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Towards High-Energy-Density Aqueous Zinc-Iodine Batteries: Multi-Electron Pathways

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KEYWORDS: Aqueous zinc batteries, zinc-iodine batteries, iodine conversion, energy density, iodine prices, iodine recycling.

ABSTRACT:

Aqueous zinc-iodine batteries (ZIBs) based on the reversible conversion between various iodine species have garnered global attention due to their advantages of fast redox kinetics, good reversibility, and multi-electron conversion feasibility. Although significant progress has been achieved in ZIBs with the two-electron I^-/I_2 pathway (2eZIBs), the relatively low energy density has hindered practical application. Recently, ZIBs with attractive four-electron $I^-/I_2/I^+$ electrochemistry (4eZIBs) has shown a marked improvement in energy density. Nonetheless, the practical use of 4eZIBs is challenged by poor redox reversibility due to polyiodide shuttling during the I^-/I_2 conversion and I^+ hydrolysis during the I_2/I^+ conversion. In this Review, we thoroughly summarize the fundamental understanding of two ZIBs, including reaction mechanisms, limitations, and improvement strategies. Importantly, we provide an intuitive evaluation on the

energy density of ZIBs to assess their practical potential and highlight the critical impacts of the Zn utilization rate. Finally, we emphasize the cost issues associated with iodine electrodes and propose potential closed-loop recycling routes for sustainable energy storage with ZIBs. These findings aim to motivate the practical application of advanced ZIBs and promote sustainable global energy storage.

1. INTRODUCTION

The ever-increasing global energy consumption has driven the search for green and sustainable energy sources to reduce greenhouse gas emissions and air pollution.[1] Renewable energy sources, like solar and wind, are intermittent, which need energy storage technologies such as batteries to integrate them into the grid.[2-3] Since the commercialization in 1991, lithium-ion batteries (LIBs) have dominated energy storage and conversion systems in portable electronic devices, electric vehicles, and smart grids.[4-5] However, they face significant drawbacks, including high cost and safety risks, which limit their large-scale application.[6-7] Aqueous Zn batteries (AZBs) present a promising alternative to LIBs for large-scale energy storage due to their high safety, low cost, excellent rate capability, acceptable energy density, and environmental friendliness.[8-9] Therefore, the development of AZBs is high promising to address environmental issues and energy shortages.

In the past decade, tremendous efforts have been devoted to improving the reversibility and lifetime of AZBs and exploring approaches for scaling up from laboratory scale to industrial level. However, significant challenges remain, including the absence of advanced cathodes and highly reversible Zn anodes.[10-11] On the Zn anodes, notorious Zn dendrites and parasitic hydrogen evolution (HER) leads to undesirable Zn reversibility.[12-13] Recent reports indicate that the poor reversibility of Zn anodes has been largely mitigated by various methods, including electrolyte component tuning,[12, 14-17] anode structure design,[18-20] and surface modification.[21] Similar to Zn

anodes, the development of advanced cathodes for AZBs is of great importance as well. Cathodes based on Zn^{2+}/H^{+} co-intercalation, primarily including one-electron MnO_2, V_2O_5, and Prussian blue analogues (PBA), have been widely reported for AZBs. However, their reversibility in aqueous media is far from satisfactory, which mainly results from following limitations: 1) the intercalation electrochemistry suffers from significant energy barriers owing to the large charge density of divalent Zn^{2+}; 2) the H^{+} co-intercalation leads to the violent pH variation at cathode interface to accelerate the insulated by-products and active mass dissolution; 3) limited electron transfer number and poor Zn^{2+} intercalation leads to low capacity of cathodes; 4) repeated intercalation/de-intercalation processes damage the crystal structure of cathodes to degrade the electrochemical performance and lifetime.[22-24] Researchers have further developed novel two-electron Zn-Mn electrolytic batteries based on a deposition/dissolution mechanism, which facilitates a two-electron Mn^{2+}/Mn^{4+} conversion, achieving a notable specific capacity of 616 mAh g^{-1} and a high discharge potential of approximately 1.95 V vs. Zn/Zn^{2+}.[25-26] However, challenges such as poor cathode conductivity, excessively high operating voltage, and significant Zn corrosion present substantial obstacles to their practical application.[11] Therefore, exploring new cathode electrochemistry is crucial for the advancement and practical deployment of AZBs.

Recently, conversion-type cathodes, including chalcogen cathodes and halogen cathodes, garnered significant attention for several advantages: 1) the Zn^{2+}/H^{+}-independence mechanism helps to avoid battery failure caused by structural degradation of the cathode[27-28]; 2) soluble intermediates allows faster conversion kinetics[29]; 3) the multi-electron conversion process significantly enhances capacity delivery and energy density[30]. For the chalcogen cathodes (*e.g.*, O_2/S/Se/Te), can provide high energy density, however, are limited by the sluggish reaction kinetics and low charge-transfer process.[11] For example, S cathodes can present a high theoretical

capacity of 1672 mAh g^{-1} and a high discharge potential of 1 V vs. Zn/Zn^{2+}. However, issues such as the insulating nature of solid S and ZnS discharge products, significant volume expansion, sluggish kinetics for sulfur speciation, and a high activation energy barrier for ZnS oxidation severely hinder battery reproducibility.[31-32] In contrast, halogen cathodes, which involve liquid-phase reactions with highly soluble intermediates and discharge products, present a promising alternative for cathodes in AZBs. Specifically, the I_2 cathodes are particularly promising due to their moderate operating potential, good redox reversibility, multi-electron conversion routes, and abundance in oceanic reserves.[33-35] As illustrated in **Figure 1**a, the I_2 cathode undergoes a two-electron I^-/I_2 conversion with a potential of *ca.* 1.28 V vs. Zn/Zn^{2+}, offering a theoretical capacity of 211 mAh g^{-1} (based on the mass of I_2).[36-37] Additionally, I_2 electrode can also experience an additional conversion between I_2 and I^+ with a discharge potential of *ca.* 1.8 V vs. Zn/Zn^{2+}.[38] Based on the reversible $I^-/I_2/I^+$ conversion pathway, the theoretical capacity can extend to 422 mAh g^{-1} (based on the mass of I_2). As elucidated in **Figure 1**b, I_2 cathode based on I^-/I_2 conversion exhibits a theoretical energy density of around 290 Wh kg^{-1} (based on the mass of I_2), which is comparable to the V_2O_5 cathodes (around 300 Wh kg^{-1}) but is still lower than one-electron MnO_2 cathodes (around 420 Wh kg^{-1}). Benefiting from the additional I_2/I^+ conversion, the theoretical energy density of I_2 cathode can be extended to over 630 Wh kg^{-1} (based on the mass of I_2), surpassing most prevailing cathodes for AZBs. Furthermore, it has been demonstrated that I_2 cathodes can couple with other halogen redox reactions (Cl^-/Cl^0 or Br^-/Br^0 redox) or undergo a twelve-electron I^-/IO_3^- conversion, indicating the potential for higher energy density out-put.[39-41] Although recent reports on 2eZIBs have achieved significant success in improving battery reproducibility, the understanding of the working mechanism and reversibility improvement of 4eZIBs remains limited, not to mention higher-valence iodine conversion chemistry. Additionally, most research

evaluates ZIBs at the coin-cell level, lacking practical assessment with industrial-level prototype cells and practical battery parameters such as high active mass loading, high Zn utilization, and lean electrolytes. Moreover, inaccuracies in evaluating the energy density of ZIBs hinder the rational judgment of their practical application.

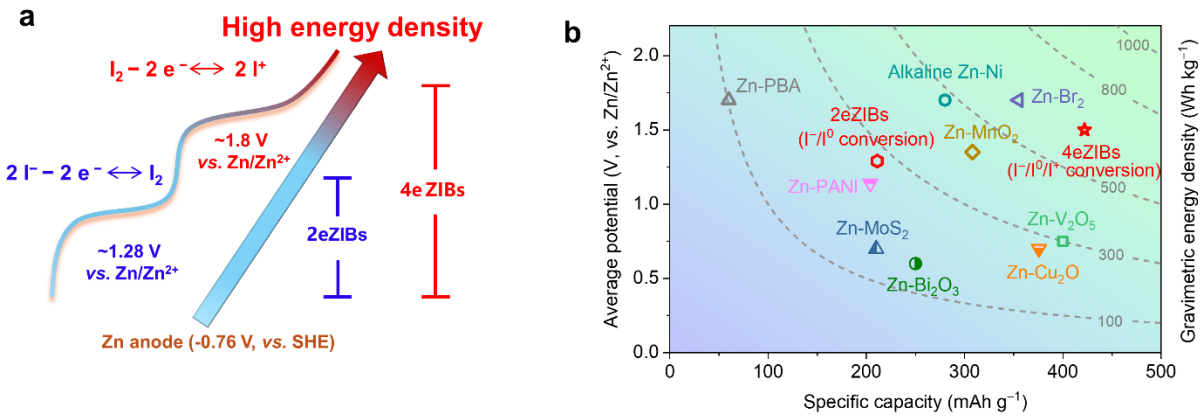


Figure 1. Comparison of energy density of ZIBs with existing AZBs. (a) Schematic for iodine conversion. (b) Theoretical energy density of cathodes for AZBs.

In this Review, we aim to highlight the remarkable progress made in advanced ZIBs in recent years and discuss their practical potential. We begin by examining the working mechanisms, critical drawbacks, and related solutions for advanced ZIBs, including 2e I^-/I_2 conversion, 4e $I^-/I_2/I^+$ conversion, and hetero-halogen conversion. In the next section, we simulate the energy density of ZIBs by considering all battery components at a practical pouch-cell level to impartially assess the competitiveness of ZIBs compared to the existing AZBs. Following that, we further elucidate the impacts of the Zn anode on the lifespan of ZIBs, identifying critical parameters and possible Zn utilization control methods in practical battery fabrication to meet the target of ten-year energy storage. Additionally, we assess the cost of ZIBs based on current global iodine reserves and iodine prices, highlighting key issues related to battery costs in their applications and proposing a closed-loop iodine recycling pathway to reduce iodine prices in the future. Finally, we

conclude that ZIBs, especially 4eZIBs, are a promising solution for large-scale applications and provide a perspective on industrial-level battery design.

2. CHALLENGES FOR IODINE CATHODES

Iodine redox undergoes the reversible conversion between variety of iodine species, reversibly storing and releasing the energy by altering the chemical valence of iodine. Traditional two-electron I^-/I_2 pathway presents good reversibility and fast reaction kinetics, however, is limited by the polyiodides shuttle and relatively low energy density. Four-electron $I^-/I_2/I^+$ pathway can offer significant energy density, whilst much inferior reversibility and reaction kinetics is plugged the practical applications. In this part, the reaction mechanism of iodine conversion process and related challenges are discussed.

2.1. Two-electron I^-/I_2 pathway. Traditional 2eZIBs process two-electron I^-/I_2 pathway, which involves the formation of a series of polyiodides, such as triiodide (I_3^-) and pentaiodide (I_5^-), as intermediates during battery cycling (top of **Figure 2**a).[37] These polyiodides, especially I_3^-, are highly soluble in aqueous electrolytes, enabling fast reaction kinetics with exceptional rate capability due to the liquid-phase reaction mechanism.[29] However, the soluble I_3^- tends to cross the separator to the anode side and spontaneously react with active Zn to consume the stored energy, which is so-called as shuttle effects.[33] The generated I^-, also highly soluble in aqueous media, can migrate back to the cathode side to participate in iodine oxidation. The severe shuttle effects would cause the low battery reversibility with low battery CEs.[42] Moreover, the parasitic reaction between shuttled polyiodides and Zn anodes would result in serious Zn corrosion and anode passivation, significantly consuming the active Zn to shorten the cycling life of 2eZIBs (**Figure 2**b).[33] Importantly, when under limited Zn supplement, the lifespan of batteries would be worsened, posing huge challenges to realize practical application of 2eZIBs. The practical use of

2eZIBs is also plagued by the serious self-discharging, gradually losing the stored energy during battery resting.[11] It should be concerned that the self-discharging cannot be simply ascribed to the shuttle effects. Typically, I_2 is instable in aqueous media, which can gradually be hydrolysed to yield polyiodides, as shown below:[43]

$$I_2 + H_2O \rightarrow HIO + H^+ + I^- \quad (1)$$

$$4HIO \rightarrow 2H_2O + 2I_2 + O_2\uparrow \quad (2)$$

$$I^- + I_2 \rightarrow I_3^- \quad (3)$$

As-generated polyiodides, especially I_3^-, initiate the shuttle effects, further accelerating the self-discharging. Therefore, suppressing the I_2 hydrolysis and shuttle effects is fundamentally effective to reduce the self-discharging. Various strategies, including confining the polyiodides inside cathodes,[44-45] suppressing the polyiodide diffusion toward anode sides,[46-47] and retarding the spontaneous reaction between polyiodides and Zn metal,[48-49] are demonstrated to lower the self-discharging of 2eZIBs. It should be concerned that most prevailing methods for suppressing self-discharging have focused on overcoming shuttle issues while largely ignoring the contribution of I_2 hydrolysis. To effectively prevent self-discharging, it is essential to suppress both shuttle effects and I_2 hydrolysis. Besides, the evaluation of self-discharging is essential to conduct under strict conditions to meet the requirement of practical application, such as reasonable mass ratio of I_2 in cathode materials (*e.g.*, >70%), high area capacity (*e.g.*, >3 mAh cm^{-2}), and lean electrolyte (*e.g.*, <5 g Ah^{-1}). So far, the self-discharge rate of 2eZIBs remains unsatisfactory, especially at the practical pouch-cell level.

2.2. Four-electron $I^-/I_2/I^+$ pathway. The iodine electrochemistry further enables the additional I_2/I^+ redox when the cut-off voltage was enlarged up to over 1.8 V vs. Zn/Zn^{2+} (bottom of **Figure 2**a). This redox is generally infeasible unless the presence of nucleophilic species like halides (X^-,

X = F, Cl, and Br), cyanide, and amines.[38, 50] This is due to the interaction between electrophilic I^+ and nucleophilic species forms charge-transfer complexes to stabilize the I_2/I^+ redox. Unfortunately, the reversibility of I_2/I^+ reversibility is far from satisfactory, primarily resulting from the hydrolysis of I^+ due to the nucleophilic attack of water (**Figure 2**d), as showing following:[51]

$$IX + H_2O \rightarrow HIO + H^+ + X^- \quad (4)$$

$$4HIO \rightarrow 2I_2 + 2H_2O + O_2\uparrow \quad (5)$$

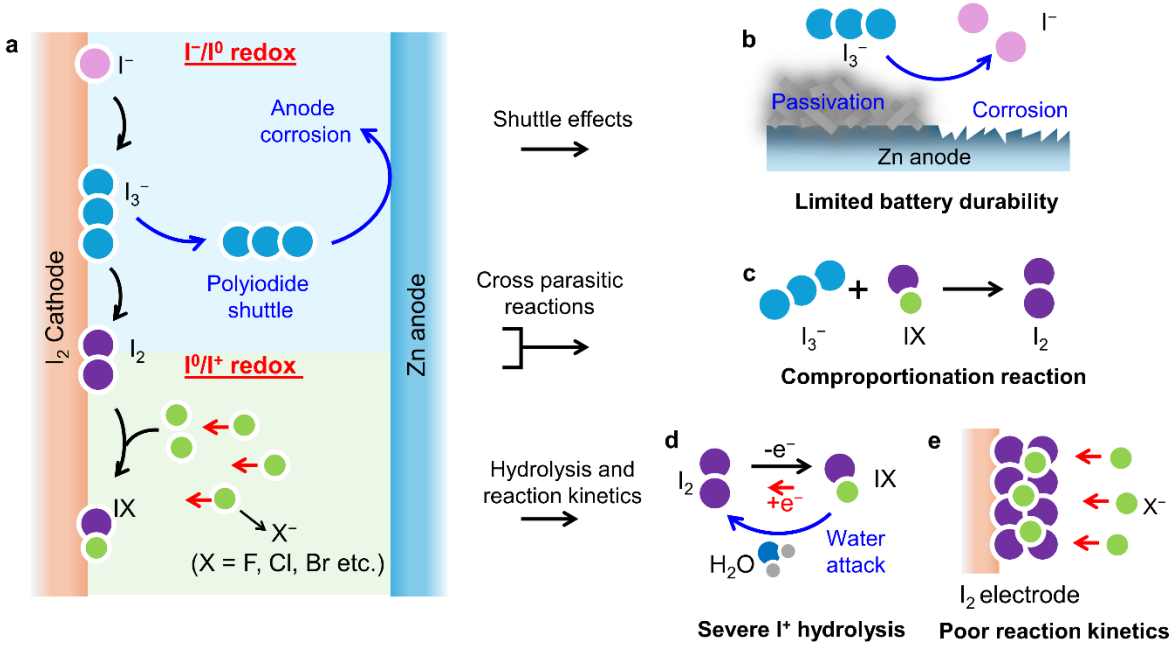


Figure 2. Reaction mechanisms and critical issues for ZIBs. (a) Schematic for reaction mechanism of ZIBs. (b) Shuttle effects induced limited battery durability. (c) Cross parasitic reactions between polyiodides and I^+ species. (d) Poor I_2/I^+ reversibility caused by I^+ hydrolysis. (e) Insufficient I_2/I^+ conversion due to sluggish kinetics.

Besides, unlike the I^-/I_2 conversion, the I_2/I^+ conversion is highly related to the formation of charge-transfer complexes between I^+ and nucleophilic species. The mass transportation of these nucleophilic species within the electrode is sluggish, leading to the insufficient contribution of I_2/I^+

redox in practical batteries, especially when elevating the active mass loading (**Figure 2**e). Nevertheless, the I^-/I_2 and I_2/I^+ redox presents the cross parasitic reactions to degrade the battery performance. The incomplete conversion of polyiodides in I^-/I_2 conversion would neutralize the I^+ species generated in I_2/I^+ conversion, which further deteriorate the reversibility of 4eZIBs (**Figure 2**c).[52] Therefore, advanced 4eZIB should overcome the shuttle effect of polyiodides, hydrolysis of I^+ species, together with sluggish reaction kinetics between variety of iodine species.

3. SOLUTIONS FOR HIGH-PERFORMANCE IOIDNE CATHODES

3.1. Suppressing the shuttle effect of 2eZIBs. Shuttle effects of 2eZIBs are initialized by the dissolution and migration of soluble polyiodides towards the Zn anodes. The spontaneous chemical reaction between polyiodides and Zn anodes leads to the capacity loss of batteries. suppression of shuttle effects is highly demanded for the practical adoption of 2eZIBs. In this section, we systematically concluded the proposed solutions for 2eZIBs, including host confinement, functional binders, cation coordination, I_3^- diffusion limitation, electrolyte optimization, and physical shield for Zn anodes.

3.1.1 Host confinement. I_2 is a purple-black molecular crystal with poor electrical conductivity ($\approx 10^{-6}$–10^{-9} S m^{-1}), resulting in inferior redox reversibility and poor reaction kinetics.[53] Additionally, I_2 has high vapor pressure and undesirable thermal stability, leading to easy sublimation even at room temperature.[54] Dispersing I_2 into porous conductive hosts to fabricate composite cathodes is an effective approach to address above issues (**Figure 3**a). Porous carbon-based materials with high electrical conductivity, rich pore structures, and chemical/electrochemical stability not only facilitate electron transfer for iodine conversion but also adsorb the polyiodide intermediates to suppress shuttle effects.[55-57] However, this physical adsorption is relatively weak, posing challenges in effectively eliminating the shuttle effect.

Methods such as heteroatom (*e.g.,* N, O, S, and P) doping and functional group modifications can create rich defects and active sites to strengthen polyiodide anchoring.[58-60] Nevertheless, relatively weak iodine carrying capability of carbon-based hosts still challenges the stable cycling of ZIBs under conditions of high I_2/host ratios and high specific I_2 loading.

Transition metals can provide strong orbital hybridization between the *d* orbitals of metal sites and the *p* orbitals of iodine species, which strengthens polyiodide capture to mitigate shuttle effects.[61] Additionally, the catalytic effects of metal sites can further promote the iodine conversion process by reducing the energy barrier.[30] Consequently, modification of carbon-based hosts by various catalyst materials, such as single-atom catalysts,[62-65] metal clusters, and molecular catalysts,[66] have been proposed to enhance the electrochemical performance of 2eZIBs. Ample catalyst loading in the host materials is essential for effectively catalysing the iodine conversion, however high catalyst loading lowers the specific surface area and blocks the pore structure of host materials as well, posing difficulty in realizing high I_2 carrying. To trade-off the high I_2 carrying capability and abundant catalytic metal sites, various metal-coordinated networks, such as MXenes, metal-organic frameworks (MOFs), and Prussian blue analogues (PBAs), have been proposed (**Figure 3**b).[67-69] These metal-coordinated networks do not sacrifice I_2 carrying capability due to their sufficient inner conductive channels but provide rich metal active sites for a more efficient iodine conversion pathway.

In addition to porous materials, polymer-based materials have also been demonstrated to serve as effective hosts for I_2 (**Figure 3**c). For example, inspired by the chromogenic reaction between starch and I_2, researchers have utilized starch to confine I_2, achieving excellent cycling life for over 50,000 cycles.[33] The unique double helical structure of starch enables polyiodides to embed inside its helical structure *via* hydrogen bonding. However, polymer-based hosts often have poor

electrical conductivity and lack a porous structure, leading to slow charge transfer. Conductive polymer materials, such as polyaniline and polypyrrole, offer solutions to address the inherent electrical insulation of I_2.[70-71] Additionally, designing the electrode structure or preparing porous conductive polymer materials can further address the limited I_2 carrying capability of polymer-based hosts.[72]

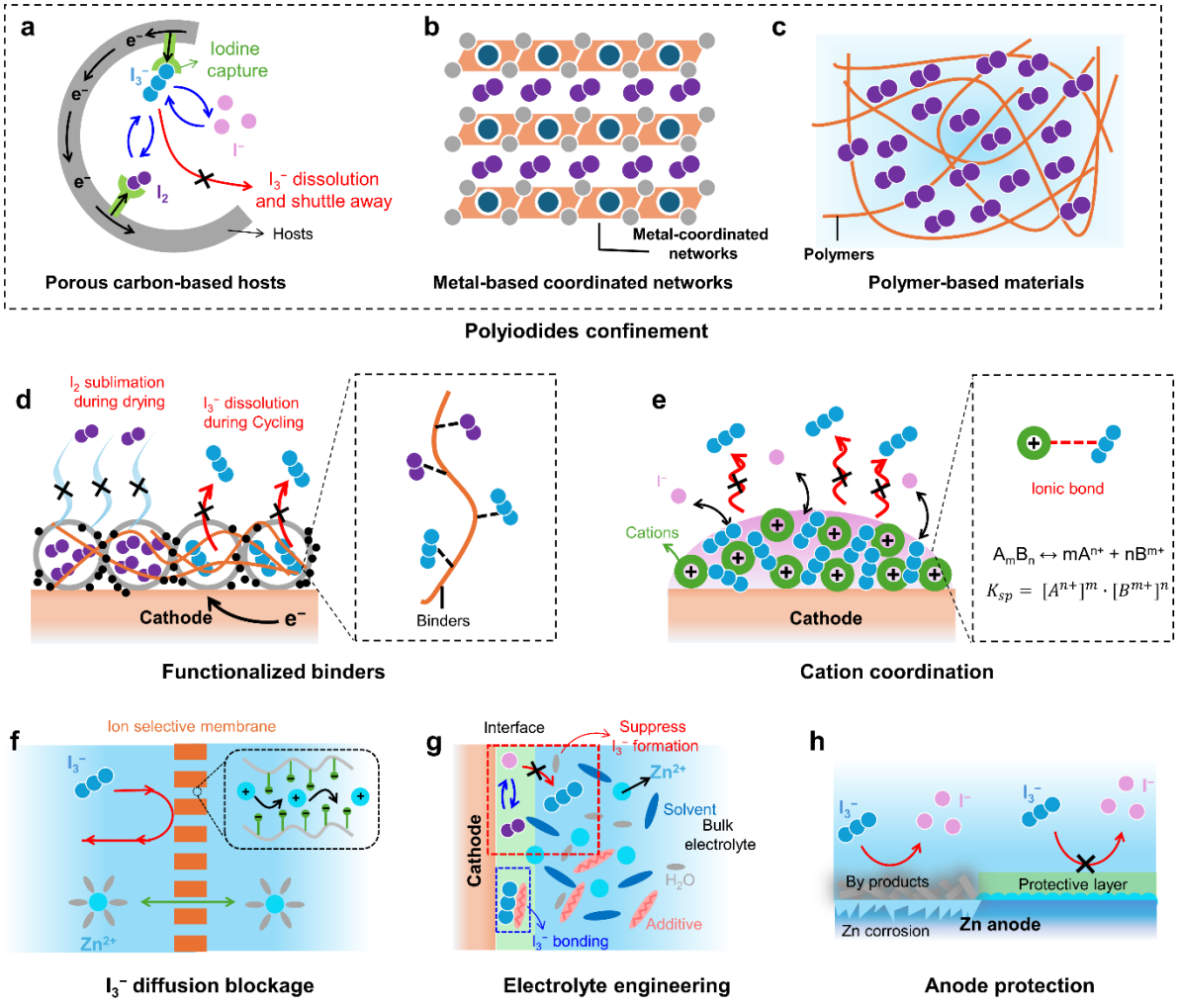


Figure 3. Strategies for 2eZIBs. (a-c) Host confinement by (a) porous carbon-based materials, (b) metal-based coordinated networks, and (c) polymer-based materials. (d) Functionalized binders. (e) Cation coordination, (f) I_3^- diffusion limitation, (g) electrolyte engineering, and (h) anode protection.

Despite the successful application of various hosts to overcome the shuttle effect and enhance the charge transfer process of ZIBs, the mass fraction of I_2 in composite cathodes remains relatively low, generally below 50%. Moreover, the rich pore structure and large surface area result in low tap density of composite cathodes, challenging the fabrication of high-area-capacity electrodes (*e.g.,* > 3 mAh cm^{-2}). Thus, there is a high demand for finding desirable hosts that can achieve high I_2 mass ratios and enable the fabrication of thick electrodes.

3.1.2. Functional binders. Binders play a critical role in integrating I_2 composite cathodes into real electrodes. An ideal binder for 2eZIBs should inhibit I_2 sublimation during electrode preparation and suppress shuttle effects during battery cycling (**Figure 3**d). However, commonly used binders, such as polyvinylidene fluoride and polytetrafluoroethylene, have weak interactions with iodine and polyiodides, resulting in poor battery performance. Moreover, the use of organic solvents in electrode preparation exacerbates I_2 loss during drying. Water-soluble binders might be suitable for I_2 electrode preparation as insoluble nature of I_2 solid. However, the good binders must overcome issues such as dissolution and exfoliation from current collectors during battery operation in aqueous media. Recently, water-soluble binders like chitosan and polyacrylonitrile copolymer have been successfully used to reduce I_2 loss during electrode preparation and mitigate I_3^- shuttle during battery operation due to stronger interactions between their polar polymer chains and iodine species.[73-74] Various water-soluble polymers, such as sodium alginate, can stabilize in Zn^{2+}-based electrolytes due to the cross-linking effect of Zn^{2+}, indicating their potential application as binders.[75-76] This solubility retardance of various binders in Zn^{2+}-based electrolyte can broaden the options for binder design, paving the way for high-performance ZIBs in the future.

3.1.3. Cation coordination. The strong ionic bond between cation species and polyiodide anions provides a new approach for shuttle-free 2eZIBs (**Figure 3**e). In previous reports, a series

of iodide salts, including methyl ammonium iodide, tetrabutylammonium triiodide, and iodine-based perovskite materials, were directly used as cathodes for iodine batteries.[77-79] Due to the intrinsic thermal stability of these iodide salts, I_2 sublimation during electrode preparation was completely avoided. Moreover, the large cations of these salts strongly coordinate with the polyiodides to suppress shuttle effects. However, these salts are almost electrically insulating, resulting in slow charge transfer and poor reaction kinetics. Recently, it was discovered that the coordination between some quaternary ammonium cations and I_5^- anions can form an ionic liquid state.[80] These polyiodide ionic liquids exhibit high electrical conductivity to enhance charge transfer and boosting iodine conversion under practical areal capacities of >3 mAh cm^{-2}.

Typically, the confinement of polyiodides by functional cations originates from the ionic bond between them. However, a stronger ionic bond does not necessarily mean fewer shuttle effects. Instead, the solubility product (*Ksp*) stands for the solubility of substances, which is more suitable for estimating the solubility retardance of polyiodides (right of **Figure 3**e). The cations-polyiodides composites that exhibit a large *Ksp* indicate less solubility of polyiodides for more efficient shuttle suppression. One should keep in mind that despite the significant success achieved by these cation coordination strategies in 2eZIBs, large cations reduce the active mass ratios of iodine, significantly compromising the energy density of ZIBs.

3.1.4. I_3^- diffusion limitation. Preventing the diffusion of I_3^- across the separator to the anode side can directly avoid loss of active materials and undesirable chemical reactions between I_3^- and Zn, thereby eliminating shuttle effects. Commonly used glass fibre separators allow the diffusion of both cations and anions, thus contributing less to retarding I_3^- shuttle. Cation exchange membranes (CAMs) are effective for suppressing shuttle effects because they conduct cations while repelling anions (**Figure 3**f). Nafion membrane, a commercial CAM, was demonstrated to

effectively prevent the shuttle of I_3^-.[81] However, the high price of Nafion membrane hinders its further application. Therefore, various inexpensive substituted CAMs have been proposed. Essentially, immobilizing anionic groups (*e.g.,* sulfonic groups and carboxyl groups) in the polymer chains of CAMs can improve the selective conduction of Zn^{2+} cations to block the I_3^- diffusion (inset in **Figure 3**f).[46, 82-83] Moreover, the selective conduction of Zn^{2+} further homogenizes the ion flux to regulate Zn plating, extending the cycling life of Zn anodes.

The blockage of I_3^- diffusion has also been achieved through ionic sieve strategies using porous membranes.[34, 42] For example, a zeolite membrane fabricated from a zeolite molecular sieve ($Na_{12}(AlO_2)_{12}(SiO_2)_{12}\cdot xH_2O$) was used to confine the shuttle of I_3^-. The pore size of zeolite molecular sieve is 4 Å, which is smaller than the ionic diameter of I_3^- (5.14 Å), limiting the diffusion of I_3^- over the zeolite membrane. Similarly, the zeolite-based membrane was also attached to the Zn anode to prohibit the diffusion of I_3^- toward the Zn anodes, thus preventing Zn corrosion.[84] Despite such advantages of functional membranes on suppressing shuttle effects, the practical use of these membranes still features significant drawbacks such as high cost, limited ionic conductivity, larger charge transfer resistance.

3.1.5. Electrolyte optimization. Electrolytes play a crucial role in enhancing the reversibility of both cathodes and anodes, making their design critical for practical ZIBs (**Figure 3**g). The anions in Zn^{2+}-based electrolytes significantly influence the electrochemical behaviour of iodine conversion.[85] During this conversion, I^- tends to coordinate with I_2 to form I_3^-, which can dissolve and shuttle to the anode. Therefore, the competitive coordination of I_2 between salt anions and I^- can regulate the CE of ZIBs by modulating the diffusion rates of polyiodides. Among various anions, SO_4^{2-} exhibits a stronger interaction with I_2, which retards the formation of I_3^- and thereby improves the CE of ZIBs in $ZnSO_4$-based electrolytes.[85] Additionally, highly concentrated $ZnSO_4$

can increase the acidity of electrolytes, which is beneficial for suppressing the self-discharge of ZIBs.[86] However, unmodified $ZnSO_4$ electrolytes exhibit inferior performance for Zn anodes. Introducing co-solvents into aqueous electrolytes has also been demonstrated to modulate both Zn reversibility and shuttle issues. For example, ethylene glycol has been used as a co-solvent in $ZnSO_4$-based electrolytes to smooth Zn dendrites by altering Zn^{2+} solvation and inhibiting the I_3^- shuttle through complexation with polyiodides.[87] In addition to the bulk electrolyte modification, various additives present significant functions to interact with iodide species to inhibit the polyiodides diffusion. The functions of additives on suppressing shuttle effects can be classified as following: 1) inhibiting I_3^- formation by preferentially coordinated with I_2;[88] 2) restraining the I_3^- dissolution by forming insoluble composites;[44, 89-90] 3) modulating the diffusion rates of I_3^- in electrolytes;[47, 91] 4) mitigating the Zn corrosion by strong anode adsorption.[88] Beyond conventional aqueous electrolytes, novel systems like eutectic electrolytes offer different iodine electrochemistry due to their unique Zn^{2+} solvation structures.[10, 92] It has been shown that the $I_2 \rightarrow I_3^-$ conversion presents a high Gibbs free energy in eutectic electrolytes, thermodynamically prohibiting the formation of I_3^- and eliminating shuttle effects. However, the organic solvent in eutectic electrolytes increases the solubility of I_2, which may cause the shuttle of I_2 as well.

Compared to liquid-based electrolytes, solid-state or hydrogel electrolytes can effectively block the diffusion of I_3^- due to improved selective Zn^{2+} conduction. Solid-state electrolytes offer a fundamental solution to shuttle issues by eliminating the liquid medium for I_3^- dissolution.[93] However, their limited ionic conductivity compromises battery rate performance. Hydrogel electrolytes, on the other hand, constrain a certain amount of water within their polymer networks, providing good interfacial affinity, high Zn^{2+} conductivity, desirable redox kinetics, and mechanical flexibility.[94-95] The improvement of selectivity for Zn^{2+} conduction is the primary

target for hydrogel electrolytes, which regulating the Zn plating behaviour and repel the unwanted polyiodides diffusion.[94, 96] However, the hydrogel electrolytes are hardly to completely avoid the anion conduction, implying the potential of I_3^- shuttle. Modifying the hydrogel electrolyte near the cathode sides by iodophilic functional groups can compensate for the imperfect Zn^{2+} selectivity of hydrogel electrolytes, benefiting to the shuttle-free ZIBs design.[97]

3.1.6. Physical shield for Zn anodes. The root of the shuttle effect can be attributed to the spontaneous reaction between shuttled I_3^- and Zn metal. Therefore, preventing contact between I_3^- and Zn can be effective to eliminate the shuttle effect. Constructing protective layers on the Zn anode to prevent I_3^- corrosion has been widely reported to suppress the shuttle effect (**Figure 3**h). An ideal protective layer for 2eZIBs must possess several features: 1) high Zn^{2+} conductivity and selectivity to facilitate fast Zn^{2+} transportation while inhibiting I_3^- diffusion; 2) good chemical and electrochemical stability to resist water/polyiodide-induced corrosion; 3) robust mechanical strength and flexibility to prevent dendrite formation; 4) good affinity and cohesion with Zn anodes to prevent exfoliation. Various types of protective films, including alloy-type films,[48, 98] conversion layers,[99-100] and ionically selective films,[84, 101] have been constructed on the Zn surface to hinder polyiodide-initiated Zn corrosion, Zn dendrite formation, and water-related parasitic reactions. However, due to the significant volume variation during Zn plating/stripping, the protective layer is susceptible to breaking and exfoliation, especially under conditions of high Zn cycling capacity (*e.g.,* >3 mAh cm^{-2}) and high Zn utilization (*e.g.,* >50%). The effectiveness of protective layers under such stringent battery cycling conditions has yet to be fully established.

3.2 Stabilizing the I^+ species for 4eZIBs. The activation of additional I_2/I^+ conversion provides significant improvement in energy density of ZIBs, nevertheless, the reversibility of I_2/I^+ conversion is much poor compared to the I^-/I_2 conversion. The root of poor reversibility of I_2/I^+

conversion can be ascribed to the strong tendency of hydrolysis of I^+ species in aqueous media and large energy barrier for the conversion owing to the slow charge/mass transportation. In this section, we comprehensively summarized the methods for addressing the reversibility issues of 4eZIBs, including host confinement, catalytic effects, electrolyte engineering, and coordination chemistry, providing the guidance for designing high-performance 4eZIBs.

3.2.1. Host confinement. For the 4e conversion reaction, the challenges posed by highly soluble reaction intermediates, the strong tendency for I^+ species hydrolysis, and sluggish reaction kinetics significantly reduce its reversibility. Host materials offer a potential solution by facilitating electron transfer and promoting reaction kinetics through their high electrical conductivity and abundant pore structure for confining critical intermediates (**Figure 4**a). While carbon-based materials have shown success in I^-/I_2 redox reactions, they often fail in achieving highly reversible I_2/I^+ redox due to their limited ability to retard I^+ hydrolysis and promote kinetics. Metal-based coordination frameworks, however, exhibit stronger electrostatic interactions with I^+ species, which is crucial for improving conversion reversibility.[102-103] In a pioneering study, an iodine-terminated halogenated $Ti_3C_2I_2$ MXene derived from the reaction between Ti_3AlC_2 and CuI was directly used as a cathode for 4eZIBs.[102] Leveraging the excellent electrical conductivity and abundant internal active sites of $Ti_3C_2I_2$ MXene, reversible $I^-/I_2/I^+$ conversion was successfully achieved in a $ZnCl_2$/KCl electrolyte. However, due to the relatively low iodine content of $Ti_3C_2I_2$ MXene, the overall specific capacity of 4eZIBs was limited to approximately 200 mAh g^{-1} at 0.5 A g^{-1}.

3.2.2. Catalytic effect. Catalysts play a crucial role in enhancing the interaction between iodine species and catalytic substrates, addressing the poor reversibility and sluggish reaction kinetics of $I^-/I_2/I^+$ conversion (**Figure 4**b). Porous carbon materials are well-suited for hosting iodine species

within their pore structure, promoting the charge-transfer process during iodine conversion due to their high electrical conductivity and abundant porous architecture. However, the limited catalytic activity of carbon materials alone is insufficient to effectively facilitate iodine conversion. Therefore, a rational design approach involves the hybridization of metal-based active sites with porous carbon substrates.[104] Various modifications of porous carbon materials using metal-based catalysts, such as single-atom catalysts,[61, 64] metal-phthalocyanine compounds,[105] Co_9S_8,[106] and others, have been proposed for this purpose. For example, Liang et al. proposed a Fe single-atom catalyst with highly Fe-N_4 coordination centres for 4eZIBs.[61] It demonstrated that the orbital hybridization between *p* orbitals of Fe metal sites and *p* orbitals of iodine species strengthens the interaction with I^+ species to suppress the hydrolysis by elevating the energy barrier for proton detachment from the ICl·HOH intermediate. Additionally, the *d-p* hybridization further accelerates electron transfer among iodine species, facilitating their conversion. As a result, 4eZIBs have demonstrated high reversibility with nearly 100% battery CEs under practical areal capacities of > 3 mAh cm^{-2} and outstanding long-term stability of over 10,000 cycles at 2 A g^{-1}. Furthermore, it has been observed that the I_3^- shuttle during I^-/I_2 conversion can neutralize I^+ species through the comproportionation reaction, accelerating the failure of 4eZIBs.[52] Therefore, catalyst design should focus on facilitating the I^-/I_2 conversion to inhibit I_3^- formation and stabilizing I^+ species to improve I_2/I^+ conversion. Very recently, Lu et al. developed a copper phthalocyanine/graphene heterostructure (CuPc@rGO) as a host for I_2, effectively enhancing the stability of the $I^-/I_2/I^+$ conversion process.[105] The study demonstrated that the charge transfer interaction between CuPc and I^+ species stabilizes the I^+ ions. Additionally, the electron-outflow effect resulting from the π-π conjugation between CuPc and the carbon hosts further strengthens this charge transfer

interaction, thereby improving the reversibility of the $I^-/I_2/I^+$ conversion. Such metal/carbon hybrid catalysts provide a feasible approach to enhancing the reaction kinetics for 4eZIBs.

The development of catalysts for 4eZIBs is still in its early stages, and further efforts are needed to elucidate the functional roles and design principles of highly effective catalysts. A deeper understanding of the catalytic activity and mechanisms of metal-based materials in 4eZIBs is currently lacking, which is crucial for the rational selection and design of efficient catalysts. Additionally, it is important to consider that catalysts may also enhance the reaction kinetics of the oxygen evolution reaction (OER), potentially accelerating water decomposition. Therefore, improving catalytic selectivity is equally critical in the design of catalysts for 4eZIBs.

3.2.3. Electrolyte engineering. The stabilization of I^+ species in aqueous electrolytes relies on the formation of interhalogen compounds between I^+ and X^- (X = Br, Cl, and F) ions, making the electrolyte critical for the reversibility of $I2/I^+$ electrochemistry (**Figure 4**c). Unlike the I^-/I_2 conversion, 4eZIBs based on I_2/I^+ conversion require the participation of nucleophilic X^- ions, similar to a "dual-ion battery" mechanism. This mechanism means the reaction equilibrium is highly dependent on the concentration of X^- ions in the electrolyte, which can be elaborated by the Nernst equation (right of **Figure 4**c). The concentration of X^- is a denominator, suggesting the easier conversion from I_2 to I^+ under higher concentration of X^-. In diluted Zn^{2+}-based electrolytes, the improvement of X^- concentration is feasible by introducing alkali metal halide salts (*e.g.,* LiCl, KCl, etc.) in electrolytes.[102] However, I^+ exhibits a strong tendency for hydrolysis in diluted electrolytes due to high water activity. The hydrolysis of IX can be suppressed in environments with low water content, high X^- concentration, and strong acidity. Highly concentrated electrolytes are primarily used to reduce I^+ hydrolysis due to their low free water content. As an example, a Cl^- based highly concentrated electrolyte composed of $ZnCl_2$, LiCl, and acetonitrile (ACN) in a

molarity ratio of 19:19:8 was proposed to enable highly reversible $I^-/I_2/I^+$ conversions.[38] This high-concentration electrolyte provided sufficient free Cl^- ions to effectively trigger the I_2/I^+ conversion, resulting in a reversible capacity of 594 mAh g^{-1}. Additionally, the fraction of free water in this electrolyte was significantly reduced, which further retarded the hydrolysis of I^+ species. As a result, outstanding electrochemical performance of 4eZIBs for over 6,000 cycles was achieved at 2 A g^{-1}. However, significant drawbacks of highly concentrated electrolytes, such as high viscosity hindering ion transport and leading to sluggish electrode kinetics, should be noted.

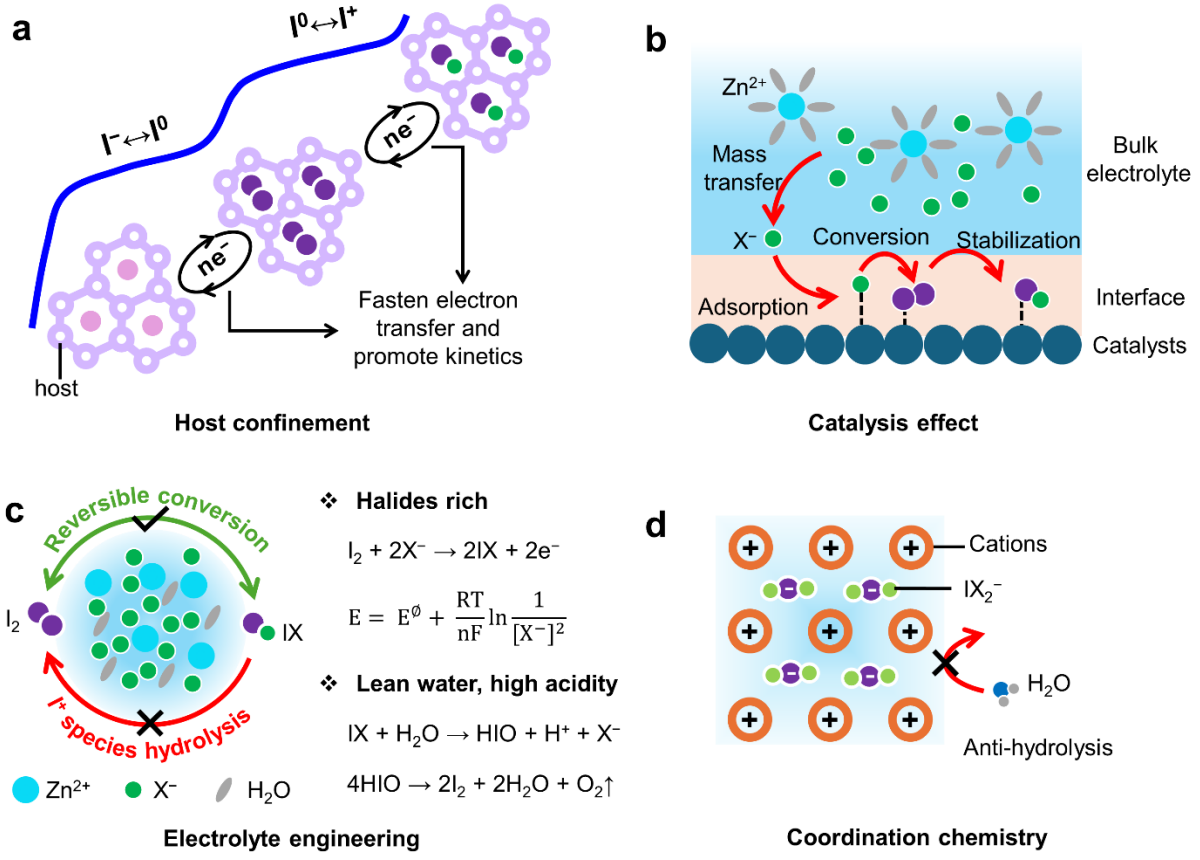


Figure 4. Strategies for high-reversible 4eZIBs. (a) Host confinement. (b) Catalysis effect. (c) Electrolysis engineering. (d) Coordination chemistry.

Effectively activating the I_2/I^+ conversion often requires electrolytes rich in X^- ions. However, X^- ions are prone to corrode ordinary battery components and are not readily available for forming a stable and ionically conductive interfacial phase on the Zn anode, posing challenges for practical applications. Early work by Hickam demonstrated the feasibility of stabilizing I^+ with nucleophilic species such as quinoline, piperidine, or pyridine.[50] These compounds, containing N atoms with rich lone pair electrons, can coordinate with I^+ species. Drawing inspiration from this, a non-halide ternary hydrated eutectic electrolyte composed of $Zn(ClO_4)_2{\cdot}6H_2O$, dimethyl sulfone (DMS), and niacinamide (NA) in a molar ratio of 1:3:0.5 was proposed for 4eZIBs.[107] The lone pair electrons on the N atoms of NA molecules can bond to I^+ species, forming stable I^+-NA_2 complexes to activate the I_2/I^+ conversion. Additionally, the hydrated eutectic electrolyte has a low water content, inhibiting the hydrolysis of I^+. With this electrolyte, highly reversible $I^-/I_2/I^+$ conversion with a near-theoretical specific capacity of 412 mA h g^{-1} at 500 mA g^{-1} was achieved. However, the relatively weak coordination capability between these N-containing compounds and I^+ may lead to poor cycling stability.

3.2.4. Coordination chemistry. Enhancing the inherent anti-hydrolysis ability of I^+ species in aqueous environments is significant for achieving reversible $I^-/I_2/I^+$ conversion. Typically, in X^--rich environments, I^+ species can form IX_2^- anions (*e.g.*, ICl_2^- in Cl^- based electrolytes). Therefore, embedding the IX_2^- anions in cations-domain coordinated networks should be feasible for stabilizing I^+ (**Figure 4**d). Previous reports have achieved stable 4e conversion in organic Li-I_2 batteries by directly using ammonium methyl iodide as a cathode.[77] Later, tin-based iodine-rich $ODASnI_4$ (ODA is 1,8-octanediamine) perovskite materials were adopted as cathodes for 4eZIBs.[79] The strong coordination networks between ODA^{2+} cations and $[SnI_6]^{4-}$ anions could stabilize I^+ species, resulting in a high specific capacity of 421 mAh g^{-1}. A significant breakthrough

in reversible 4eZIBs was demonstrated by using quaternary ammonium cations (QA^+) to improve the anti-hydrolysis capacity of I^+ species (ICl_2^-).[108] It was found that QA^+ with long-chain alkyl groups can form stable insoluble composites with ICl_2^- anions, significantly enhancing anti-hydrolysis of I^+ species in aqueous media. Through the coordination of QA^+, high-reversible $I^-/I_2/I^+$ conversion was realized, presenting a new pathway for advanced 4eZIBs. Nevertheless, the selection of QA^+ should be carefully concerned as it would sacrifice the energy density owing to large molecule wight of QA^+.

3.3 Hetero-halogen electrochemistry for higher energy density out-put. In pursuit of enhancing energy density, introducing hetero-halogen conversion chemistry in ZIBs have been regarded as a promising approach. This strategy involves the utilization of mixed halogen species to improve the energy density of halogen-based batteries. Specifically, the focus lies on two main categories: halogen redox coupling (**Figure 5**a) and iodate (IO_3^-) electrochemistry (**Figure 5**b).

The activation of the I_2/I^+ redox reaction has been achieved through the formation of interhalogens with hetero-halogen ions (*e.g.,* Cl^- and Br^-). By elevating the upper limit potential for charging, the Cl^-/Cl^0 or Br^-/Br^0 conversion can be realized, presenting a three-stage conversion process with significantly enhanced energy density (*e.g.,* > 900 Wh kg^{-1} when coupling $I^-/I_2/I^+$ redox with Cl^-/Cl^0 redox) (**Figure 5**c).[39-40] However, achieving reversible Cl^-/Cl^0 or Br^-/Br^0 conversion is challenging because the products, liquid Br_2 or gaseous Cl_2, are difficult to capture and stabilize. Notably, iodine plays a crucial role in stabilizing Cl^-/Cl^0 and Br^-/Br^0 redox by forming interhalogens with liquid Br_2 and gaseous Cl_2.

The I^-/IO_3^- redox couple enables twelve-electron conversion per I_2 molecule can provide an ultra-high theoretical capacity of 1,266 mAh g^{-1} (based on the mass of I_2), indicating an unparalleled energy density among AZBs. Previous studies have shown that IO_3^- is the direct

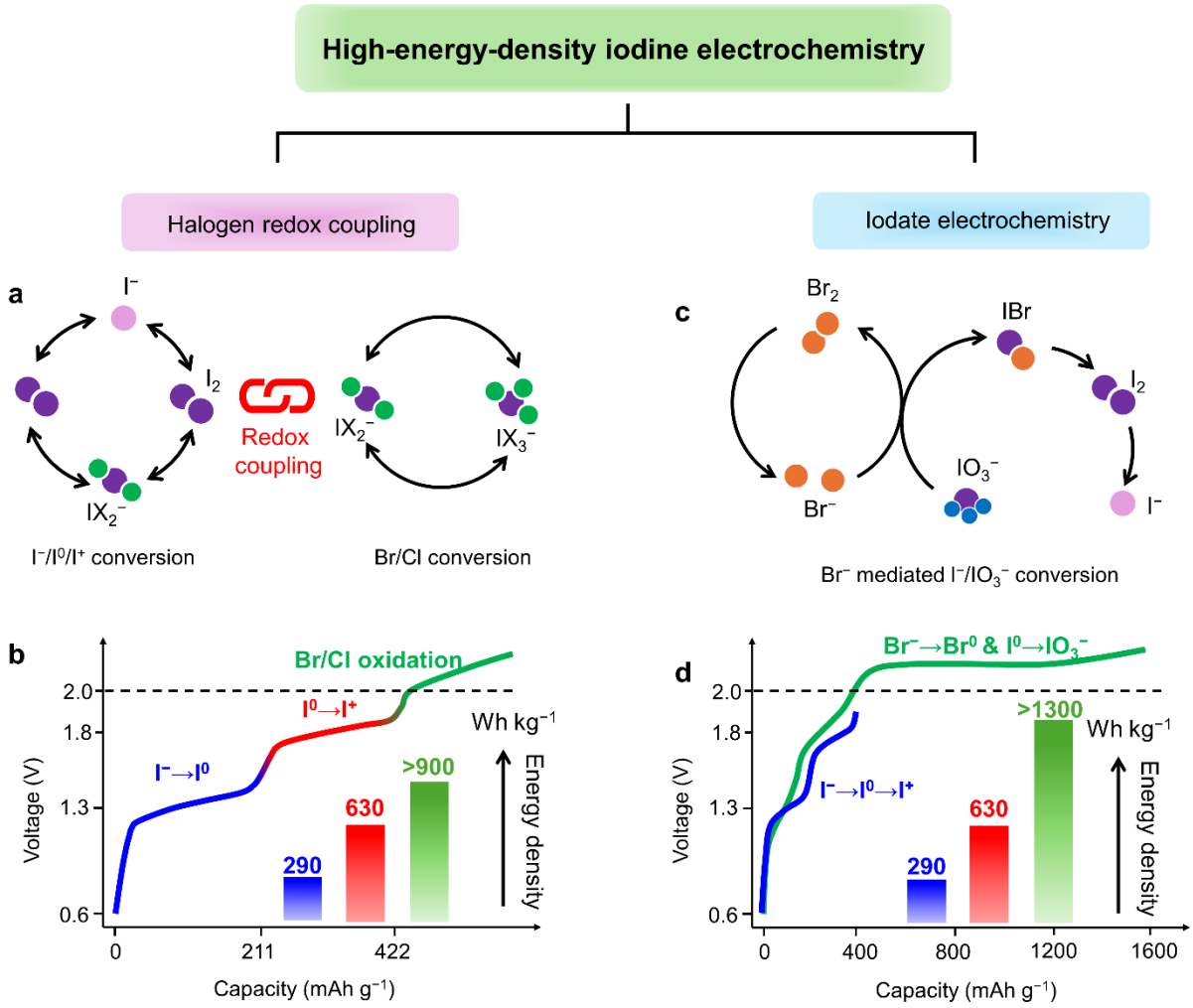


Figure 5. Multi-electron hetero-halogen conversions. (a) Halogen redox coupling and (b) Related typical charge curves. (c) Iodate electrochemistry and (d) Related typical charge curves.

oxidation product of iodine in the absence of halides (Cl^-, Br^-) or cyanide (CN^-) in aqueous solution.[109] However, this reaction typically requires a high overpotential to overcome the substantial H_2O dissociation energy to form IO_3^-. Recently, it was demonstrated that the Br^-/Br^0 redox is beneficial for activating the $I^-/I_2/IO_3^-$ redox in an acidic electrolyte.[41, 110] For example, Liang et al. introduced Br^- into the electrolyte, establishing a redox pathway known as the bromide-iodate loop (**Figure 5**b).[41] This approach effectively mitigates the kinetic obstacles for

the charge and discharge processes of the $I^-/I_2/IO_3^-$ redox couples, delivering a high specific capacity of 1,200 mAh g^{-1} and a high energy density of 1,357 Wh kg^{-1} (**Figure 5**d).

Despite the attractive energy density of these hetero-halogen conversion routes, several challenges must be addressed before practical applications can be realized: 1) the shuttle effect in hetero-halogen systems is exacerbated compared to single-halogen systems because all halogens are soluble and can shuttle to the anode; 2) the high operating potentials of hetero-halogen systems (1.36 V vs. SHE for Cl^-/Cl^0, 1.20 V vs. SHE for I_2/IO_3^-, 1.08 V vs. SHE for Br^-/Br^0) trigger severe OER; 3) the poor reversibility of hetero-halogen conversion limits the improvement of electrode loading, falling short of meeting the requirements for real applications. In summary, the exploration of hetero-halogen conversion chemistry represents a significant step forward in improving the energy density of ZIBs. However, substantial challenges hinder their real-world applications, necessitating further research and development to overcome these obstacles.

4. ENERGY DENSITY EVALUATION

The practical energy density of ZIBs in pouch-cell configurations, especially the 4eZIBs, remains inadequately estimated. The practical energy density is often much lower than the theoretical value due to the presence of multiple inactive components, including binders, conductive agents, electrolytes, separators, and packaging materials.[111] For ZIBs, substantial amounts of conductive hosts are required to compensate for the poor electrical conductivity of iodine species and to confine reaction intermediates, further reducing the energy density of the pouch cells. Additionally, controlling the zinc supplement is critical, as excessive zinc significantly compromises the energy density of the batteries.[112] Therefore, an objective evaluation of the energy density of ZIBs is necessary for bridging laboratory research to further actual application.

Table 1. Critical parameters for fictional ZIBs under 50% ZUR.

Cell Component	Cell Parameters	Value			
		2eZIBs	**4eZIBs**		
Cathode	Active materials	I_2	IF	ICl	IBr
	Capacity (mAh g^{-1})	211.0	367.1	329.8	258.9
	Mass ratios of active materials and hosts	7:3	7: 3	7: 3	7: 3
	Unilateral loading mass (mg cm^{-2})	40.62	23.35	25.99	33.11
	Unilateral capacity (mAh cm^{-2})	6.0	6.0	6.0	6.0
	Active material mass ratio (%)	96	96	96	96
	Electrode length × width (mm)	100 × 100	100 × 100	100 × 100	100 × 100
	Thickness of Ti collector (μm)	5	5	5	5
	Number of Ti collector	10	10	10	10
Anode	Active materials	Zn	Zn	Zn	Zn
	Unilateral Zn capacity (mAh cm^{-2})	12.0	12.0	12.0	12.0
	Unilateral mass of Zn (mg cm^{-2})	14.63	14.63	14.63	14.63
	ZUR (%)	50	50	50	50
	Electrode length × width (mm)	102 × 102	102 × 102	102 × 102	102 × 102
	Thickness of Ti collector (μm)	5	5	5	5
	Number of Ti collectors	11	11	11	11
Electrolyte	Injection parameter (g Ah^{-1})	2.5	2.5	2.5	2.5
Separator	Mass of glass fibre (g cm^{-2})	0.005	0.005	0.005	0.005
	Separator length × width (mm)	104 × 104	104 × 104	104 × 104	104 × 104
	Thickness (μm)	50	50	50	50
	Number of separators	20	20	20	20
Packing materials	Al-plastic film mass (g cm^{-2})	0.0192	0.0192	0.0192	0.0192
	Length × width (mm)	120 × 120	120 × 120	120 × 120	120 × 120
	Thickness (μm)	115	115	115	115
	Number of Al-plastic film	2	2	2	2

Ni tabs	Mass of Ni Tab (g)	0.4	0.4	0.4	0.4
	Out-put potential (V)	1.25	1.45	1.45	1.45
Cell	Capacity (Ah)	12.0	12.0	12.0	12.0
	Total mass (g)	165.5	129.5	135.0	149.8
Gravimetric Energy density (Wh kg^{-1})		**90.6**	**134.3**	**128.8**	**116.1**

To assess the energy density of ZIBs under practical pouch-cell configurations, a hypothetical pouch cell with a total capacity of 12 Ah was proposed, as shown in **Table 1**. This evaluation includes high-area-capacity cathodes (6 mAh cm^{-2}), high mass ratios of active materials (70 wt.%), a high zinc utilization rate (ZUR, 50%), a low electrolyte/capacity (E/C) ratio (2.5 g Ah^{-1}), and the necessary inactive battery components. For the energy density simulation of 4eZIBs, interhalogen compounds (IX, such as IF, ICl, and IBr) were selected as active materials, as at least an equal molar amount of X^- ions to iodine is essential for activating the I_2/I^+ conversion. Based on the active mass of IF, ICl, and IBr, the specific capacities of the cathodes were calculated as 367.1, 329.8, and 258.9 mAh g^{-1}, respectively. Furthermore, the relationship between energy density and ZUR was illustrated to guide the control of limited zinc conditions for practical pouch cells (**Figure 6**a). The 2eZIBs can achieve an energy density of 90.6 Wh kg^{-1} at a 50% Zn utilization rate (ZUR) and approximately 100 Wh kg^{-1} at a 100% ZUR. This indicates that increasing ZUR from 50% to 100% contributes less to the energy density. Conversely, excessively high ZUR significantly compromises the battery lifespan. According to our assessment, an optimal ZUR should be controlled at around 50% to balance high energy density and long lifespan. Additional contributions from the I_2/I^+ conversion significantly improve the energy density. With increasing molecular weights of IX compounds, the energy density of 4eZIBs follows the order of IF > ICl > IBr. Among the X^- ions, Cl^- is abundant and inexpensive, making it an ideal choice for

activating the I_2/I^+ redox. Cl^- activated 4eZIBs demonstrate a remarkable energy density of 128.5 Wh kg^{-1} at 50% ZUR and can reach 140.3 Wh kg^{-1} at 80% ZUR, showing promise for large-scale energy storage applications.

For comparison, prevailing AZBs, including Zn-MnO_2 (308 mAh g^{-1} and 1.35 V), Zn-V_2O_5 (400 mAh g^{-1} and 0.8 V), and Zn-PBA (*ca.* 60 mAh g^{-1} and 1.7 V), are shown as dash curves in **Figure 6**a. Under a ZUR of 50%, the energy density of the Zn-MnO_2 batteries is predicted to be 128.4 Wh kg^{-1}, whilst only 85.6 Wh Kg^{-1} and 70.5 Wh kg^{-1} for Zn-V_2O_5 and Zn-PBA batteries. Hence, the energy density of 2eZIBs is predicted to surpass Zn-V_2O_5 and Zn-PBA batteries but remains significantly lower than Zn-MnO_2 batteries. However, the long-term durability of Zn-MnO_2 batteries lacks solid evidence, especially in practical pouch-cell configurations, suggesting that 2eZIBs could be a feasible alternative for large-scale energy storage. Furthermore, Cl^- activated 4eZIBs present a comparable energy density to Zn-MnO_2 batteries, indicating that 4eZIBs have significant potential as next-generation aqueous-based energy storage systems.

We calculated the contribution of various battery components to the energy density of ZIBs, as shown in **Figure 6**b and 6c. In the designed battery, the cathodes and anodes account for over 60% of the total mass of the pouch cells. This suggests that reducing the electrochemically inert components in the cathodes (such as host materials, binders, and conductive agents) and improving the ZUR of the Zn anodes can significantly enhance the energy density of ZIBs. Notably, the electrolyte also occupies a substantial mass fraction, accounting for 22.2% in 2eZIBs and 18.1% in 4eZIBs, highlighting that using a lean electrolyte is another effective strategy to improve energy density.

To better illustrate the impacts of battery components on energy density, we explored the relationship between energy density and several critical parameters, including the active mass

ratios in composite cathodes, area capacity, and electrolyte/capacity (E/C) ratios, under a fixed ZUR condition of 50%. **Figure 6**d shows that the mass ratios between active materials and host materials have a critical impact on energy density. This assessment was performed at an area capacity of 6 mAh cm^{-2} and an E/C ratio of 2.5 g Ah^{-1}. High mass ratios of active materials (I_2 or ICl) are essential for achieving high energy density outputs. For 2eZIBs, the mass ratio of I_2 in composite cathodes should exceed 70% to ensure an energy density of over 90 Wh kg^{-1}, while for 4eZIBs, a mass ratio of ICl higher than 60% is necessary to achieve an energy density surpassing 120 Wh kg^{-1}. We then evaluated the impact of area capacity on the energy density of ZIBs, keeping the active mass ratio and E/C ratio fixed at 70% and 2.5 g Ah^{-1}, respectively (**Figure 6**e). A low area capacity increases the mass fractions of electro-inert components, such as current collectors and separators, which decreases the overall energy density. Our simulations indicate that energy density increases sharply when the area capacity is below 3 mAh cm^{-2} and levels off at higher area capacities. Therefore, an area capacity greater than 3 mAh cm^{-2} is crucial for achieving high energy density. Lastly, we investigated the impact of E/C ratios on energy density, with active mass ratio and area capacity fixed at 70% and 6 mAh cm^{-2}, respectively (**Figure 6**f). For 2eZIBs, a high energy density of 90.6 Wh kg^{-1} is achieved at an E/C ratio of 2.5 g Ah^{-1}, whereas it drops to 40 Wh kg^{-1} under a high electrolyte condition of 20 g Ah^{-1}. Similarly, the energy density of 4eZIBs decreases significantly from 128.6 Wh kg^{-1} to 50.4 Wh kg^{-1} when the E/C ratio increases from 2.5 g Ah^{-1} to 20 g Ah^{-1}. These results clearly demonstrate the importance of a lean electrolyte condition in practical applications.

From the above discussion, achieving high active mass ratios, high area capacity, and lean electrolyte conditions are key to maximizing the energy density of ZIBs. However, several challenges remain. For 2eZIBs, poor electrical conductivity of iodine species, inferior reaction

kinetics, and severe shuttle effects limit the realization of high active mass ratios and area capacities. Additionally, the use of a large amount of porous conductive host materials in the cathodes complicates efforts to maintain lean electrolyte conditions. The challenges are even greater for 4eZIBs, as they must simultaneously address the shuttle effects associated with I^-/I_2 conversion, I^+ instability, and sluggish reaction kinetics for I_2/I^+ conversion. Moreover, in practical conditions, 4eZIBs often use I_2 as the active material and Cl^--containing solutions as electrolytes due to the inherent instability of ICl, which increases the E/C ratios and reduces the overall energy density. Furthermore, insufficient kinetics for I_2/I^+ conversion often necessitate high Cl^- concentrations in the electrolytes (>0.5 M), further detracting from the energy density.

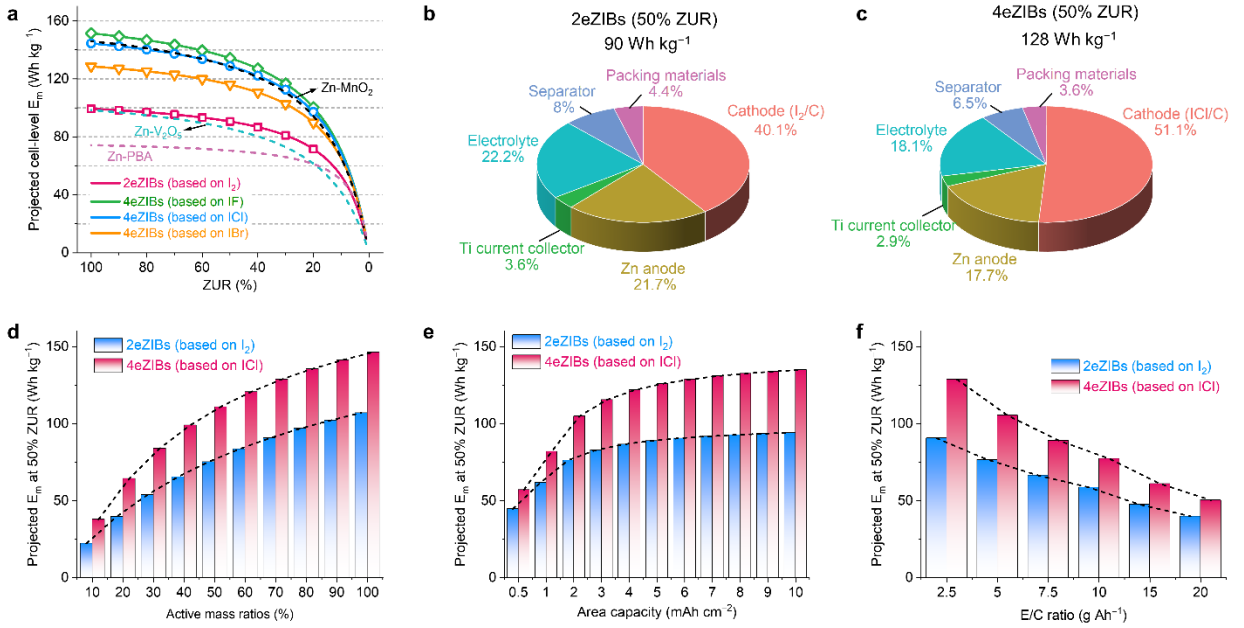


Figure 6. Energy densities for ZIBs. (a) The relationship between simulated energy densities and ZUR. The mass fractions of battery components for (b) 2eZIBs and (c) 4eZIBs at 50% ZUR. The impact of critical parameters on the energy density of ZIBs: (d) active mass ratios, (e) area capacity, and (f) E/C ratios.

In previous studies, researchers have developed various pouch cells to demonstrate the potential of AZBs for practical applications (**Table 1**). Although Zn-MnO_2 and Zn-V_2O_5 batteries offer significant theoretical energy densities, their cycling stability and lifespan at the pouch cell level remain unsatisfactory. In contrast, 2e Zn-I_2 pouch cells have shown superior electrochemical performance. For instance, a recent study reported the successful fabrication of a 0.4 Ah 2e Zn-I_2 pouch cell with a high active mass loading of 35 mg iodine cm^{-2} and an ultra-high ZUR of 68.3%.[44] Under these rigorous conditions, the pouch cell achieved an impressive lifespan of 5000 cycles with a capacity retention of 87.5%, highlighting the promise of 2eZIBs for practical applications. However, 4e Zn-I_2 pouch cells have not yet been reported, and their practical applications require further robust evaluation.

Table 2. Summary of the reported pouch cells.

Strategy	**Loading (mg cm^{-2})**	**Zn Anode**	**Capacity (mAh)**	**Performance**	**Energy Density (Wh kg^{-1})**	**Ref.**
Zn-V pouch cells						
ZLT-DMC electrolyte	22.5	43% ZUR	–	81.8% (500 cycles)	100	113
CarraChi-$ZnSO_4$ gel electrolyte	15	100 μm	900	84% (200 cycles)	~26	114
$Zn(OTf)_2$-H_2O-sulfolane electrolyte	20	31.2% ZUR	1,000	80% (390 cycles)	94	115
$Me_3EtNOTf$ additive	~3	100% ZUR	50	80% (90 cycles)	136	16
SPS additive	~ 7.0	–	20.7	82.8% (200 cycles)	<10	116
Zn-Mn pouch cells						

$Zn(OTf)_2$+$Mn(OTf)_2$ electrolyte	–	–	1,550	85% (50 cycles)	158.5	117
Zn-In alloy powder anode	5 mAh cm^{-2}	–	2,400	80% (200 cycles)	52	118
Zn-I_2 pouch cells						
$ZnSO_4$ eutectic electrolytes	~33.3	–	78.5	96.7% (500 cycles)	~45.4	10
Molecular interface modified Zn anode	~35	20 μm	1,200	87.5% (600 cycles)	63.5 (Wh L^{-1})	119
Silk protein additive	~37.5	20% ZUR	500	95% (1,000 cycle)	80	90
PolyPTX membrane	35	–	460	99.57% (400 cycles)	–	120
TOP/Carra@Zn	~38	–	1,050	80% (500 cycles)	–	121
BMIS additive	~35	68.3% ZUR	400	88.3% (5,000 cycles)	–	44

5. UTILIZATION OF ZN ANODES

The lifespan of AZBs is also of importance for large-scale energy storage, which highly depends on the Zn reversibility. Anode-free design, equally to the ZUR is 100%, can fulfill the energy density of AZBs, however, the lifespan is unsatisfactory owing to the irreversible Zn loss during battery cycling. **Figure 7**a elucidates the capacity retention of anode-free AZIBs under different Zn CEs, the relationship is showed following:

$$\text{Capacity retention} = \frac{Q_n}{Q_0} \times 100\% = CE^n \quad (6)$$

Where Q_n is the retained capacity after n cycles and Q_0 is initial capacity. The capacity retention of 70% is set as the end of life (EOL) of batteries. For a ten-year energy storage system, it would require a lifespan of battery of over 3000 cycles (based on one charge/discharge cycle per day). To achieve this aim, the Zn CE should attain >99.98%. Unfortunately, such a high Zn CE is hardly

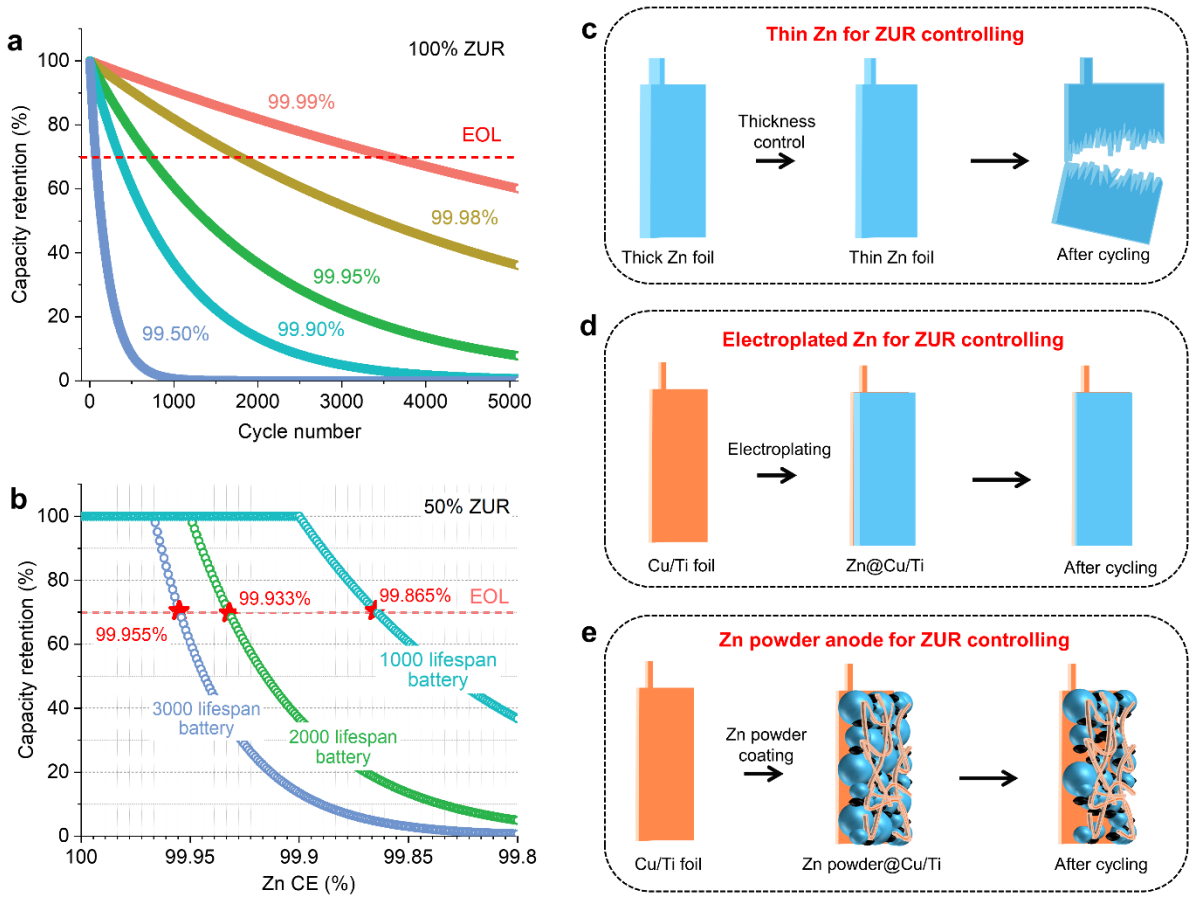


Figure 7. Critical issues for Zn anodes. (a) The battery capacity retention at various Zn CEs under 100% ZUR. (b) The required Zn CEs for batteries with designed cycling life. Methods for the realization of ZUR controlling: (c) Thin Zn foils, (d) Electroplated Zn anodes, and (e) Zn powder anodes.

achieved, especially under small current density. According to our estimation above, the condition of 50% ZUR can satisfy the requirement of high energy density. Extra Zn can serve as Zn reserve to compensate irreversible Zn loss during Zn plating/stripping. **Figure 7**b presents the impact of Zn CE on the capacity retentions after designed cycling life (1000, 2000, and 3000 cycles). Under a ZUR of 50%, irreversible Zn plating/stripping would consume the Zn reserve but would not lead to capacity loss until Zn reserve is consumed without current collector function. The cycle number (n) for the depletion of Zn reserve can be calculated as:

$$n = \frac{1}{1-\mathrm{CE}} \quad (7)$$

When n is larger than the designed cycling life (N_d), the capacity retention after N_d cycles would remain 100%. While when n is smaller than the N_d, the capacity of battery would start to decay after n cycles as the Zn reserve runs out at this time. Thereafter, the tenday for capacity decay for the battery is similar to the case of that with 100% ZUR (**Eq. 6**). Therefore, the relationship between capacity retention and Zn CE can be described as:

$$\text{Capacity retention} = \mathrm{CE}^{\left(N_d - \frac{1}{1-\mathrm{CE}}\right)} \times 100\% \quad (8)$$

Obviously, a 1000 lifespan battery would require a Zn CE higher than 99.865%. However, when setting the designed lifespan to 3000 cycles, the Zn CE should still reach 99.955%. When considering the degradation of cathode together, the required Zn CE will be larger, suggesting the Zn reversibility is still the biggest obstacle for practical application of AZBs.

For practical AZBs, methods for fabricating Zn anodes with controlled ZUR are critical. These methods can be divided into three strategies: thin Zn anodes, electroplated Zn anodes, and Zn powder anodes. Using a thin Zn foil as an anode is a convenient method for ZUR control (**Figure 7**c). However, uneven Zn plating and stripping can deplete local active Zn, leading to breakage of the Zn foils. This breakage results in the isolation of part of the active Zn, accelerating battery degradation. Compared to thin Zn anode designs, electroplated Zn anodes on inert metal substrates (*e.g.*, Ti and Cu) are an effective approach for ZUR control (**Figure 7**d).[12] Ti and Cu are chemically inert, ensuring good electrical contact between Zn and the substrates, which prevents Zn isolation and extends the cycling life of Zn anodes. Zn electroplating technology is well-established in traditional electroplating industries, making large-scale production of electroplated Zn anodes feasible. Additionally, electroplated Zn anodes can be optimized by adjusting the components of electroplating solutions or modifying the substrates with zincophilic sites to improve Zn

reversibility. Zn powder is also widely explored for the large-scale production of Zn anodes with controlled Zn capacity.[122] Typically, Zn powders are mixed with conductive agents and binders, then cast onto inert substrates to prepare Zn powder anodes. This preparation method is compatible with existing electrode technology, which is beneficial for large-scale production. Previous studies have shown that various methods, including coating Zn powders with protective layers,[123-124] designing conductive scaffolds,[125] and applying advanced binders,[126] can enhance the reversibility of Zn powder anodes.

6. IODINE PRICES AND RECYLING ROUTE

As a candidature for grid-scale energy storage, the prices of critical elements are important. For ZIBs, relative high prices of iodine would become one of the largest concerns that impede the further application. According to statistic data, the total global reserve of iodine is around 6.16 million metric tons and Japan had the largest reserves of iodine across the globe, estimated at *ca.* 4.9 million metric tons with a fraction of *ca.*79.5% (**Figure 8**a). Limited global reserve of iodine leads to its high price. **Figure 8**b presents the iodine prices within latest ten years. It can be observed that, the price of iodine increases rapidly in recent years. In 2023, the iodine price reaches 61 USD kg^{-1}, suggesting the prices of I_2 cathodes based on I^-/I_2 conversion can achieve around 210 USD kWh^{-1} (based on the I_2). Activating the additional I_2/I^+ conversion can reduce this cost to 97 USD kWh^{-1}. However, this price remains significantly higher than that of MnO_2 (5.7 USD kWh^{-1}) and V_2O_5 cathodes (39 USD kWh^{-1}). When considering the whole pouch-cell configuration, the price of ZIBs would be larger, implying the ZIBs would suffer from critical price issues if applicating.

The fact is that iodine element is rich in reserve on the earth, especially in the ocean (50-60 μg L^{-1}), indicating the potential for price lowering in the future.[35] The root of high price of iodine

can be concluded into two aspects: difficulty in iodine exploiting and limited application scenarios. Through rich reserve in the ocean, the low concentration makes the iodine exploiting from ocean is uneconomical. Some marine products, especially seaweeds, can gathering the iodine from the ocean water, leading to the large-scale iodine exploiting from them become realistic.[127-128] Besides, the application of iodine is mainly limited at in the field of medicine. Small market adoption also is a critical factor for high price. In the future, the widespread application of I_2-based batteries in the field of energy storage will have significant potential for price reduction.

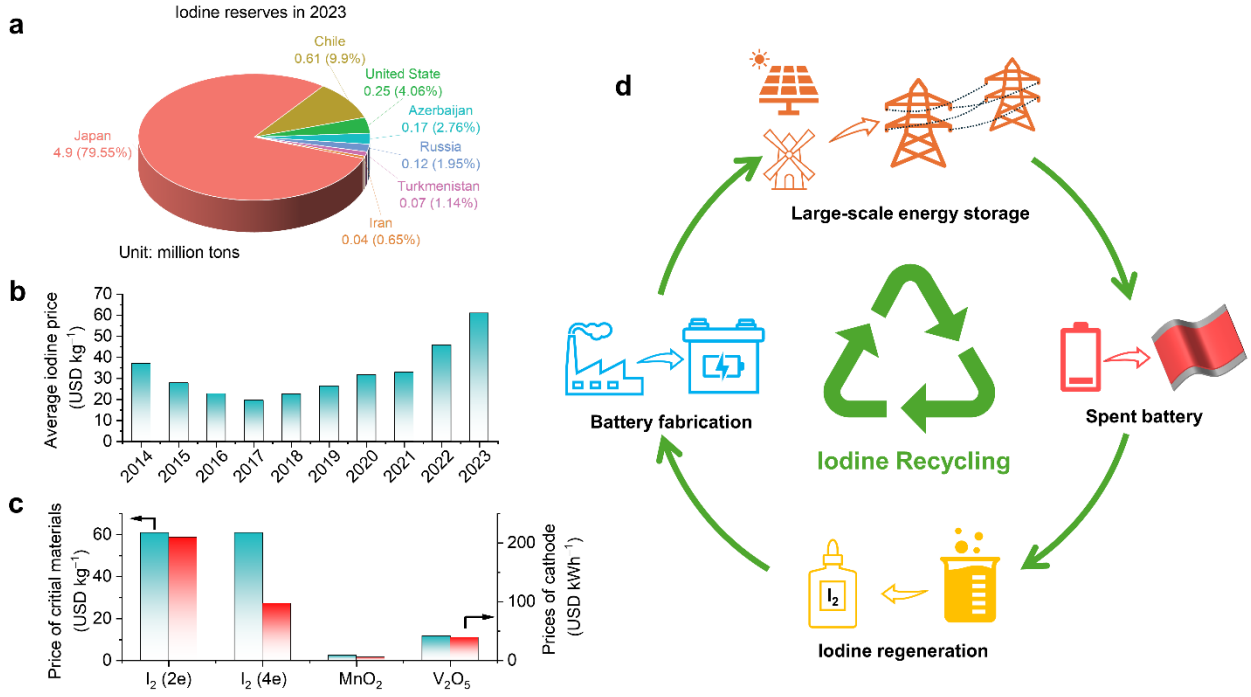


Figure 8. Iodine recycling for sustainable energy storage of ZIBs. (a) The iodine reserves around the world in 2023 (data sources: Statista). (b) Prices of iodine within ten years (data sources: Statista). (c) The comparison of the price of iodine cathodes with MnO_2 and V_2O_5 cathodes. (d) Possible iodine recycling route for the sustainable energy storage of ZIBs.

Apart from the iodine exploiting, cyclic utilization of iodine is another approach to reduce the iodine prices. With the large-scale application of I_2-based batteries, the iodine recycling is of

importance for sustainable iodine utilization. **Figure 8**c proposed a possible route for iodine closed-loop recycling. The application of iodine batterie for large-scale energy storage plays a critical role on integration of intermittent sustainable energies (*e.g.* wind and solar) into a grid. The iodine in spent iodine batteries is possible to re-collected by feasible an oxidizing route. Due to the characteristics of iodine being easily oxidized and sublimated, the iodine element in spent electrodes can be oxidized into I_2 by an oxidizing agent such as Cl_2. By increasing the temperature, iodine is prompted to sublimate from the liquid phase, allowing for the collection of the iodine element. The regenerated I_2 can be used for battery re-fabrication and put into use in the energy storage again. This iodine closed-loop recycling provides solutions for sustainable utilization of iodine and further contribute to the iodine price reduction.

7. SUMMARY AND PERSPECTIVE

ZIBs have shown rapid development as promising candidates for large-scale applications, however, they are hampered by poor redox reversibility. This review provides a comprehensive overview of recent advancements in advanced ZIBs based on I^-/I_2, $I^-/I_2/I^+$, and hetero-halogen conversion chemistry, analysing the advantages and disadvantages of various strategies and suggesting future developments. Additionally, a robust simulation of the energy density of ZIBs in industrial-level pouch cells was conducted to elucidate their practical potential for energy storage. The simulation highlighted the significant impact of Zn utilization on the energy density and lifespan of the batteries. Furthermore, we propose that electroplated Zn anodes or Zn powder anodes could be feasible approaches for fabricating practical Zn anodes with controlled Zn utilization rates. This review also underscores the critical cost factors of ZIBs, identifying key elements influencing the price of iodine. Finally, a potential closed-loop iodine recycling route is

proposed to reduce iodine costs and promote the sustainable energy storage potential of ZIBs. Additional perspectives on the future development of ZIBs are also proposed as follows.

(1) *In-depth understanding of 2eZIBs.* The reaction mechanism for 2eZIBs has been clarified as an I_3^- and I_5^- mediated electrochemical process. Various studies have examined the shuttle effects initiated by soluble I_3^- anions and investigated the parasitic reactions between shuttled I_3^- and Zn anodes. However, self-discharging is a critical issue for effective energy storage that is often overlooked. We concluded that both I_2 hydrolysis and shuttle effects contribute to the self-discharging of 2eZIBs. Nonetheless, the process of I_2 hydrolysis and methods for its inhibition remain unclear.

(2) *Incomplete understanding of 4eZIBs.* The development of 4eZIBs remains in its early stages, with unclear conversion mechanisms and a lack of effective guidance for improving reversibility. Firstly, there is controversy over whether ICl or ICl_2^- is the I^+ product during charging. Clarifying the form of I^+ is crucial for developing strategies to stabilize the I_2/I^+ conversion reaction. For example, ICl_2^- anions can be coordinated with functional cations to inhibit hydrolysis. Secondly, identifying the reaction pathways and potential intermediates for I_2/I^+ conversion is essential for designing host materials and catalysts to enhance the conversion efficiency of 4eZIBs. Thirdly, 4eZIBs generally exhibit a much shorter lifespan compared to 2eZIBs. Failure analysis of 4eZIBs is necessary to develop effective approaches for long-life battery design. Lastly, improving the active mass loading for 4eZIBs remains a significant challenge for practical use, and strategies to address this issue are still unclear.

(3) *Poor reversibility of hetero-halogen conversion.* Despite the coupling between various halogen redox or the I^-/IO_3^- conversion route can provide overwhelming energy density,

the reversibility of these conversions are rather poor. The most important thing is the limited stability of electrochemical stable window of aqueous electrolytes, because these conversions often require very high upper voltage limit, which triggers the OER. Secondly, the oxidative products of these conversions are highly active against water, making the reversibility much lower compared to 2e or 4eZIBs. More efforts are needed to explore their mechanism and the methods for redox reversibility improvement.

(4) *Long-term stability of Zn anodes under high ZUR.* Zn anodes face severe challenges due to dendrite formation, parasitic hydrogen evolution reactions (HER), and corrosion, which hinder their practical application. Although extensive research has proposed various strategies to improve Zn reversibility, there is a lack of focus on practical Zn anodes under high ZUR, especially in pouch cells. Additionally, H_2 release is detrimental to practical systems, particularly at relatively low charge/discharge rates. Successful demonstrations suggest that using highly concentrated electrolyte systems can nearly eliminate H_2 generation.[113] However, these electrolytes often come with high costs and high viscosity, which can compromise the price advantage and fast redox kinetics of AZBs. Designing optimal electrolyte systems to completely eliminate Zn dendrites and HER is therefore imperative. Furthermore, electroplated Zn anodes or Zn powder anodes may be feasible for practical Zn anode fabrication to control the ZUR, but the pathway for realization and additional modifications still require further efforts.

(5) *Practical industrial-level batteries.* In 2eZIBs, the suppression of shuttle effects often necessitates limiting the I_2 content in composite cathodes and specific I_2 loading in electrodes, thereby compromising the realistic energy density of the batteries. For 4eZIBs, this issue is exacerbated by their inferior reversibility compared to 2eZIBs. Achieving a

high active mass content of ≥70% and a high loading of >15 mg cm^{-2} (> 3 mAh cm^{-2}) is crucial for meeting commercialization requirements. Additionally, the ZUR significantly affects the energy density of ZIBs, and practical batteries must ensure a long lifespan under strict ZUR conditions. However, parasitic reactions between Zn and iodine species pose challenges to achieving high ZUR. Potential HER and OER during battery operation also need to be addressed to ensure the safety of ZIBs. Moreover, as electrolytes constitute a significant mass fraction in practical batteries, lean electrolyte design is necessary to improve the energy density of ZIBs. Nonetheless, the use of massive porous materials and unfavorable redox reversibility significantly impedes long-term durability under lean electrolyte conditions.

(6) *Iodine exploiting and close-loop recycling.* Exploiting iodine from natural reserves is crucial for reducing the cost of iodine batteries. Iodine element is abundant in the seawater, its concentration however is rather low. Some marine products, such as seaweeds, can concentrate iodine from seawater, making them an important source of iodine. Advanced technologies for artificial cultivation and iodine extraction from these marine products are highly needed to facilitate the practical use of iodine batteries. Additionally, technologies for recycling iodine from spent iodine batteries are currently lacking. Developing efficient iodine recycling methods is essential for the sustainability and market adoption of iodine batteries.

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Notes

The authors declare no competing financial interest.

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