The solvation structure of the central ion (Zn^{2+} or halide ion) in an electrolyte is a hierarchical entity primarily consisting of a primary solvation shell (inner sphere) and a secondary solvation shell (outer sphere).⁹⁰ The solvation structure forms through a complex interplay of intermolecular forces. The most fundamental forces are coordination bonds (Lewis acid–base interactions), hydrogen bonding, and dipole–dipole interactions.⁹¹ The relative strength and synergy of these forces determine the final spatial arrangement, stability, and dynamics of the solvation structure.

Coordination bonds represent the primary and strongest interactions in forming the primary solvation shell, which directly impact the desolvation energy barrier. This interaction is fundamentally a Lewis acid–base reaction, where the metal ions (Zn^{2+}) act as the electron-pair acceptor (Lewis acid) and a solvent molecule or anion functions as the electron-pair donor (Lewis base) (Figure 5a).⁹² The strength of the Zn^{2+} -solvent coordination is predominantly influenced by the donor number (DN) and polarizability of the solvent. The donor number, a quantitative measure of Lewis basicity, reflects its

ability to donate an electron pair to the central Zn^{2+} . Solvents with a high DN, such as dimethyl sulfoxide (DMSO), form stronger and more stable coordinate bonds with Zn^{2+} compared to weaker donors like water.⁹³ Concurrently, the polarizability, quantified by the ease of electron cloud distortion, influences the covalent character of the bond. Highly polarizable solvent can engage in more effective orbital overlap with Zn^{2+} , leading to stronger interactions. For the coordination strength between Zn^{2+} and anion, the higher charge and smaller radius of anions result in greater charge density, strengthening the electrostatic attraction (e.g., $\text{SO}_4^{2-} > \text{Ac}^- > \text{NO}_3^- > \text{Cl}^- > \text{BF}_4^- > \text{ClO}_4^- > \text{CF}_3\text{SO}_3^- > \text{TFSI}^-$).²² However, for the anions with a large radius, polarizability, that is, the ease with which the electron cloud distorts, must be considered. Highly polarizable anions (e.g., I^- , SCN^- , TFSI^-) induce additional polarization interactions or charge transfer, thereby enhancing the overall coordination strength.⁹⁴ The strong coordination interactions within the primary solvation shell enhance structural stability; they concomitantly raise the desolvation energy barrier.

Hydrogen bonds (HBs) govern the secondary solvation shell and the extended solvent network. The HBs typically occur between solvent molecules and between solvents and anions, influencing the mobility of ions and the overall viscosity of the electrolyte. More critically, the HBs can occur between the primary solvation shell and the outer solvent molecules, mediating the exchange of solvent molecules. The HBs exhibit partial covalent character and are defined as an electrostatic attraction between a hydrogen atom covalently bonded to a highly electronegative atom (HB donor, D) and another electronegative atom bearing a lone pair of electrons (HB acceptor, A). The general notation of HBs is $\text{D}-\text{H}\cdots\text{A}$ (Figure 5b).⁹⁵ The HBs are typically stronger than van der Waals forces but weaker than the coordination bonds. The strength of HBs arises with the polarity of the D–H bond and the electron density of HB acceptor A. Besides, it is also enhanced by a shorter $\text{H}\cdots\text{A}$ distance and is maximized when the D–H $\cdots$ A angle approaches 180° due to optimal orbital overlap and electrostatics. Strong HBs among solvents or between solvents and ions can restrict the activity of the solvents or stabilize the solvated ions.⁹⁶

Dipole–dipole interactions are essential for the solvation of ions by polar aprotic solvents and for the overall stability of the solvation structure. The interactions are universal electrostatic forces between molecules with permanent dipole moments (Figure 5c). A polar solvent molecule possesses a permanent dipole moment. When an ion is introduced, the electric field of the ion exerts a torque on the solvent dipoles, causing them to reorient to align their opposite charges toward the ion, a process sometimes described as electrostriction. The strength of the interaction is proportional to the product of the involved dipole moments and inversely proportional to the cube of the distance between them, which is weaker than both the coordination and hydrogen bonds. The strong dipole–dipole interactions between polar solvents and ions could promote salt dissociation, thereby weakening the interactions between cations and anions and thus increasing the free ion concentration.⁹⁷

The formation of distinct ion-pairing configurations—solvent-separated ion pairs (SSIP), contact ion pairs (CIP), and ion aggregates (AGGs)—is governed by the competitive balance between cation–solvent, cation–anion, and solvent–solvent interactions (Figure 5d).⁹⁸ In an SSIP, ions are fully

solvated and separated by at least one solvent layer, where strong cation–solvent coordination effectively screens the direct Coulombic attraction. A CIP forms when an anion directly coordinates to the cation, entering its primary solvation shell. This occurs when the combined Lewis acid–base interaction and Coulombic attraction between the ion pair overcome the binding energy of the displaced solvent molecule. The progression of this anion-for-solvent substitution can lead to AGGs, where anions bridge multiple cations, forming clusters dominated by intensive ion–ion interactions.⁹⁹

Solvation Structure of Zn^{2+}

In conventional aqueous electrolytes, especially in a conventional anolyte, Zn^{2+} ions predominantly exist as the SSIP structure, specifically the octahedral $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ complex. This solvation structure presents several intrinsic drawbacks for zinc anode reversibility: (i) The strong polarization of coordinated H_2O molecules weakens the O–H bond, lowering their reduction potential and intensifying the hydrogen evolution reaction (HER). (ii) The high thermodynamic stability of the complex translates into a high desolvation energy barrier, slowing Zn^{2+} charge transfer kinetics. (iii) The abundance of active water at the electrode–electrolyte interface promotes parasitic reactions and byproduct formation.²⁹

A well-established strategy to mitigate these issues involves modulating the solvation structure to transform the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ SSIP into CIP or AGGs (Figure 5d). This can be achieved by using Zn salts with higher lattice energy, increasing the concentration of typical Zn salts, or introducing species with high Zn^{2+} affinity (e.g., halide ions like I^- or Cl^-). These anions can partially displace water molecules from the primary solvation shell to form a CIP—a process rooted in the enhanced coordination interaction between the anion and Zn^{2+} . In the resulting mixed solvation shell $[\text{Zn}(\text{H}_2\text{O})_{6-x}(\text{anion})_x]$, electron-donating anions reduce the electron deficiency of the remaining coordinated H_2O molecules. Computational studies on model solvation clusters suggest that this modification is associated with an increase in the energy of the lowest unoccupied molecular orbital (LUMO), an indicator that is often correlated with improved reduction stability of coordinated water.¹⁰⁰ This elevated LUMO energy is considered to raise the thermodynamic barrier for the reduction of H^+ , thereby contributing to the suppression of the HER. However, it is important to recognize that in bulk aqueous electrolytes, HER inhibition arises from collective solvation effects, including the disruption of the hydrogen-bond network, altered interfacial electric double layer, and reduced water activity, rather than from isolated molecular orbital changes alone.

The total capacity of ZHFBs hinges on the amount of zinc that can be reversibly deposited and stripped on the electrode.

With stronger ion-pairing, these CIPs can further associate into water-lean AGGs (e.g., ZnCl_4^{2-}), drastically reducing overall water activity.¹⁰¹ However, this conventional approach of promoting strong anion coordination has inherent trade-offs: while effectively minimizing free water, it can significantly

increase electrolyte viscosity, slightly compromise ionic conductivity, and in the case of dense AGGs, may even raise the Zn^{2+} desolvation barrier, counteracting the initial kinetic benefit.¹⁰² Higher viscosity increases pressure drop and pumping power, reducing overall system efficiency—a key concern for grid-scale storage, where round-trip efficiency dictates economic viability. It may also slow convective mass transport, exacerbating concentration polarization at high current densities and partially offsetting the benefits of reduced water activity.

An innovative design is the high-entropy solvation strategy, inspired by the modification strategy of static zinc-based batteries. This approach utilizes a mixture of different anions—typically including various halide ions—to create a diverse solvation environment. The term “high-entropy” here is used conceptually to describe the increased compositional complexity and configurational disorder introduced by the multianion mixture. This structure prevents the system from forming a single, dominant, and strongly bound solvation structure (such as a specific multihalogenated AGG). Instead, it promotes a tailored distribution of various contact ion pairs (CIPs) and anion-aggregated structures (AGGs). For example, in the 2 M ZnSO_4 base electrolyte with 0.02 M additions of ZnCl_2 , ZnBr_2 , and ZnI_2 , the competitive coordination among the different halide ions results in a solvation sphere dominated by monohalogenated CIPs.⁹⁸ This specific composition avoids the excessively high desolvation energy typically associated with homogeneous multihalogenated AGGs, thereby optimizing Zn^{2+} transport kinetics. The primary consideration for this strategy is the increased formulation complexity of the electrolyte.

Another prominent strategy involves the introduction of organic solvent additives. Organic additives are broadly categorized into protic solvents and polar aprotic solvents, each exhibiting distinct mechanisms in modulating the solvation structure based on their molecular structure and interactions with ions (Figure 5e). The protic solvents, characterized by the presence of protons that can donate hydrogen bonds, function as Lewis bases to coordinate with Zn^{2+} and as HB donors to interact with anions or other water molecules.¹⁰³ The dipolar aprotic solvents have a nonsolvation effect on anions, resulting from the outer negative charge and the inner positive charge in structure, coupled with the absence of HB donors. The relatively weak interaction of cations and anions of salts could promote participation of both protic solvent and dipolar aprotic solvents in the primary solvation shell of Zn^{2+} , forming an SSIP solvation shell. When the interaction between cations and anions is relatively strong, the protic solvents can incorporate into the Zn^{2+} primary solvation shell, partially replacing water, to form a CIP shell. The Zn^{2+} –organic solvent strategy is currently the most common solvation regulation strategy for ZHFBs, which can effectively inhibit water-related side-reactions. However, due to the strong coordination interaction between Zn^{2+} and organic solvent molecules, it leads to slow Zn^{2+}/Zn charge transfer kinetics.

Drawing on the solvation modification measures of static zinc-based batteries, the construction of a weak solvation structure with an organic solvent-free primary shell can effectively promote fast reaction kinetics while limiting H_2O side reactions. Introducing a small amount of dipolar aprotic solvents under weak ion-pairing conditions favors the dipolar aprotic solvent exclusion from the Zn^{2+} primary shell, creating organic solvent-free solvation structure.⁸⁵ Besides, when the

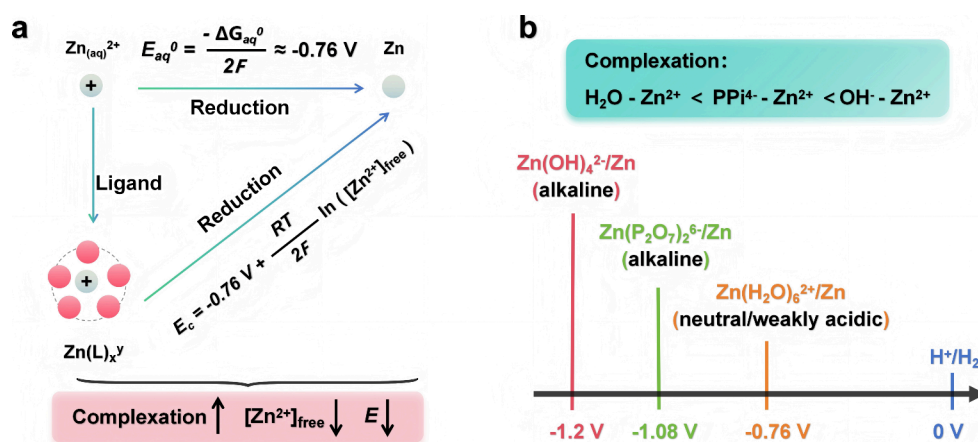


Figure 6. Zn deposition potential. (a) The relationship between the Zn deposition potential and Zn²⁺ coordination environment. (b) Deposition potentials of Zn(OH)₄²⁻, Zn(P₂O₇)₂⁶⁻, and Zn(H₂O)₆²⁺.

interaction between cations and anions is relatively strong, the dipolar aprotic solvents are more likely to be excluded from the inner coordination sphere of Zn²⁺, forming an organic solvent-free solvation environment.¹⁰⁴

Notably, this HER suppression mechanism is primarily electrolyte-driven as it originates from modified solvation chemistry that reduces water availability and alters the LUMO energy of coordinated species. However, the actual HER rate at the electrode interface also depends on the adsorption energy of hydrogen intermediates on the Zn surface—a factor that can be influenced by the electric double layer composition, which is itself affected by electrolyte ions. Therefore, while solvation engineering provides the fundamental thermodynamic basis for HER mitigation, the observed kinetic improvements may involve coupled electrolyte–electrode effects.

Solvation Behavior of Halogen Ions

The solvation structure of halogen ions critically governs the oxidation kinetics by influencing both the desolvation activation energy and the mass transport. However, the solvation structures of halogen ions have rarely been studied or reported in ZHFBs. The oxidation reaction of 2X⁻ → X₂ + 2e⁻ begins with the desolvation from the solvation shell. The energy barrier of this process is highly dependent on the solvation strength. The inherent physicochemical properties of halogen ions, such as ionic radius, charge density, and polarizability, fundamentally preset their solvation tendency. In aqueous environments, small ions with high hydration energy like Cl⁻ tend to formSSIP structures, tightly surrounded by water molecules. Although this strong solvation results in good solubility and high ionic conductivity, it also creates a high desolvation energy barrier, leading to sluggish kinetics for the Cl₂ evolution reaction. In contrast, large ions with weak hydration like I⁻ exhibit more significant direct electrostatic attraction to counter-cations (Zn²⁺) in solution, readily forming CIPs, and further assembling via halogen bridging. Such structures make I⁻ more easily desolvated from the coordination shell, thus exhibiting faster oxidation kinetics. However, the relatively loose solvation also makes its oxidation products (e.g., I₃⁻) more soluble and mobile, triggering severe shuttle effects. Br⁻ exhibits intermediate behavior, shifting fromSSIPs at a low concentration to CIPs at a high concentration.

With the introduction of organic solvents, protic solvents (e.g., alcohols) and dipolar aprotic solvents (e.g., DMSO)

create two distinct solvation microenvironments for halogen ions due to their different molecular structures. Protic solvents could solvate halogen ions via ion-dipole interactions and HBs, increasing the desolvation barrier by the breaking of HBs. The dipolar aprotic solvents with an inner positive charge and the absence of HB donors interact weakly with halogen ions, enhancing relative attraction between cations and halogen ions to form a CIP/AGG structure. This can lower the desolvation barrier, but the formation of large ion pairs may lead to slow diffusion.

It is important to note that these insights into solvation structures, often derived from static or equilibrium battery studies, operate within a dynamic environment in actual flow batteries. The continuous flow of electrolyte affects local concentrations at the electrode interface, mass transport of all species, and shear force near surfaces. Parameters such as flow rate and electrode architecture determine the residence time of electrolyte in the reaction zone, which can influence the steady-state composition of the interfacial solvation layer and, consequently, the kinetics of Zn²⁺ or X⁻ ion desolvation. Therefore, optimizing solvation structures for ZHFBs requires a consideration of their stability and function under convective flow, not just in a quiescent state.

Electrode Potential for Zn Deposition

The electrode potential for the Zn deposition—one of the critical parameters influencing ZHFB performance—is the direct manifestation of the solvation structures discussed previously. Together with the halogen reaction potential, the Zn deposition potential determines the theoretical voltage of the ZHFBs. The more negative the Zn deposition potential, the higher the open-circuit voltage of ZHFBs typically becomes.

The coordination surroundings of Zn²⁺ ions govern the Zn deposition potential. For the Zn deposition reaction, Zn²⁺ + 2e⁻ ⇌ Zn(s), its equilibrium electrode potential (*E*) is determined by the Nernst equation:

$$E = E^0 + \left(\frac{RT}{2F} \right) \ln([Zn^{2+}]_{\text{free}})$$

where *E*⁰ is the standard electrode potential (−0.76 V vs SHE), *R* is the gas constant, *T* is the absolute temperature, *F* is the Faraday constant, and [Zn²⁺]_{free} is the free activity of Zn²⁺ (Figure 6a).¹⁰⁵

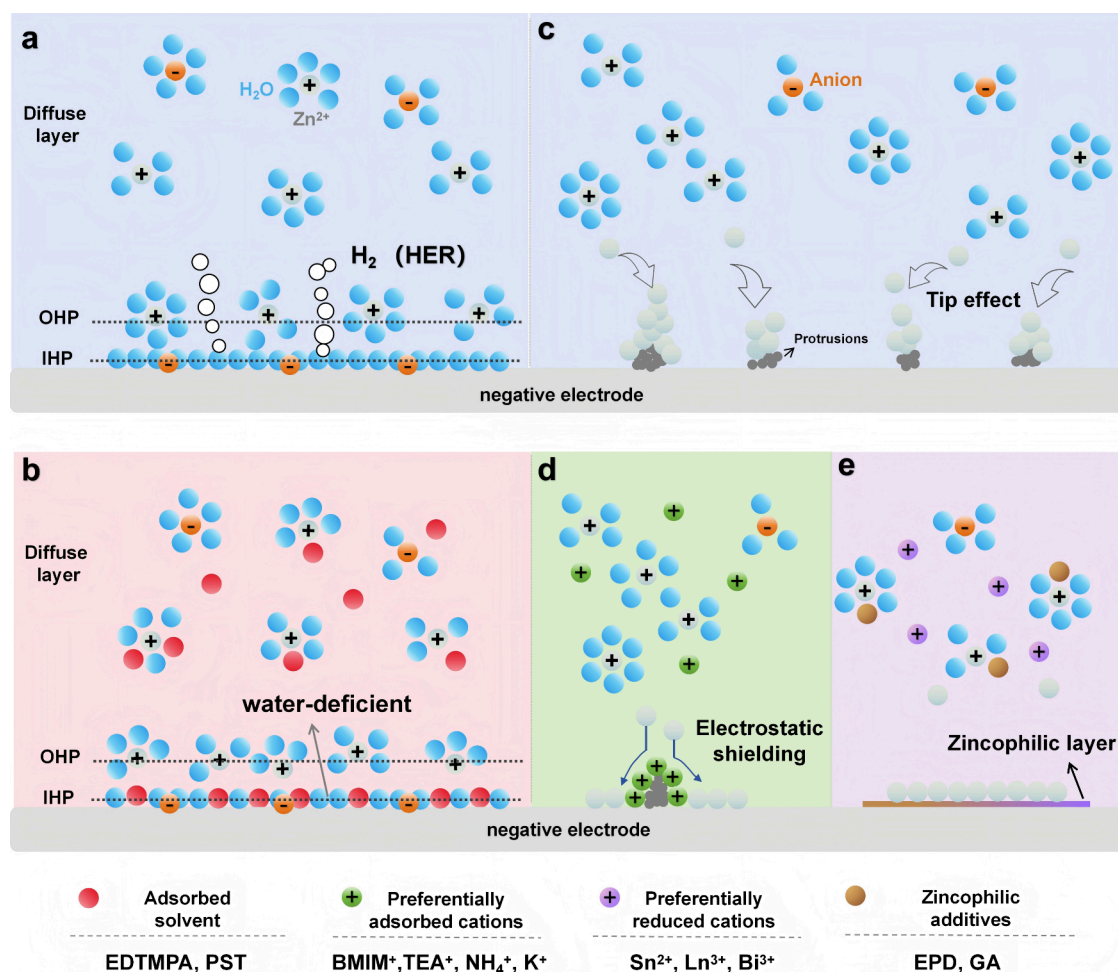


Figure 7. Zn deposition is interfacial electrochemistry. Schematic diagram of (a) the electric double layer in a conventional electrolyte, (b) the optimized electric double layer, (c) Zn nucleation and growth in a conventional electrolyte, (d) electrostatic shielding modification, and (e) zincophilic layer modification.

In a conventional aqueous anolyte, Zn^{2+} ions exist primarily as simple hydrated ions of $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, which makes $[\text{Zn}^{2+}]_{\text{free}}$ near the Zn^{2+} concentration of 1 mol/L. In this case, Zn deposition potential is close to the standard value of -0.76 V vs SHE. When anions or organic solvent molecules replace solvated H_2O molecules to form stronger coordination bonds with Zn^{2+} , the free activity of Zn^{2+} is further reduced, leading to a more negative deposition potential. For example, in ZnCl_2 with potassium pyrophosphate ($\text{K}_4\text{P}_2\text{O}_7$), the Zn^{2+} ions exist as $\text{Zn}(\text{P}_2\text{O}_7)_2^{6-}$ clusters. The strong coordination between Zn^{2+} ions and $\text{P}_2\text{O}_7^{4-}$ anions shifts the Zn deposition potential to -1.08 V vs SHE and correspondingly raises the voltage of zinc–iodine flow batteries to 1.61 V.¹⁰⁶ Additionally, in common alkaline anolytes, Zn ions form stronger coordination with OH^- , resulting in the formation of $\text{Zn}(\text{OH})_4^{2-}$. This shifts the Zn deposition potential to a more negative value of -1.21 V vs SHE, thereby further increasing the cell voltage (Figure 6b).³⁶

Although a negative shift in Zn deposition potential increases the battery voltage, an excessively negative deposition potential leads to unstable Zn deposition and aggravates the HER.⁹⁰ A more negative deposition potential corresponds to a stronger driving force for Zn deposition, which causes a significant increase in the number of nucleation sites. Consequently, a large number of fine crystal nuclei

instantaneously generate on the electrode surface. However, as these nuclei form too rapidly, they may fail to establish robust bonding with the substrate, leading to unstable Zn deposition. The equilibrium potential for the HER (E_{HER}) remains fixed under constant pH conditions. When strong ligands shift the Zn deposition potential to more negative values, a more negative applied working potential (E_{applied}) must be used. Consequently, the overpotential for HER, defined as $\eta_{\text{HER}} = |E_{\text{applied}} - E_{\text{HER}}|$, increases further.¹⁰⁷ Since the electrode reaction current follows an exponential dependence on overpotential as described by the Butler–Volmer equation, the elevated overpotential resulting from a more negative zinc deposition potential ultimately enhances the HER kinetics.

Beyond this straightforward overpotential argument, it is important to recognize that the modified solvation environment may also influence other kinetic parameters governing HER. For instance, changes in the Zn^{2+} coordination shell can alter the exchange current density (i_0) for HER by modifying the availability and reactivity of proton donors at the electrode interface.¹⁰⁸ Additionally, the electrode surface state—including the coverage of adsorbed intermediates and the nature of active sites—may be affected by the presence of strongly coordinating ligands or organic additives.^{109,110} In some cases, the dominant HER pathway (Volmer–Heyrovsky

vs Volmer–Tafel) could even shift under significantly altered interfacial solvation conditions.^{111,112} These factors collectively determine the net HER rate rather than overpotential alone. Therefore, while the increased overpotential provides a primary driving force, a complete understanding requires considering the coupled effects of solvation-modified exchange current density and surface reactivity.

Notably, in the alkaline anolyte, the strong ligand OH[−] itself participates in the HER. At sufficiently negative Zn deposition potentials, a vigorous HER consumes a large amount of H⁺ (or H₂O), leading to a rapid increase in pH at the electrode/electrolyte interface. This elevated pH favors the more stable formation of the Zn(OH)₄^{2−} cluster, which can further shift the Zn deposition potential to more negative values. As a result, HER is further exacerbated, creating a self-amplifying detrimental cycle that couples thermodynamic potential shifts with kinetic feedback. As a result, HER is further exacerbated, creating a self-amplifying detrimental cycle.¹¹³

Interfacial Electrochemistry during Zn Deposition

As mentioned in [Redox Reaction Supports](#), Zn deposition behavior at the negative electrode is critical for the capacity of ZHFBs. Zn deposition behavior is a direct consequence of the solvation structures discussed previously. The overpotential for nucleation and growth, as well as the competition with side reactions like hydrogen evolution, is profoundly influenced by the desolvation energy and the local chemical environment created by the engineered solvation sheath. Analyzing these interfacial processes provides the essential link between molecular-scale electrolyte design and the macroscopic cycling performance. This section will systematically elaborate on the main challenges during Zn deposition in conventional anolytes and detail current mainstream regulation strategies based on anolyte design.

The core of the Zn plating–stripping process occurs at the solid–liquid interface between the negative electrode and the anolyte. This interface is not an ideal geometric plane but possesses a complex structure of charge distribution and ion arrangement, known as the electrochemical double layer (EDL) ([Figure 7a](#)).¹¹⁴ The formation of the EDL originates from charge transfer, ion adsorption, or the oriented arrangement of dipole molecules when the electrode contacts the anolyte solution. The classical Gouy–Chapman–Stern model describes the EDL as comprising three key regions: the inner Helmholtz plane (IHP), outer Helmholtz plane (OHP), and diffuse layer. The IHP is the layer closest to the electrode surface, formed by partially desolvated anions or specifically adsorbed molecules tightly bound to the electrode surface through chemical or physical interactions.¹¹⁵ The OHP is located outside the IHP and is composed of solvated zinc ions arranged under electrostatic attraction. The diffuse layer is the region extending outward from the aqueous surface of the OHP to the bulk anolyte, where ion distribution is governed by both electrostatic interactions and thermal diffusion. In conventional anolyte, the IHP is typically composed of partially desolvated anions and a large number of free water molecules, resulting from the hydrated ions of [Zn(H₂O)₆]²⁺. However, in this IHP, the highly active free water molecules on the electrode surface are prone to undergo vigorous HER, consuming electrons and protons to produce H₂ and OH[−]. Furthermore, the H₂ bubbles generated and the passivation byproducts formed from the combination of OH[−] with Zn²⁺ and anions can block the active sites for Zn deposition on the

electrode surface. This blockage elevates the ion transport resistance and induces uneven zinc plating ([Figure 7a](#)).

The key counter-strategy addressing the above issue is to reconstruct the EDL, repelling or replacing free water molecules within the IHP ([Figure 7b](#)). The common approaches include the following: (i) Introducing polar or amphiphilic molecules with strong adsorption capabilities replaces the free water in the IHP. (ii) Engineering the Zn²⁺ solvation sheath by incorporating strong-adsorbing solvents displaces solvation water, thereby reducing water cotransport to the IHP. Li et al. discovered that ethylenediamine tetramethylene phosphonic acid (EDTMPA) with six potent zincophilic sites can preferentially adsorb onto the IHP over H₂O, thereby creating a water-deficient IHP. This enabled stable Zn plating/stripping cycling for 800 h at 40 mA cm^{−2}, approximately three times longer than that in the baseline anolyte.¹⁰⁴ Additionally, Tang et al. developed a water-deficient IHP by introducing potassium sodium tartrate (PST) to form a solvation structure of Zn(OH)₂(H₂O)(PST) in place of solvated water. The system sustained the cycling of Zn plating/stripping for 180 h, significantly outperforming the control (~80 h) that contained ample solvated water.³⁶

Fundamentally, Zn deposition is a phase transition where solvated Zn²⁺ ions accept electrons at the electrode interface to form metallic Zn. In conventional anolyte (typically ≤ 2 M in concentration), this process is highly prone to nonuniform nucleation and growth, ultimately leading to the formation of Zn dendrites. The root cause lies in a self-reinforcing vicious cycle triggered jointly by mass transport limitations and interfacial reaction kinetics. First, once deposition begins, the interfacial Zn²⁺ ions are rapidly consumed. The Zn²⁺ diffusion from the bulk anolyte cannot replenish the consumed Zn²⁺ due to the limited concentration and the low transference number of Zn²⁺, which creates a pronounced concentration polarization.¹¹⁶ Under the diffusion-controlled regime driven by concentration polarization, the initially formed nuclei can preferentially capture and consume the vast majority of surrounding Zn²⁺ by virtue of their positional or size advantages, leading to rapid growth and the formation of initial protrusions. Subsequently, the stable [Zn(H₂O)₆]²⁺ solvation sheath easily undergoes desolvation on these protrusions due to their intensified local electric field, lowering the desolvation barrier and significantly accelerating the deposition kinetics. Notably, Zn deposition at a protrusion could lead to a new protrusion with stronger local electric field. The vicious cycle of this process gives rise to the tip effect, and the accumulation of the tip effect ultimately results in the formation of zinc dendrites ([Figure 7c](#)).¹¹⁷

Two primary strategies to fundamentally suppress the tip effect—the root cause of dendrite growth—are electrostatic shielding and the construction of a preferential zincophilic layer. The electrostatic shielding approach introduces cationic additives with a more negative reduction potential than Zn²⁺, such as TEA⁺ (tetraethylammonium ions),¹¹⁸ BMIM⁺ (1-butyl-3-methylimidazolium ions),¹¹⁹ NH₄⁺,⁸⁸ and K⁺.⁸⁹ These cations are electrochemically inert at Zn deposition potentials. Driven by the electric field, they preferentially migrate and accumulate in protrusion regions with the highest field strength, forming a dynamic, positively charged shield ([Figure 7d](#)). The zincophilic layer construction strategy aims to preferentially form an interfacial layer with high Zn affinity. The zincophilic layer supplies many low-barrier nucleation sites for Zn²⁺, guiding homogeneous zinc deposition from the

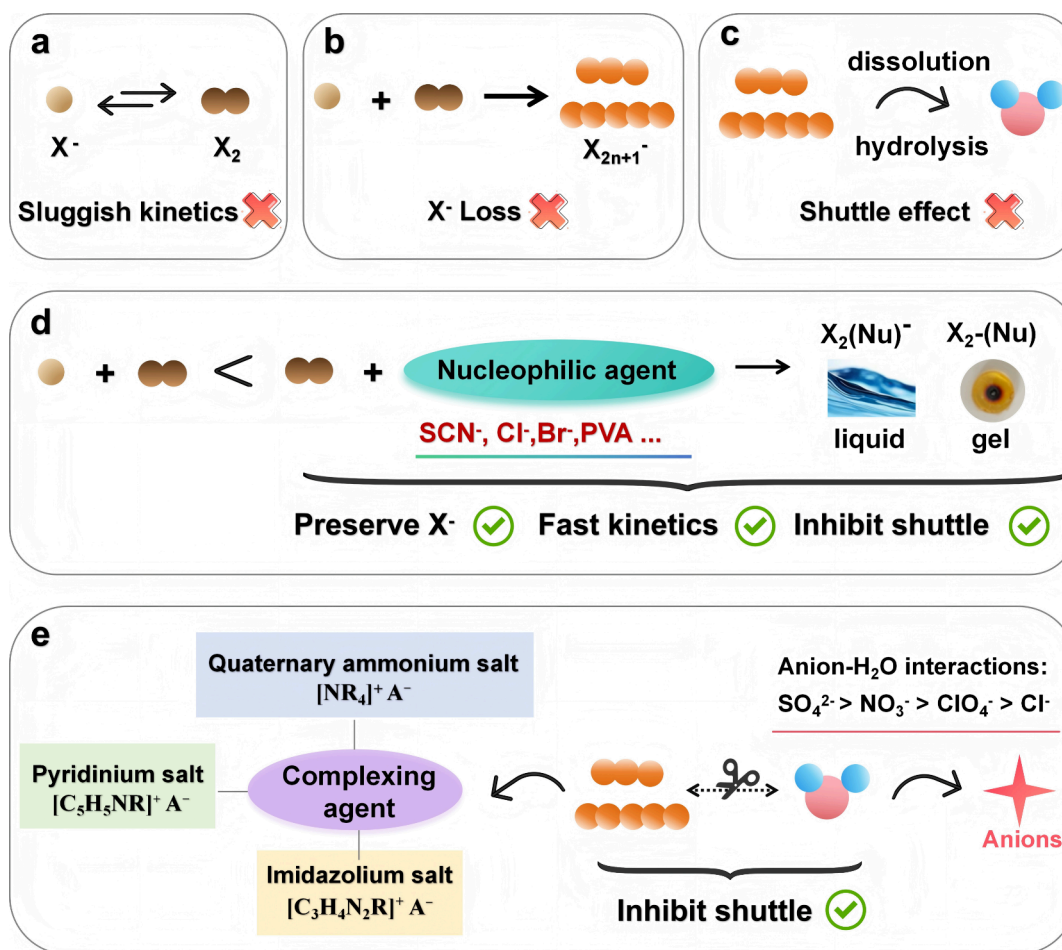


Figure 8. Halogen reaction behaviors. (a) X⁻/X₂ conversion. (b) Homogeneous reactions between X⁻ and X₂. (c) Hydrolysis of polyhalide anions. Modification strategy via (d) nucleophilic agent and (e) complexing agents and anion coordination.

initial stage. This strategy typically involves two approaches (Figure 7e): (i) Introducing metal cations (e.g., Sn²⁺, Ln³⁺, Bi³⁺) with more positive reduction potentials than Zn²⁺ allows them to be preferentially reduced into metal nanoparticles on the electrode. These metal nanoparticles exhibit strong adhesion to subsequently deposited Zn and possess uniform surface energy, significantly lowering Zn nucleation overpotential and guiding Zn to deposit preferentially on the (002) plane.^{86,120,121} (ii) Incorporating zincophilic organic additives rich in electronegative O/N-based functional groups, such as -COOH or -NH₂. These molecules can adsorb onto the zinc anode surface, forming a stable adsorption layer. These molecules function to form a zincophilic layer on the electrode surface through direct adsorption or reductive decomposition, which act as zincophilic sites to guide uniform nucleation. Zhi et al. demonstrated that 1-ethylpyridinium bromide (EPD) adsorbs on the electrode via its heterocyclic N atom, forming a uniform charge-modulating layer, which enables a Zn-Br₂ flow battery with 4000 stable cycles.¹²² Similarly, Byon et al. showed that glutaric acid (GA) facilitates a robust zinc-glutarate-rich zincophilic layer, achieving stable Zn plating/stripping for 4000 h.⁸²

It is important to clarify that while the strategy of EDL regulation, shielding effect, and zincophilic layer is enabled by electrolyte additives, its effectiveness depends on the adsorption behavior of these cations or solvent on the Zn deposition or electrode surface; thus, the observed perform-

ance improvement arises from a synergistic interaction between the electrolyte species and the electrode interface rather than from bulk electrolyte properties alone.

Interconnection of Solvation Structure and Interfacial Electrochemistry

The preceding discussions on the solvation structure and interfacial electrochemistry are intrinsically linked, forming a causal chain that dictates battery performance. This chain originates from the molecular design of the Zn²⁺ solvation sheath, which fundamentally governs both bulk transport and interfacial processes.

First, the solvation structure directly dominates ion transport characteristics in the bulk electrolyte. The binding strength and configuration between Zn²⁺ and its primary solvation sheath ligands—whether water molecules, anions, or additive molecules—determine the activation energy for ion migration. A strongly coordinating solvation structure increases the energy barrier for Zn²⁺ migration, thereby exacerbating ohmic polarization and reducing the voltage efficiency.

Second, the solvation structure serves as the thermodynamic and kinetic origin of both deposition potential and interfacial reactions. Strong interactions between Zn²⁺ and its ligands typically lower the reduction potential of the Zn²⁺/Zn couple; however, an excessively negative zinc reduction potential aggravates the HER. More critically, the key step in interfacial reactions—the desolvation of Zn²⁺—requires energy that is directly dictated by the stability of the primary solvation

sheath. A water-rich, overcoordinated solvation sheath (such as the classic $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ complex) leads to a high desolvation energy barrier, which in turn induces large nucleation overpotential and sluggish deposition kinetics, ultimately compromising Coulombic efficiency.

Therefore, an ideal solvation structure capable of synergistically promoting fast ion migration; low-overpotential deposition; and uniform, stable interfacial reactions typically exhibits characteristics of “weak solvation yet dynamic coordination” or “high entropy”. For example, solvation environments formed by organic-solvent-free configurations or competitive coordination among multiple anions (e.g., Cl^- , Br^- , SO_4^{2-}) can maintain high ionic conductivity while avoiding overly stable, kinetically sluggish coordination structures. Such architectures synergistically reduce water activity and optimize the desolvation process, providing a thermodynamically and kinetically favorable interfacial environment for zinc deposition. This represents an effective pathway toward achieving a high Coulombic efficiency, high voltage efficiency, and extended cycle life.

Halogen Reaction Behavior

The electrochemical behavior of halogens constitutes a cornerstone for the efficiency, longevity, and energy density of ZHFBs. The ideal halogen reaction involves reversible redox between halide anions (X^-) and halogen molecules (X_2). However, the practical operation of halogen reaction is plagued by parasitic reactions and kinetic limitations. This section aims to systematically elucidate the key challenges of halogen reactions, and summarize the advanced strategies to address these issues.

The oxidation of X^- to X_2 involves the cooperative coupling of two X^- ions, requiring desolvation, overcoming Coulombic repulsion, and formation of a new $\text{X}-\text{X}$ bond.¹²³ This process has a high activation energy and a small reaction rate constant (Figure 8a). Consequently, the kinetics of halogen conversion are sluggish, leading to a high electrochemical overpotential, poor rate-capacity, and limited power density.¹²⁴ Additionally, the generated neutral X_2 molecules are highly reactive and undergo further homogeneous chemical reactions with the abundant X^- ions in the electrolyte, forming polyhalide anions with less electrochemically active (e.g., I_3^- , I_5^- , Br_3^-) (Figure 8b).¹²⁵ This process results in the loss of electrochemically active X^- , thus leading to a limited capacity. Moreover, the polyhalide anions can dissolve in the H_2O solvent, migrate from the positive electrode side across the separator to the negative electrode driven by the concentration gradient, and then chemically react with Zn deposition ($3\text{X}_3^- + 2\text{Zn} \rightarrow 2\text{Zn}^{2+} + 9\text{X}^-$) (Figure 8c).¹²⁶ This process can result in poor Coulombic efficiency, poor cycling performance, and severe self-discharge.

To address these issues, research has focused on regulating the halogen reaction pathway. This involves enhancing the conductivity of the X_2 product, hindering the reaction between X^- and X_2 , or anchoring the highly soluble polyhalides. First, the introduction of strong nucleophilic agents represents a direct and efficient strategy. As Lewis bases, nucleophiles are the species rich in electrons and prone to attack electron-deficient centers.⁷⁶ During charging, the crucial role of the nucleophile is to preferentially react with the generated X_2 over X^- ions, forming halogen-nucleophiles (X_2Nu^- or X_2-Nu) (Figure 8d).¹²⁷ This approach offers three key benefits: (i) As X_2 is immediately immobilized by the nucleophile, hindering

the reaction of X_2 with abundant X^- , the free active X^- ions maintain a high concentration in the electrolyte, thereby enhancing the capacity. (ii) The formed halogen–nucleophiles complex, serving as a new oxidized-state carrier, typically has a lower energy barrier for reduction than the direct reduction of X_2 molecules, accelerating halogen reaction kinetics and improving the rate capability. (iii) The shuttle effect is effectively suppressed by reducing the generation of polyhalides, due to the hindered reaction between X^- and X_2 . Studies show that the nucleophiles like SCN^- , Cl^- , and Br^- can react with I_2 to form liquid complexes of I_2SCN^- , I_2Cl^- , and I_2Br^- , respectively, and the poly(vinyl alcohol) (PVA) can form a gel I_2 –PVA complex, which improves iodine conversion kinetics and achieves excellent cycling stability and increased capacity.^{77,79}

In contrast to the nucleophile strategy that alters the reaction pathway, the core of complexing agents and electrolyte anion regulation is to directly target already-formed polyhalides, suppressing the dissolution and migration of polyhalides (Figure 8e). Complexing agents typically employ salts with bulky organic cations, such as quaternary ammonium salts, pyridinium salts, and imidazolium salts. The strong electrostatic or partial coordination interactions between bulky cations and polyhalide anions promote the formation of an ion pair or coordination compound.⁵⁰ This interaction lowers the overall Gibbs free energy, which makes the resulting complexes thermodynamically more stable. It is important to note that the strategies for mitigating polyhalide shuttling differ fundamentally between static and flow battery architectures. In static zinc-halogen batteries, the formation of solid or gel-like polyhalide complexes is often acceptable, as these nonuniform phases can be physically confined within the cathode structure or at the electrode interface.¹²⁸ However, such heterogeneous products are detrimental in flow batteries, where any precipitate or viscous gel can block porous electrodes, clog flow channels, and impair pump operation, leading to rapid system failure.

Consequently, ZHFBs demand fully homogeneous reaction environments, necessitating complexing agents that form soluble, low-viscosity adducts or alternative strategies such as nucleophilic scavenging that convert halogens into stable, dissolved species without phase separation. This distinction underscores that electrolyte design for ZHFBs must prioritize not only chemical efficacy but also hydrodynamic compatibility. The key design principle involves tailoring the molecular structure of complexing agents to suppress crystallization or gelation while maintaining strong polyhalide affinity (Table 1).

The solvation structure of halogen ions critically governs the oxidation kinetics by influencing both the desolvation activation energy and mass transport.

For conventional quaternary ammonium salts, such as *N*-methyl-*N*-ethylpyrrolidine bromide (MEP), the localized positive charge on the sp^3 -hybridized nitrogen atom provides a strong initial electrostatic attraction to polyhalides. However, the core driving force for shuttle suppression relies more on the strong hydrophobic effect and steric hindrance induced by the long alkyl chains.⁷⁴ These interactions can effectively

Table 1. Comparison of Complexing Agents of Quaternary Ammonium Salts, Pyridinium Salts, and Imidazolium Salts

Complexing agent	Quaternary ammonium salt	Pyridinium salt	Imidazolium salt
Geometric shape	Tetrahedron	Planar	Planar
Cationic charge density	High (N sp ³)	Low (N sp ²)	Medium (N sp ² and C2–H)
Interaction	Electrostatic interaction and steric hindrance	Electrostatic and π – π interaction	Electrostatic and HBs interactions (C–H...X ₃ [−])
Complexation ability	Strong	Medium	Weak
Solubility of complex	Low	Medium	High
Reaction kinetics of complex	Sluggish	Medium	Fast
Modification	Hydrophilic	Quaternization	Soft–hard zwitterionic

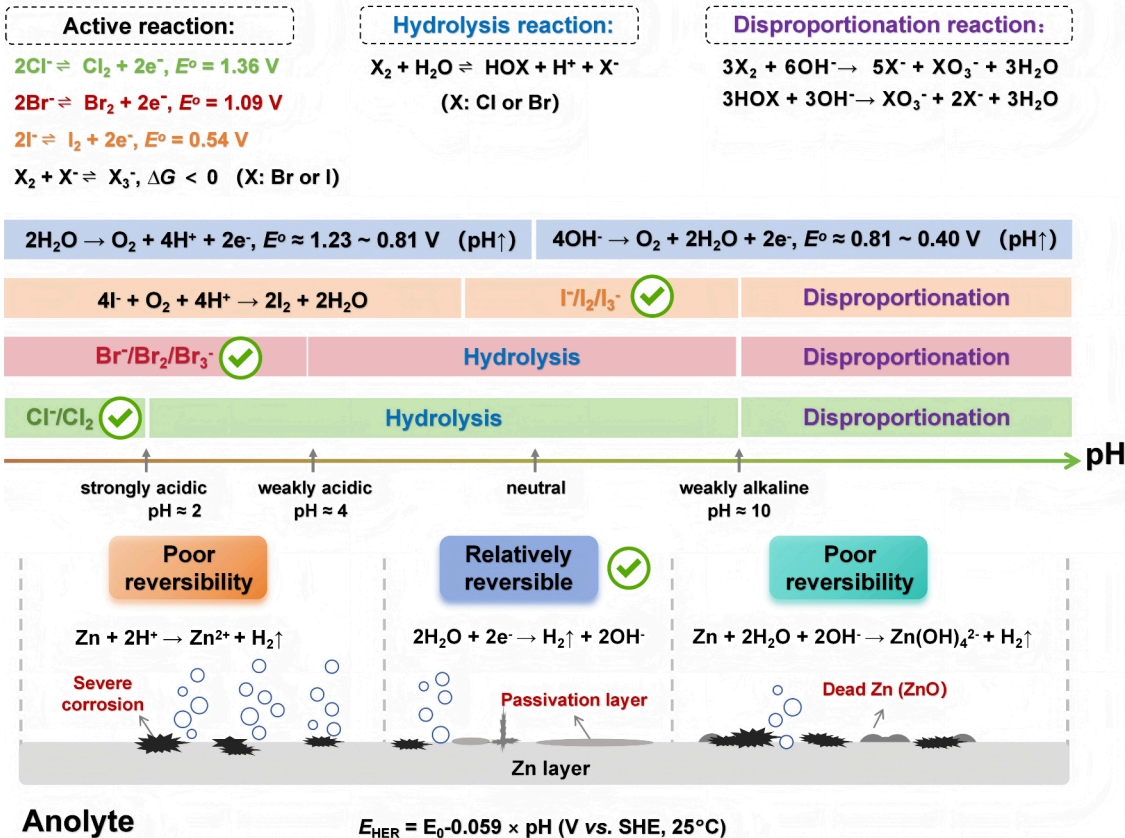
induce macroscopic phase separation such as oil state or precipitation of the complexes, significantly hindering polyhalide migration. Nevertheless, as the alkyl chain lengthens, excessive hydrophobicity may cause excessive oil phase or precipitation, blocking electrode pores and the flow channel and leading to sluggish reaction kinetics. The representative solution is the hydrophilic modification of a molecule to balance hydrophobic precipitation and interfacial compatibility. For example, introducing a hydroxyl group (–OH) at the terminus of the alkyl chain in MEP forms a hydroxyl-

functionalized quaternary ammonium salt.⁷⁵ This modification retains the fundamental electrostatic and steric hindrance effects while preventing excessive precipitation of complexes through the hydrophilicity of –OH.

Conventional pyridinium salts, such as N-ethylpyridinium (EPY⁺), are characterized by a planar aromatic conjugated structure. The central nitrogen atom is sp²-hybridized, and the positive charge is delocalized over the entire aromatic ring. This charge dispersion results in weaker electrostatic attraction compared with quaternary ammonium salts, whereas the planar rigid structure promotes the π – π stacking interactions of pyridinium salts and polyhalides, manifesting a moderate complexation ability.⁷³ However, the complexing agent of pyridinium salts has insufficient chemical stability. The aromatic ring is susceptible to electrochemical oxidative degradation at high voltage, leading to deactivation of pyridinium salts. Additionally, the generated complexes sometimes exhibit a relatively high solubility, resulting in incomplete suppression of the shuttle effect. A strategy to address these issues is quaternization modification. For example, transforming N-ethylpyridinium to N-hexylpyridinium can significantly improve the oxidative stability.

Conventional imidazolium salts, represented by 1-ethyl-3-methylimidazolium, also possess a planar aromatic structure with sp² hybridization, but the positive charge is delocalized between the two nitrogen atoms. Due to the strong electron-withdrawing effect of the adjacent nitrogen, the hydrogen atom at the C2 position exhibits significant acidity and can act as a strong hydrogen, forming specific HBs with polyhalides.

Catholyte

**Figure 9.** Behaviors of halogen reactions and Zn deposition at different pH.

However, the relatively low charge density and small steric hindrance of imidazolium salts enable the generated complexes to possess relatively high solubility, which, while beneficial for interfacial mass transfer, may lead to incomplete suppression of the shuttle effect. Beyond alkylation, a more advanced optimization method is to construct the soft–hard zwitterionic trappers (SH-ZITs).⁷⁴ This design covalently links a soft imidazolium cation with a hard anionic group (such as SO_3^-) to form SH-ZITs. Such SH-ZITs can capture the polyhalides to form a hydrophilic bulky group, maintaining a homogeneous state with the electrolyte, thereby simultaneously achieving shuttle inhibition and favorable reaction kinetics.¹²⁹

Complementarily, the dissolution and migration of polyhalides are highly dependent on their surrounding hydration shell. Introducing anions—which interact strongly with water—can reduce the hydration effect of H_2O on polyhalides, thereby limiting solubility and mobility of polyhalides. Research indicates the order of interaction strength between different anions and water molecules is $\text{SO}_4^{2-} > \text{NO}_3^- > \text{ClO}_4^- > \text{Cl}^-$. Anions with stronger interactions can more effectively lowering the solubility of polyhalides in the water, thus suppressing shuttling.⁷³

This shuttle suppression mechanism is predominantly electrolyte-driven as it relies on altering the chemical speciation of polyhalides within the bulk electrolyte and does not require direct interaction with the electrode surface. However, in practical flow battery operation, the porous carbon electrode may provide additional physical confinement or adsorption sites for the resulting complexes, introducing a secondary synergistic effect that enhances the overall suppression efficiency.

Notably, the flow battery architecture introduces unique factors influencing halogen speciation and shuttle. During long-term cycling, the electrolyte undergoes continuous circulation between the stack and storage tanks. In the tanks, halogen and polyhalide species may experience prolonged residence times, allowing for slow thermal relaxation, disproportionation, or interactions with tank materials, potentially altering the speciation from that immediately after electrochemical generation. This “aging” in storage, coupled with the gradual chemical degradation of complexing agents or membranes over thousands of cycles, can dynamically shift the equilibrium of halogen species, making long-term shuttle suppression a moving target that is more complex than static cell tests.

pH Regulation

Electrolyte pH critically governs the cycling stability of ZHFBs by simultaneously influencing the halogen redox chemistry and the Zn plating/stripping behavior. This section systematically elucidates the mechanisms of pH regulation on the reversibility and side reaction pathways of the halogen redox and the efficiency and morphology of the Zn plating/stripping process (Figure 9).

The reversibility of the halogen redox couples (Cl^-/Cl_2 , $\text{Br}^-/\text{Br}_2/\text{Br}_3^-$, $\text{I}^-/\text{I}_2/\text{I}_3^-$) is strongly dependent on the electrolyte pH, which is primarily related to the chemical species and reaction pathways of halogen ions or elemental halogens in aqueous solution (Table 2).¹³⁰ In a strongly alkaline environment ($\text{pH} > 10$), all halogens undergo two-step disproportionation reactions ($\text{X}_2 + 6\text{OH}^- \rightarrow 5\text{X}^- + \text{XO}_3^- + 3\text{H}_2\text{O}$ and $3\text{HOX} + 3\text{OH}^- \rightarrow \text{XO}_3^- + 2\text{X}^- + 3\text{H}_2\text{O}$) making reversible reaction of all halogens redox couples impractical.⁴⁰ In addition, all halogen elements undergo hydrolysis in water

Table 2. Comparative Analysis of Zn–Cl, Zn–Br, and Zn–I Systems

Aspect	Zn–Cl	Zn–Br	Zn–I
Potential (vs SHE)	+1.36	+1.09	+0.54
Volatility	Very High (gas)	High (liquid, volatile)	Low (solid, sublimates)
Corrosivity	Extremely High	High	Moderate
Hydration energy of halide ion (kJ mol^{-1})	–381	–347	–305
Hydrolysis constant	$\sim 7.2 \times 10^{-9}$	$\sim 4.2 \times 10^{-4}$	$\sim 2 \times 10^{-13}$
Shuttle Species	Cl_2	Br_3^- , Br_5^-	I_3^- , I_5^-
Available pH	$\text{pH} < 2$	$\text{pH} < 4$	$6 < \text{pH} < 10$

($\text{X}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOX} + \text{H}^+ + \text{X}^-$). In the chlorine system, with the largest hydrolysis constant ($K \approx 7.2 \times 10^{-9}$), Cl_2 hydrolysis is significant across a wide pH range. To achieve reversible Cl^-/Cl_2 electrochemistry, a strongly acidic medium ($\text{pH} < 2$) is essential to shift the equilibrium left, suppressing hydrolysis. In the bromine system, although the hydrolysis constant for Br_2 ($K \approx 4.2 \times 10^{-4}$) is magnitude smaller than that for Cl_2 , the hydrolysis equilibrium can shift right as pH increases. Consequently, the reversible $\text{Br}^-/\text{Br}_2/\text{Br}_3^-$ couple is effectively limited to $\text{pH} < 4$ to minimize hydrolytic losses. In the iodine system, due to the extremely low hydrolysis constant ($K \approx 2 \times 10^{-13}$), I_2 hardly hydrolyzes.¹³¹ However, the relatively low redox potential of the I^-/I_2 couple (0.54 V vs SHE), combined with the potential of the $\text{O}_2/\text{H}_2\text{O}$ couple ($E^\circ = 1.23 - 0.059 \times \text{pH}$, at 25 °C), introduces a different constraint. In acidic media, the oxidation reaction of I^- by dissolved oxygen ($4\text{I}^- + \text{O}_2 + 4\text{H}^+ \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O}$) is a spontaneous process, resulting from the relatively large thermodynamic driving force ($\Delta E^\circ = E^\circ(\text{O}_2/\text{H}_2\text{O}) - E^\circ(\text{I}^-/\text{I}_2) = 0.69 - 0.27 \text{ V}$). Therefore, the optimal window for reversible $\text{I}^-/\text{I}_2/\text{I}_3^-$ operation is a near-neutral to weakly alkaline environment ($6 < \text{pH} < 10$) to avoid both acid-driven oxidation and alkaline disproportionation.

Therefore, the three halogen systems exhibit distinct pH windows for reversible operation: chlorine requires strongly acidic conditions ($\text{pH} < 2$) to suppress hydrolysis; bromine requires mildly acidic environments ($\text{pH} < 4$); while iodine operates optimally in near-neutral to weakly alkaline conditions ($6 < \text{pH} < 10$).

The morphology and stripping efficiency of Zn deposition governed by the pH environment, as the pH directly influences the kinetics of competitive side reactions, such as HER, and the formation of surface passivating species.¹³² In strongly acidic environments, a high H^+ concentration dominates the interfacial reactions. The core mechanism is the intense competition between the HER and Zn deposition. In terms of thermodynamics, the standard potential of H^+/H_2 (0 V vs SHE) is much more positive than that of Zn^{2+}/Zn (-0.76 V vs SHE). However, on the electrode surface, the overpotential for H^+ reduction is high, while that for Zn^{2+} reduction is relatively low, allowing Zn deposition to occur kinetically. Nonetheless, the reduction of high H^+ concentration on the electrode consumes electrons, competing with Zn^{2+} for charge. This leads to an uneven distribution of the effective reduction current density for Zn^{2+} . In addition, the H^+ reacts with Zn via a displacement reaction ($\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\uparrow$), causing severe chemical corrosion. The HER-induced H_2 bubble agitation instability of Zn^{2+} mass transport leads to a loose, porous deposit layer highly prone to dendrite formation.¹³³ When the pH approaches neutral, the significantly reduced H^+

Table 3. Summary of ZHFBs, Including Electrolyte Composition, Solvation Structure, Membrane, Testing Conditions, and Electrochemical Performance

Anolyte	Solvation structure	Catholyte	Membrane	Current density (mA cm ⁻²)	Capacity, Cycle	ref.
2 M ZnBr ₂ +3 M KCl+0.4 M MEP +1g/L EDTMPA	Zn(H ₂ O) _x (EDTMPA) _{6-x}	Same as anolyte	Daramic membrane	80	20 mAh cm ⁻² , 400 cycles	104
2 M KI+1 M ZnBr ₂ +2 M KCl	[Zn(H ₂ O) ₆] ²⁺	Same as anolyte	polyolefin porous membrane	40	90 mAh cm ⁻² , 1000 cycles	137
2 M ZnBr ₂ +3 M KCl+0.4 M EPD	[Zn(H ₂ O) _n] ²⁺ (4 < n < 6)	Same as anolyte	polyolefin porous membrane	40	20 mAh cm ⁻² , 4000 cycles	122
1 M ZnCl ₂ +2 M KCl	ZnCl ₄ ²⁻	2 M KI+1 M KCl	Nafion 115	40	20 mAh cm ⁻² , 300 h	102
3.0 M ZnBr ₂ +2.0 M KBr+0.80 M PMDA	/	Same as anolyte	Porous polyolefin membrane	40	57 Ah L ⁻¹ 100 cycles	75
1 M ZnBr ₂ +2 M KCl+0.4 M MEP	/	Same as anolyte	Porous polyolefin membrane	40	40 mAh cm ⁻² , 450 cycles	138
2 M ZnBr ₂ +2.4 M KCl+0.6 M KBr +0.6 M N[1,1,1,2OH]Cl	[Zn(Br ⁻) _x (H ₂ O) _y] ^{2-x}	Same as anolyte	Porous Polyolefin Membrane	40	20 mAh cm ⁻² , 250 cycles	139
1 M ZnI ₂ +7.5 vol % ACN	[Zn(H ₂ O) ₄ (ACN) ₂] ²⁺	Same as anolyte	Nafion-115	100	166 Wh L ⁻¹ 170 cycles	140
2 M ZnBr ₂ +1 M MSA	/	Same as anolyte	Nafion-212	40	75 Wh kg ⁻¹ 50 cycles	59
1 M ZnBr ₂ +3 M KCl+0.6 M TMSO	[Zn(H ₂ O) _x (TMSO) ₂] ²⁺	Same as anolyte	Nafion-212	30	60 mAh cm ⁻² , 500 cycles	141
1.25 M ZnCl ₂ +1.25 M NH ₄ Cl	Zn(NH ₃) _x (Cl ⁻) _y	2.5 M NH ₄ I+1.25 M NH ₄ Cl	Nafion-117	20	120 Ah L ⁻¹ 2500 cycles	77
5 M ZnI ₂ +2.5 M ZnBr ₂	/	Same as anolyte	Nafion-115	10	87 Ah L ⁻¹ 50 cycles	142
1 M ZnI ₂ +1 M NH ₄ Br	/	Same as anolyte	Nafion-211	40	35 Ah L ⁻¹ 100 cycles	78
2 M ZnBr ₂ +3 M KCl+0.8 M ChCl +0.2 M MEM	/	Same as anolyte	Porous Polyolefin Membrane	40	20 mAh cm ⁻² , 1200 cycles	143
0.5 M ZnI ₂ +4 M NaBr+3 M ZnBr ₂	/	Same as anolyte	Nafion-211	40	65.8 Wh L ⁻¹ , 100 cycles	144
1 M ZnI ₂ +1 M NH ₄ OAc	[Zn(OAc ⁻) _x (H ₂ O) _y] ^{2-x}	Same as anolyte	Nafion-115	80	20 mAh cm ⁻² , 200 cycles	88
0.2 M Zn(PPI) ₂ ⁶⁻ +0.6 M KCl	Zn(PPI) ₂ ⁶⁻	2 M KI+1 M KCl	JCM-D membrane	200	606 mW cm ⁻² 250 cycles	106
2.5 M ZnCl ₂ +2.5 M NH ₄ Cl	/	Same as anolyte	Daramic membrane	80	45 Ah L ⁻¹ 370 cycles	145
2 M ZnBr ₂ +3 M KCl+0.4 M MEP +DMSO	[Zn(Br ⁻) _x (H ₂ O) _y (DMSO) _z] ^{2-x}	2 M ZnBr ₂ +3 M KCl + 0.4 M MEP	Daramic membrane	120	24 mAh cm ⁻² , 2000 cycles	85
1 M ZnSO ₄ +0.01 M GA	[Zn(H ₂ O) _x (GA) _y] ²⁺	1 M KI+1 M KCl	Nafion-212	10	5 mAh cm ⁻² , 300 h	82

concentration weakens H⁺ side effects. Charge can then be efficiently utilized for Zn²⁺ reduction, creating a more favorable thermodynamic and kinetic window for reversible Zn plating/stripping. However, new challenges arise from water decomposition (2H₂O + 2e⁻ → H₂↑ + 2OH⁻). The generated OH⁻ readily reacts with zinc ions and anions to form electrochemically inert basic zinc salts, such as Zn₄SO₄(OH)₆·xH₂O, which block ion transport.¹³⁴ In alkaline environments, Zn can directly react with OH⁻ to form a Zn(OH)₄²⁻ passivation layer, hindering subsequent Zn electrodeposition and increasing the polarization. Moreover, under strong alkaline conditions, the further reactions can generate inactive dead-Zn (ZnO), causing irreversible capacity loss.¹³⁵

To mitigate the dominant failure modes in different pH regimes—HER/corrosion in acid and passivation in alkali—pH buffering agents such as ammonium acetate (NH₄OAc) or acetic acid/sodium acetate (CH₃COOH/CH₃COONa) pairs can be employed.^{85,88} Specifically, the conjugate acid (e.g., NH₄⁺, CH₃COOH) neutralizes locally generated OH⁻, while the conjugate base (e.g., CH₃COO⁻) consumes excess H⁺. This dynamic equilibrium stabilizes the interfacial pH. Notably, interfacial challenges at near neutral pH are primarily

linked to the water activity. As detailed in the preceding section on solvation structure design, strategies that suppress water activity offer a direct solution to this issue.

The management of the pH in a flowing system presents distinct challenges and opportunities. While continuous flow can help mitigate extreme local pH shifts at the electrode surfaces by rapidly removing generated OH⁻ or H⁺ ions, it also facilitates the transport of these ions across the cell. For example, OH⁻ generated at the zinc anode can be carried to the cathode compartment, where it may trigger an unfavorable disproportionation of halogens. This highlights that pH management in ZHFBs is not just about maintaining a static value in each reservoir but about managing pH gradients and transients created and sustained by the flowing electrolytes.

This pH stabilization is achieved through homogeneous buffering reactions in the bulk electrolyte and is therefore primarily electrolyte-driven. However, the effectiveness of pH regulation at the electrode interface may be modulated by the local electric field and adsorption of buffer species, introducing a secondary electrode-dependent factor that can influence the uniformity of pH stabilization across the electrode surface.

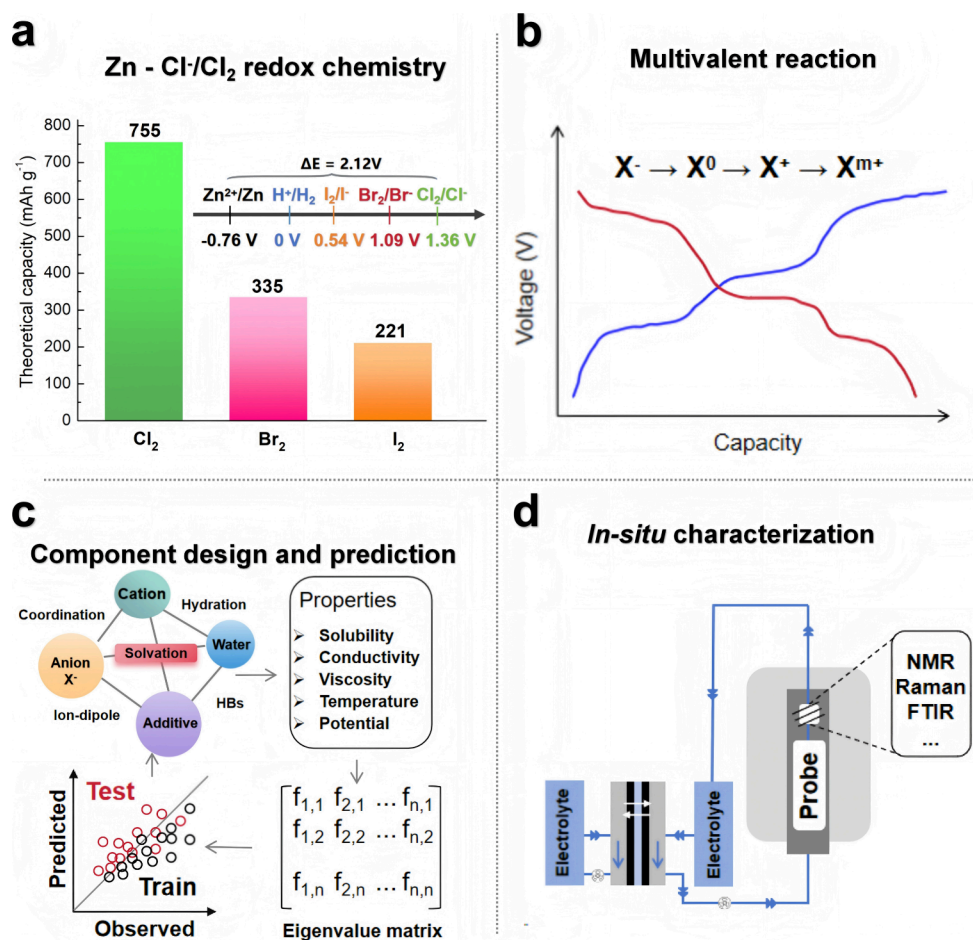


Figure 10. Future prospects of ZHFBs. (a) Zinc chloride flow batteries. (b) Multivalent halogen reactions. (c) Intelligent screening of electrolytes. (d) *In situ* characterization techniques.

Dynamic Considerations in Flow Battery Electrolyte Chemistry

The mechanistic discussions above are largely based on equilibrium or static conditions. However, in practical ZHFB operation, continuous electrolyte circulation introduces dynamic factors that critically influence the solvation equilibria and halogen speciation. Unlike static cells, where local equilibrium can be established, flowing electrolytes experience the following: (i) Flow rate effects on mass transport and reaction kinetics. The velocity of electrolyte flow affects the thickness of the diffusion boundary layer at the electrode interface, directly impacting Zn²⁺ supply and polyhalide removal. Higher flow rates can mitigate concentration polarization and dendrite formation but may also accelerate undesirable species transport across the membrane.¹³⁶ (ii) Tank storage and electrolyte aging. The decoupling of energy and power in flow batteries means that large electrolyte volumes reside in external tanks for extended periods (hours to days). During this residence time, slow equilibria involving polyhalide complexes can shift, potentially leading to phase separation or gas evolution even without an applied current. Long-term aging phenomena—including gradual degradation of complexing agents, hydrolysis of halogen species, and accumulation of side products—become magnified over thousands of operating hours.¹²⁹ (iii) Dynamic solvation structures under flow. While static studies reveal equilibrium solvation structures, flowing conditions may induce shear-

driven perturbations to ion coordination, particularly for weakly bound complexes. Computational modeling suggests that solvation shell configurations can fluctuate under hydrodynamic stress, potentially affecting desolvation kinetics at the electrode.⁶⁵

These dynamic considerations underscore that electrolyte design for ZHFBs must extend beyond equilibrium thermodynamics to encompass flow-dependent kinetics, long-term stability, and system-level integration. Future research should combine *in situ* spectroscopic monitoring under realistic flow conditions with multiscale modeling to capture these transient phenomena.

In summary, ZHFBs are promising for grid storage due to their high energy density, low cost, and material abundance. This Review highlights key aspects of electrolyte design in ZHFBs, focusing on composition, solvation structure, zinc deposition behavior, halogen redox chemistry, and the influence of pH. An overview of the electrolyte composition, solvation structure, membrane, testing conditions, and electrochemical performance is provided in Table 3. Although significant progress has been made in specific systems such as zinc–bromine and zinc–iodine flow batteries, the path to full commercialization remains hindered by persistent scientific and engineering challenges. To advance ZHFBs toward maturity and widespread adoption, future efforts must combine deeper fundamental insights into these complex electro-

chemical systems with integrated advances in multidisciplinary device engineering.

Exploration of the Zinc-Chlorine Flow Battery (ZCFB).

The high potential of the Cl^-/Cl_2 couple (1.36 V vs SHE) positions ZCFBs as a promising path to ultrahigh energy density, but they remain underexplored due to chlorine's extreme corrosiveness and shuttle effect (Figure 10a).¹⁴⁶ Drawing from the halogen reaction mechanisms discussed above, future efforts must go beyond generic strategies. First, research should focus on developing chlorine evolution reaction (CER) catalysts with tailored active sites that minimize the formation energy of Cl_2 and suppress the competing OER in the highly corrosive, high-potential environment.¹⁴⁷ Second, inspired by the complexing agents used in Zn–Br or Zn–I systems, a critical direction is to design novel nucleophilic agents capable of forming reversible, stable, and ideally water-immiscible complexes with Cl_2 to fundamentally mitigate Cl_2 crossover. Third, we developed an electrolyte with low-activity H_2O to suppress Cl_2 solubility. Fourth, ultrasensitive, chlorine-resistant membranes (e.g., advanced perfluorinated or hydrocarbon-based polymers), fully sealed, negative-pressure system designs should be implemented to minimize corrosion risks and toxic chlorine exposure.^{148,149}

Multielectron Redox Pathways of Halogens. The multielectron redox pathway of halogens represents a pivotal direction to transcend the energy density limitations of zinc-halogen flow batteries. The ideal pathway involves sequential oxidation from X^- to X^0 and further to X^+ (or even higher valence states, X^{m+}) (Figure 10b). However, the core challenge lies in the thermodynamic instability of high-valence intermediates such as I^+ and Br^+ , which are prone to hydrolysis or disproportionation (e.g., $3\text{I}^+ + 3\text{H}_2\text{O} \rightarrow \text{I}_2 + \text{IO}_3^- + 6\text{H}^+$), leading to capacity decay and side reactions.⁸ In Zn–I flow batteries, constructing interhalogen species such as IBr_2^- or ICl_2^- to stabilize I^+ has preliminarily validated the feasibility of $\text{I}^-/\text{I}^0/\text{I}^+$ four-electron transfer.¹⁵⁰ However, this strategy is heavily reliant on high-concentration halide ions (Br^- , Cl^-), introducing issues such as electrolyte corrosiveness and high cost. In Zn–Br flow batteries, introducing bromine scavengers like sodium sulfamate (SANA) enables rapid reaction with electrogenerated Br_2 to form stable N-brominated sulfamate (Br-SANA , representing the Br^+ state), realizing Br^-/Br^+ transfer.¹⁵¹ Nevertheless, multielectron bromine chemistry remains at a nascent stage. To further address the stabilization of high-valence halogen intermediates, future research can draw inspiration from successful strategies in static halogen-based batteries while developing electrolyte engineering tailored to flow systems. For instance, adopting a carbon–halogen bond strategy by designing functional organic molecules chemically captures and stabilizes X^+ through reversible C-X^+ bonds (e.g., $\text{C-I}^+-\text{Br}$).¹⁵² Additionally, developing eutectic electrolytes, “water-in-salt” systems, or hybrid aqueous electrolytes to drastically reduce water activity offers another effective route to suppress hydrolytic side reactions.¹⁵³

Electrolyte Prediction and Inverse Design. Moving beyond inefficient trial-and-error methods, the integration of artificial intelligence (AI), machine learning (ML), and high-throughput computation is essential to establish an intelligent prediction platform for composition–structure–property prediction (Figure 10c).¹⁵⁴ The predictive capability of such models is fundamentally governed by the quality and relevance

of the input data, which must extend well beyond simple bulk properties (e.g., solubility, ionic conductivity, viscosity) to encompass the molecular-level interactions that dictate performance.¹⁵⁵ For ZHFBs, constructing a multidimensional parameter space anchored in the mechanistic principles discussed throughout this Review is critical. Key descriptors should include (i) calculated binding energies between Zn^{2+} and solvent molecules, supporting salts, or functional additives; (ii) fundamental physicochemical parameters such as donor numbers (DN) and the energies of HOMO/LUMO of solvation sheaths, which are predictive of electrochemical stability against HER or OER; and (iii) interaction energies between halogen intermediates (e.g., X^+ , X_3^-) and potential complexing agents, directly correlating with shuttle effect mitigation. By training ML models on databases enriched with these fundamental descriptors, the field can move beyond rapid screening of existing compositions toward genuine inverse design.¹⁵⁶

In Situ Characterization Is Used for Real-Time Monitoring of Dynamic Electrolyte Chemistry. A critical forward-looking challenge is to bridge the gap between fundamental mechanistic understanding, often gained in simplified static setups, and the dynamic, integrated operation of a full flow battery system. Future research must explicitly investigate how continuous circulation, variable flow regimes, large-volume storage, and long-term cycling collectively influence the solvation equilibria, halogen speciation kinetics, and component degradation pathways. To validate the proposed mechanisms and guide rational design, real-time observation of the dynamic electrolyte chemistry under operating conditions is indispensable (Figure 10d).¹⁵⁷ Future efforts should focus on the strategic integration of multiple *in situ* techniques to probe specific ZHFB interfaces. For instance, *in situ* Raman and FTIR spectroscopy can be deployed to monitor the dynamic evolution of Zn^{2+} solvation structures and the formation of halogen complexes in electrolyte during cycling. *In situ* NMR spectroscopy is uniquely powerful for tracking the mobility, speciation, and crossover of polyhalide ions in real time, offering a direct quantitative measure of the shuttle effect. Such multimodal, correlative approaches are essential to close the loop between electrolyte design and observed battery performance.

The reversibility of the halogen redox couples (Cl^-/Cl_2 , $\text{Br}^-/\text{Br}_2/\text{Br}_3^-$, $\text{I}^-/\text{I}_2/\text{I}_3^-$) is strongly dependent on the electrolyte pH, which is primarily related to the chemical species and reaction pathways of halogen ions or elemental halogens in aqueous solution.

Synergistic Optimization for Practical ZHFB Applications. The ultimate success of ZHFBs depends on holistic, system-level optimization tailored to the flow battery paradigm. Many component-level strategies successful in static batteries fail to translate directly due to the demands of continuous flow, scalability, and decoupled energy/power. Therefore, future efforts should focus on a synergistic design that acknowledges these unique constraints (Figure 11). Key areas for synergistic

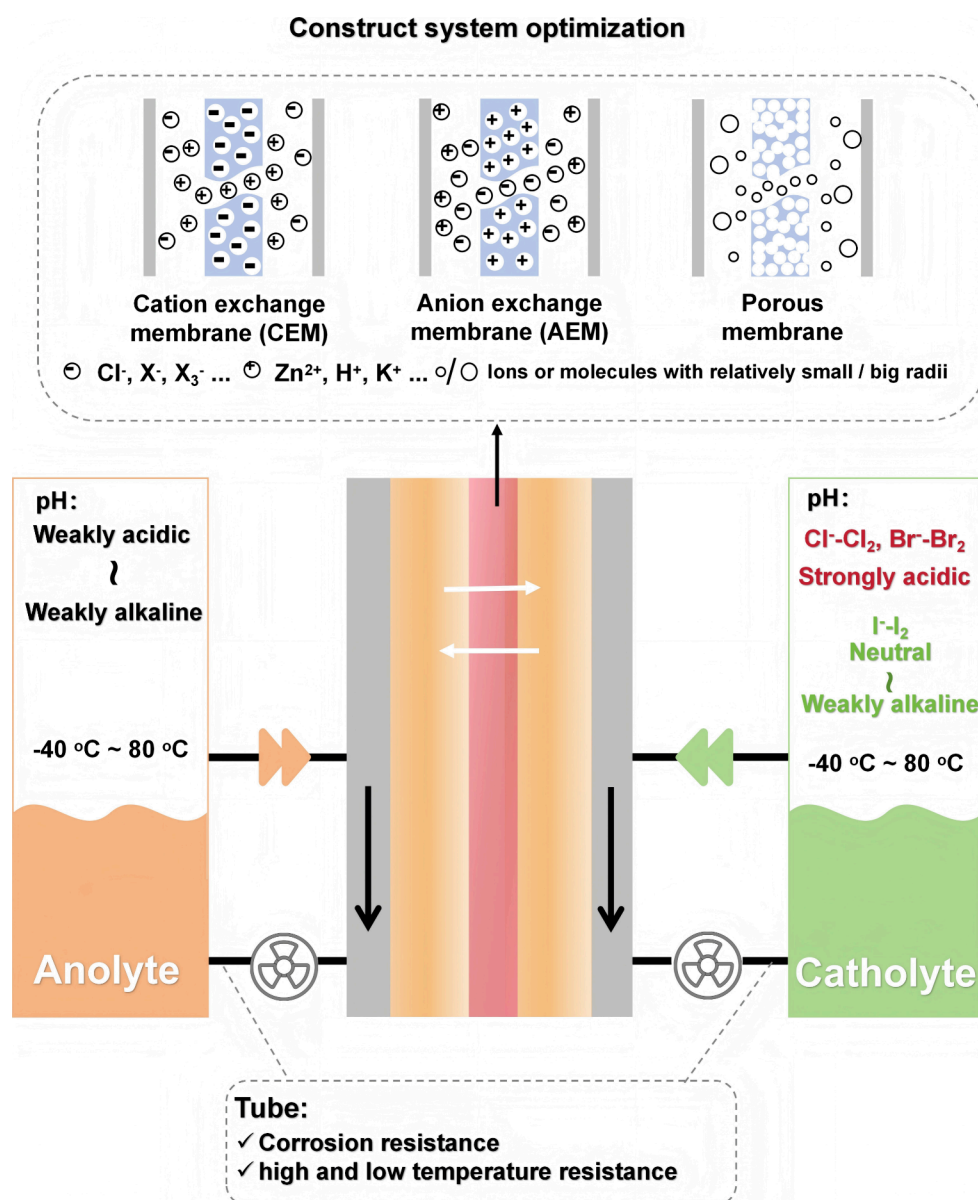


Figure 11. Future prospects of ZHFBs. Synergistic optimization for practical ZHFB applications.

optimization include the following: (i) pH management. For reversible redox reactions, differential pH management is crucial—maintaining a neutral/weakly alkaline anolyte for stable Zn plating, while optimizing the catholyte pH to enhance halogen reaction kinetics. A bypass loop with real-time sensors and automated injection could maintain an optimal and decoupled pH environment.¹⁵⁸ (ii) Membrane–electrolyte codesign. Membrane selection—whether cation exchange membranes (CEM), anion exchange membranes (AEM), or porous separators—should be tailored or combined based on the system’s specific ionic requirements to achieve optimal ion selectivity and conductivity. A porous separator with a tailored pore size might offer the lowest resistance while effectively blocking large complexes. Conversely, a CEM or AEM might be preferred in systems with simpler halide chemistry to minimize anion crossover, but their prices are relatively high. Advanced computational modeling of ion transport through membranes under specific electrolyte compositions and flow conditions is crucial for this rational

codesign.^{159,160} (iii) Corrosion-resistant and wide-temperature system architecture. The highly reactive nature of halogens demands that all contacted components—including bipolar plates, flow frames, gaskets, and tubing—be fabricated from or coated with materials exhibiting exceptional chemical stability, such as graphite–polymer composites and fluorinated polymers.^{151,161} The selection of these materials involves inherent trade-offs among corrosion resistance, mechanical properties, and cost; for example, high-performance fluoropolymers offer excellent chemical inertness but at significantly greater expense than standard engineering plastics. Furthermore, the entire system including electrolyte formulations and component materials should be designed for wide-temperature operation to ensure reliable performance across diverse geographical and climatic conditions.¹⁶² (iv) Economic, environmental, and long-term stability considerations. Practical ZHFB deployment requires addressing the electrolyte cost and sustainability. Additive cost-effectiveness must be justified by performance gains, while long-term stability under continuous

cycling remains critical yet underexplored. Environmentally biodegradable or recoverable complexing agents are preferred to mitigate ecological risks. These constraints must be integrated early to ensure that laboratory innovations translate into commercially viable technologies.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

Fundamental and Interdisciplinary Disciplines Breakthrough Plan of the Ministry of Education of China (JYB2025XDXM408).

Notes

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ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Key Research and Development Program of China (grant no. 2024YFA1211800), National Science Foundation of

China (grant nos. 52373306 and 52472244), the Key Research and Development Program Project of Hubei Province (grant nos. 2023BAB140 and 2024BAA013), the Natural Science Foundation of Hubei Province (grant nos. 2023AFA053, 2024BAA013, and 2025AFA105), the Key Research and Development Program of Henan Province (grant no. 25111240100), and the Science and Technology Special Fund of Hainan Province (ZDYF2025GXJS008).

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