

Review

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# High-energy and durable aqueous Zn batteries enabled by multi-electron transfer reactions

Qi Li<sup>1,#</sup>, Kovan Khasraw Abdalla<sup>1,#</sup>, Jiawei Xiong<sup>2</sup>, Zhihang Song<sup>3</sup>, Yueyang Wang<sup>1</sup>, Yajun Zhao<sup>1</sup>, Mengyao Liu<sup>1</sup>, Yanchen Fan<sup>4</sup>, Yi Zhao<sup>1,\*</sup> , Xiao-Ming Sun<sup>1,\*</sup> 

<sup>1</sup>State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China.

<sup>2</sup>Mary Frances Early College of Education, The University of Georgia, Athens, GA 30605, USA.

<sup>3</sup>Department Beijing Key Laboratory of Environmental Science and Engineering, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China.

<sup>4</sup>PetroChina Shenzhen New Energy Research Institute, Shenzhen 518000, Guangdong, China.

#Authors contributed equally.

\***Correspondence to:** Prof. Xiao-Ming Sun, State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: sunxm@mail.buct.edu.cn; Assoc. Prof. Yi Zhao, State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: zybattery@buct.edu.cn

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## Abstract

Aqueous Zn batteries (AZBs) have emerged as a highly promising technology for large-scale energy storage systems due to their eco-friendly, safe, and cost-effective characteristics. The current requirements for high-energy AZBs attract extensive attention to reasonably designed cathode materials with multi-electron transfer mechanisms. This review systematically overviews the development and challenges of typical cathode hosts capable of multiple electron transfer reactions for high-performance Zn batteries. Moreover, we also summarize how to trigger the multi-electron transfer chemistry of cathodes, including transition metal oxides, halogens, and organics, to further boost the energy storage capability of AZBs. Finally, perspectives on critical issues and future directions of the multi-electron transfer battery systems offer novel insights for advanced Zn batteries.

**Keywords:** Aqueous Zn battery, multi-electron transfer mechanism, cathode materials, high performance



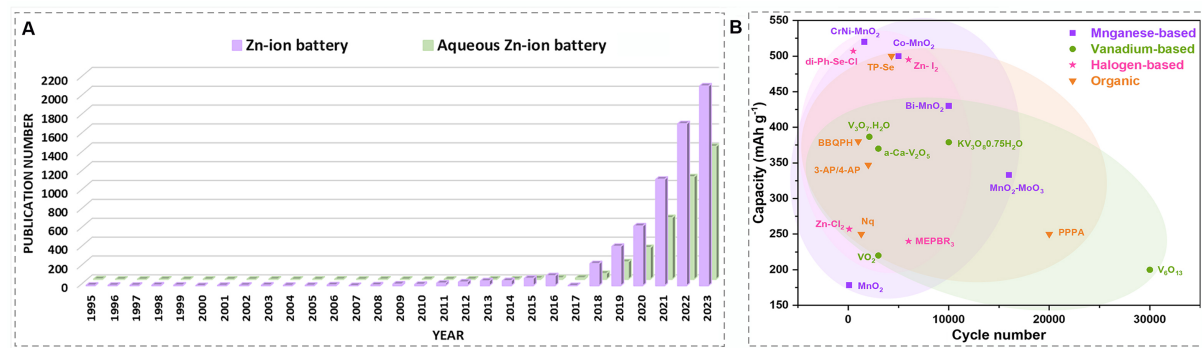
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## INTRODUCTION

As the global energy crisis in traditional fossil fuel energy continues, there is a growing urgency for developing clean and renewable energy sources, including wind, solar, hydrogen energy, and geothermal energy, towards achieving the goal of carbon peak and carbon neutrality. However, these clean energy sources are characterized by their intermittent nature, indirectness in conversion processes, and inherent instability, resulting in low energy utilization efficiency and high operational costs<sup>[1,2]</sup>. Therefore, aqueous batteries with low cost and safety play a pivotal role in efficient energy conversion and storage for large-scale energy storage<sup>[3,4]</sup>. Compared to lithium-ion and other polyvalent metal batteries, aqueous zinc (Zn) batteries (AZBs) have been regarded as promising systems due to their highly abundant Zn reserves, outstanding theoretical specific capacity (820 mAh g<sup>-1</sup>), and lower redox potential of -0.76 V versus standard hydrogen electrode (SHE)<sup>[5]</sup>. **Figure 1A** clearly represents the number of publications related to zinc-ion and aqueous Zinc-ion battery technology research, proving the great potential for AZBs in large-scale energy storage systems<sup>[6-24]</sup>. However, the current state-of-the-art Zn batteries are still limited by the challenges related to the side reactions including shape change, passivation, and hydrogen evolution reaction (HER) of Zn anodes, particularly in alkaline environments<sup>[25]</sup>. Therefore, adopting mildly acidic and neutral electrolytes has driven great progress in rechargeable AZBs such as Zn-MnO<sub>2</sub> and Zn-V<sub>2</sub>O<sub>5</sub> cells<sup>[26,27]</sup>. It is worth noting that the energy density and battery lifespan of AZBs are highly related to the electrochemical performance of cathode materials. Generally, the single-electron transfer mechanism typically results in inferior capacity and sluggish redox kinetics between electrodes for non-durable Zn batteries<sup>[28-30]</sup>. Hence, the rational design of cathode materials based on multi-electron transformation reactions is essential for advanced AZBs.

Besides Zn anode protection and electrolyte optimization, numerous strategies have been adopted to achieve high-performance cathode materials, including manganese (Mn)-based oxides, vanadium (V)-based oxides, Prussian blue analogs, organic compounds, and halogens<sup>[4,31,32]</sup>. **Figure 1B** displays the recent progress of modified cathode materials, suggesting that the electron transfer numbers can significantly enhance the capacity and stability in aqueous Zn devices. Specifically, the MnO<sub>2</sub> cathode with MnO<sub>2</sub>/Mn<sup>3+</sup> displays an energy density of ~280 Wh kg<sup>-1</sup> based on MnO<sub>2</sub> mass. Furthermore, the redox reaction of MnO<sub>2</sub>/Mn<sup>2+</sup> endows decoupled Zn-MnO<sub>2</sub> batteries with an ultra-high platform (~2.3 V) and excellent energy density of ~1,100 Wh kg<sup>-1</sup><sup>[33]</sup>. Moreover, vanadium oxide (VO) cathodes with polyvalent states and relatively low molar mass generally undergo two-electron redox reactions and exhibit exceptional theoretical capacities over 600 mAh g<sup>-1</sup> for advanced AZBs with ~450 Wh kg<sup>-1</sup><sup>[34]</sup>. Furthermore, the calix[4]quinone (C4Q) cathode containing eight carbonyls exhibits an excellent energy density of 335 Wh kg<sup>-1</sup> and a long lifespan over 1,000 cycles at 500 mA g<sup>-1</sup>. Recently, halogens involving multi-electron conversion chemistry have been proven promising conversion cathodes for high-performance AZBs<sup>[35]</sup>. For example, Chen *et al.* reported a four-electron transfer aqueous Zn-I<sub>2</sub> batteries by triggering the redox reaction of I<sub>2</sub>/I<sup>+</sup> by forming ICl inter-halogens, improving the energy density and battery lifespan to 495 Wh kg<sup>-1</sup> and 6,000 cycles, respectively<sup>[36]</sup>. Conversely, cathode materials with substantial structural frameworks, such as covalent-organic frameworks, and polyanionic cathodes generally offer lower capacity (< 200 mAh g<sup>-1</sup>) and inferior redox potential (< 1.0 V) for unsatisfied Zn batteries. Despite the substantial advancements achieved thus far, achieving industrial-scale production remains a distant objective for AZBs to exceed the target of lithium batteries of 400 Wh kg<sup>-1</sup> in the "Made in China 2025" project<sup>[36,37]</sup>. To enhance the Zn battery performance and overcome the challenges mentioned above, multi-electron transfer reactions have been considered a suitable alternative to single-electron transfer<sup>[38-40]</sup>. Therefore, it remains crucial to explore methods for achieving reversible multi-electron transfer reactions with enhanced output voltage, high energy density, and low cost-effectiveness in advancing the application of AZBs<sup>[40,41]</sup>.



**Figure 1.** (A) The number of publications related to zinc-ion battery and aqueous zinc-ion battery technology research. (B) Recently published cathode materials with improved capacity and cycling stability for high-performance AZBs, including Mn-<sup>[6-10]</sup>, V-<sup>[11-14]</sup>, and halogen-based materials<sup>[15-19]</sup> and organic hosts<sup>[20-24]</sup>.

Despite their potential for high energy density and commercial viability, we should further explore the multiple electron-transfer chemistry of cathode materials matched with the addition of redox couples in electrolytes, especially in mild acid or natural electrolytes. In order to attain stable long-term cycling and achieve high-rate performance, improvements in ion transport and storage capability are imperative for the metal oxide cathodes with sluggish ion insertion kinetics<sup>[42]</sup>. The key to realizing cathode materials with remarkable energy density lies in optimizing crystal or molecular structures while activating reversible multi-electron reactions, which requires continuous exploration and discovery of novel chemical systems. Additionally, attention must be paid to balancing the cathode output energy density with excellent cycling stability. Hence, understanding the intrinsic structure-effect relationship among the battery performance indexes is critical for designing high-energy AZBs with long lifespans<sup>[42,43]</sup>. This review aims to capture the challenges and the latest developments posed by cathode materials based on multi-electron transfer mechanisms in reported AZBs. Furthermore, we explore potential solutions to effectively trigger the multiple-electron transfer reactions for enhanced cathode materials. The ultimate goal is to offer valuable insights that can be utilized to develop better AZBs for the future energy world.

## HOW TO TRIGGER MULTI-ELECTRON CHEMICAL REACTION

Cathode materials undergo multi-electron chemical reactions triggered by the migration of electrons from the Zn anodes during the discharge process. This reaction involves converting the cathode material into different chemical forms or variations in chemical valence, which stores the energy until it is needed during the charge process. Mn-based, V-based compounds, halogen, and organic hosts are common cathode materials based on multi-electron transfer reactions for high-energy AZBs. However, activating more than single-electron transfer chemistry in these materials requires different excitation pathways. For example, the MnO<sub>2</sub>/Mn<sup>2+</sup> mechanism in Mn-based compounds can be divided into three excitation categories, including the dissolution-deposition reaction of MnO<sub>2</sub> cathodes, chemical environment optimization of cathode/electrolyte interface (CEI), and pre-deposition surface to active MnO<sub>2</sub>/Mn<sup>2+</sup> reaction. Due to the ultra-high theoretical capacity of V-based compounds with V<sup>5+</sup>/V<sup>3+</sup> reactions, it is extremely important to limit the dissolution of active substances, the generation of byproducts, and the slow diffusion kinetics to enhance the reaction activity of Zn-V batteries. Therefore, the modification strategy for more than two-electron transfer of stable V-based cathode hosts can be divided into the material design and the electrolyte modification.

Compared to the previous two types of cathodes, the number of electrons transferred in halogen (chlorine, bromine, and iodine) cathode materials is still being determined, and the conversion mechanism

exploration is urgent for constructing advanced Zn-halogen devices. For example, the maximum electron transfer from I<sup>-</sup> to IO<sub>3</sub><sup>-</sup> can reach the twelve-electron transfer reaction for high-energy Zn-I<sub>2</sub> batteries. Yet, the modification strategies are essential to ensure the realization of a multi-electron transfer mechanism with a long lifespan. Besides the halogen cathodes, it is worth noting that a multi-electron chemical reaction can be initiated in organic hosts containing multiple redox centers by optimizing molecular structures to achieve high-energy and durable Zn-organic batteries. The battery energy is determined by  $E_g = -\frac{nFE}{\Sigma M_g} \eta$ , where  $\Sigma M_g$  is the total weight of reactants (mol g<sup>-1</sup>),  $n$  represents the charge transfer number,  $E$  is the voltage (V),  $F$  is the Faraday constant, and  $\eta$  means the activity of charge carriers, including both cations and anions that participate during the redox (multi-ion effect)<sup>[44]</sup>. Thus, the strategies for higher battery energy can be achieved by enhancing the voltage, multi-electron reaction transfer number, and mass ratio of light elements in electrode materials.

The following sections are an overview of the recent development and issues of reported cathode materials. Furthermore, the corresponding strategies are provided to enhance the capability of accept/donate multiple electrons during the battery working, thereby boosting the battery practical application of high-performance AZBs.

### Mn-based cathodes with MnO<sub>2</sub>/Mn<sup>2+</sup> mechanism

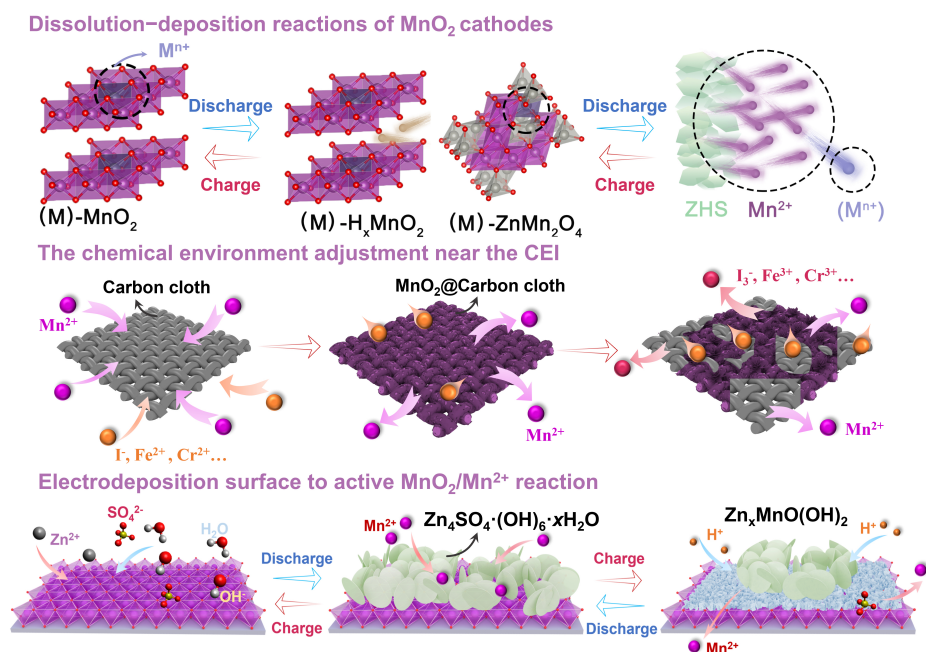
The variable valence states of Mn atoms and diverse crystal structures of manganese oxides enhance their suitability as an exceedingly captivating cathode material for high-performance AZBs<sup>[45,46]</sup>. The two-electron transfer reaction of MnO<sub>2</sub>/Mn<sup>2+</sup> endows Mn-based cathode materials with a notable theoretical specific capacity (616 mAh g<sup>-1</sup>) and an ultra-high redox voltage (~1.9 V) in acid electrolytes. Besides, electrolytic Zn-MnO<sub>2</sub> batteries significantly boost the voltage and capacity based on the dissolution-deposition reaction of MnO<sub>2</sub>/Mn<sup>2+</sup>, surpassing the energy limitation of the MnO<sub>2</sub>/Mn<sup>3+</sup> reaction. For example, Chao *et al.* proposed an electrolysis Zn-MnO<sub>2</sub> battery via proton and electron dynamics for achieving high energy of 409 Wh kg<sup>-1</sup> with a competitive battery cost of ~US\$5 per kWh<sup>[46]</sup>. However, the strong acid H<sub>2</sub>SO<sub>4</sub> as the electrolyte addition causes inferior cycling stability in electrolysis Zn-MnO<sub>2</sub> batteries. Therefore, we focus on developing and modifying strategies to active MnO<sub>2</sub>/Mn<sup>3+</sup>/Mn<sup>2+</sup> reactions in the mild acid environment, highlighting the modification methods of the dissolution-deposition reaction, chemical environment near the CEI, and the tailored electrodeposition surface for triggering MnO<sub>2</sub>/Mn<sup>2+</sup> reaction [Figure 2].

### Dissolution-deposition reactions of MnO<sub>2</sub> cathodes

Since 2016, significant advancements have been made in understanding the mechanisms of Zn-Mn batteries. Pan *et al.* discovered that adding MnSO<sub>4</sub> to the mild acid ZnSO<sub>4</sub> electrolyte can effectively suppress the dissolution of MnO<sub>2</sub><sup>[47,48]</sup>. In 2018, Fu *et al.* demonstrated that Mn<sup>2+</sup> convert into Mn(III)-based oxides could contribute additional capacity, surpassing the theoretical capacity limit of 308 mAh g<sup>-1</sup> based on MnO<sub>2</sub>/Mn<sup>3+</sup> reaction<sup>[49]</sup>. This finding underlined the importance of the two-electron transfer between Mn<sup>2+</sup> and MnO<sub>2</sub>, thereby attracting the widespread interest of researchers. Further reports by Xie *et al.* in 2019 demonstrated the electrodeposition mechanism of Mn<sup>2+</sup> from the electrolyte to form MnO<sub>2</sub>, boosting the capacity and cycling stability of electrolysis Zn-Mn batteries<sup>[48]</sup>. These insights suggest that efficient design of Mn-based oxide materials can trigger the reversible dissolution-deposition reaction of MnO<sub>2</sub>/Mn<sup>2+</sup> in the mild acid environment, facilitating the development of high-energy Zn-Mn batteries.

Henceforth, Xia *et al.* enhanced  $\delta$ -MnO<sub>2</sub> capacity and stability by incorporating high-valence Mo<sup>5+</sup> ions, altering the Mn-O bond angle and inducing structural distortion (Jahn-Teller effect) in the [MnO<sub>6</sub>] octahedron of Mo-ZnMn<sub>2</sub>O<sub>4</sub><sup>[6]</sup>. This modification promoted the dissolution of Mn(III)-based oxides into the electrolyte and enabled the activation of the MnO<sub>2</sub>/Mn<sup>3+</sup>/Mn<sup>2+</sup> reaction, doubling the specific capacity to 652 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup><sup>[6]</sup>. Furthermore, the Co-doped  $\delta$ -MnO<sub>2</sub> catalyzes the electrochemical deposition of





**Figure 2.** Schematic illustration of three ways to stimulate the dissolution/deposition reaction of MnO<sub>2</sub>/Mn<sup>2+</sup> for high-performance Zn-Mn batteries.

active Mn compounds, enhancing self-recovery and energy storage performance of Zn-Mn batteries<sup>[7]</sup>. Besides ion doping strategies, constructing Mn-based hybrid hosts also greatly facilitates two-electron transfer reactions for high-energy AZBs. For example, the MnO<sub>2</sub>/MoO<sub>3</sub> hybrid cathode with the reversible double electron transfer reaction exhibits a high capacity of 333 mAh g<sup>-1</sup> caused by the weakened energy barrier for Mn<sup>2+</sup> release and stronger attraction to Mn<sup>2+</sup> during battery cycling tests in an electrolyte without Mn<sup>2+</sup> additives<sup>[8]</sup>. Furthermore, Radha *et al.* prepared carbon-coated MnO<sub>x</sub> cathodes to achieve the reversible Mn<sup>4+</sup>/Mn<sup>2+</sup> redox chemistry for advanced Zn-Mn batteries<sup>[50]</sup>. Specifically, birnessite-type MnO<sub>2</sub> was *in-situ* generated utilizing electrolyte addition of Mn<sup>2+</sup> and finely divided MnO<sub>x</sub> particles during the charging process<sup>[50]</sup>. It is worth noting that the conductive carbon substrate further provides active sites for the MnO<sub>x</sub> cathode, yielding a peak energy density of 845.1 Wh·kg<sub>cathode</sub><sup>-1</sup> with an extended cycle life of 1,500 cycles<sup>[51]</sup>.

In the reduction process of solid MnO<sub>2</sub> to Mn<sup>2+</sup>, the absence of active sites for capturing dissolved Mn<sup>2+</sup> can lead to significant capacity decline during battery cycling. To address this, strategies such as employing a carbon coating for surface protection and incorporating a porous carbon interlayer have been proven to substantially improve the electrochemical performance of Zn-MnO<sub>2</sub> batteries by capturing dissolved Mn<sup>2+</sup> ions<sup>[52]</sup>. Ultimately, the primary challenges in the dissolution-deposition energy storage mechanism of Mn-based cathode materials are severe capacity degradation and poor cycling stability. Therefore, it is essential to optimize Mn-based cathode materials, enhancing the Mn<sup>3+</sup>/Mn<sup>2+</sup> conversion efficiency and ensuring the structural integrity for high-energy and stable Zn-Mn batteries.

### The chemical environment adjustment near the CEI

Studies have identified the root causes of capacity degradation in Zn-Mn batteries based on the MnO<sub>2</sub>/Mn<sup>2+</sup> reaction during cycling. As a result, the increased pH value and Mn<sup>3+</sup> concentration in the electrolyte and the accumulation of inactive MnO<sub>2</sub> (designed as “dead MnO<sub>2</sub>”) near the CEI severely hinder ion diffusion and reaction efficiency of MnO<sub>2</sub>/Mn<sup>2+</sup><sup>[53-56]</sup>. Therefore, efforts are currently focused on preventing the

disproportionation of  $\text{Mn}^{3+}$ , eliminating “dead  $\text{MnO}_2$ ”, and enhancing the applications for Zn-Mn batteries<sup>[15]</sup>. To address these issues, strategies such as increasing proton concentration, introducing ligand ions such as  $\text{F}^-$  or  $\text{P}_2\text{O}_7^{3-}$ , and employing innovative electrolytes have been explored<sup>[57]</sup>. Xie *et al.* used  $\text{Mn}(\text{AC})_2$  rather than conventional  $\text{MnSO}_4$  electrolytes to boost the direct conversion of  $\text{Mn}^{2+}$  to  $\text{MnO}_2$ , resulting in a lower initial oxidation potential for fast-charging Zn- $\text{MnO}_2$  devices in the  $\text{Mn}(\text{Ac})_2$  system<sup>[48]</sup>. More importantly, incorporating redox couples such as  $\text{Cr}^{3+}/\text{Cr}^{2+}$  or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in acetate-based electrolytes further endows electrode functionality by removing inert species and optimizing cathodic potential, thereby improving the energy density and battery life<sup>[58,59]</sup>. *In-situ* electrochemical quartz crystal microbalance (EQCM) techniques provide insights into the deposition/dissolution chemistry of  $\text{MnO}_2$  cathodes, promoting the development of high-performance AZBs<sup>[59]</sup>. Very recently, iodide ( $\text{I}^-$ ) as a catalyst addition can boost the reduction of solid  $\text{MnO}_2$  to  $\text{Mn}^{2+}$ , optimizing electrolysis kinetics and conversion efficiency<sup>[60,61]</sup>. More importantly, the effective removal of “dead  $\text{MnO}_2$ ” also temporarily reduces capacity attenuation and increases the cycle life, contributing to the industrialization of high-energy Zn-Mn batteries.

### Electrodeposition surface to active $\text{MnO}_2/\text{Mn}^{2+}$ reaction

Very recently, the cathode-free Zn- $\text{MnO}_2$  battery system has demonstrated the deposition/dissolution reaction of  $\text{MnO}_2/\text{Mn}^{2+}$  on the cathode side for the higher energy density<sup>[45]</sup>. This system, characterized by a high redox potential ( $\sim 1.99$  V vs.  $\text{Zn}/\text{Zn}^{2+}$ ), benefits from carbon felt on the cathode side, providing active sites for efficient deposition of  $\text{MnO}_2$  and reduced capacity decay caused by  $\text{Mn}^{2+}$  dissolution<sup>[46,62-64]</sup>. These findings offer fresh insights into the operation of Zn- $\text{MnO}_2$  batteries, especially in stationary applications, where the energy storage mechanism remains complex due to pH fluctuations and the formation of intermediate products during charge-discharge cycles<sup>[65-67]</sup>. In-depth studies using diverse *in-situ* detection techniques reveal that weakly acidic sulfate electrolytes can induce subtle changes in pH values, forming byproducts such as  $\text{Zn}_x\text{SO}_4 \cdot (\text{OH})_y \cdot x\text{H}_2\text{O}$  (ZSH)<sup>[68-70]</sup>. These byproducts are essential in the dissolution-deposition reaction and provide insights into the  $\text{MnO}_2/\text{Mn}^{2+}$  redox processes with non- $\text{MnO}_2$  cathode materials. In electrolytes containing  $\text{Mn}^{2+}$ , ZSH actively participates in the electrochemical reaction and forms layered zinc vernadite ( $\text{Zn}_x\text{MnO}(\text{OH})_2$ ) nanosheets on the cathode side. During the discharge process, these  $\text{Zn}_x\text{MnO}(\text{OH})_2$  nanosheets react with proton ions to alter the surface pH and promote ZSH re-deposition. This process enhances the dissolution-deposition reaction of  $\text{Mn}^{2+}/\text{Zn}_x\text{MnO}(\text{OH})_2$  catalyzed by ZSH, which is crucial for enhancing cycle stability and better battery performance of Zn-Mn batteries<sup>[71]</sup>.

In a weakly acidic electrolyte environment of zinc sulfate,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ , *etc.*, can further be used as cathode catalytic materials to activate the two-electron transfer reaction in electrolytic Zn-Mn devices. However, these catalytic substrates with varying performances exhibit distinct properties in inducing the deposition mechanism for Zn batteries. For example, the Zn- $\text{CaO}$  battery shows remarkable capacity retention compared to the Zn/ $\text{MgO}$  battery, possibly due to the stable  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  phase deposition on the  $\text{CaO}$  cathode<sup>[72]</sup>. This study contributes to a better understanding of Zn-Mn batteries and guides the design of high-capacity ones in mild acid environments.

Long-cycle Zn-Mn batteries with stable and high capacity are required for their commercialization in large-scale energy storage applications. Based on the above three excitation methods of two-electron transfer of Mn-based oxide materials, the introduction of defects in Mn-based dioxide, the electrolyte addition of redox couple, and substrate design for catalytic deposition of active Mn-based oxides are promising excitation methods for high-performance Zn-Mn batteries with the two-electron mechanism of  $\text{MnO}_2/\text{Mn}^{2+}$  for high-energy and durable Zn-Mn batteries.

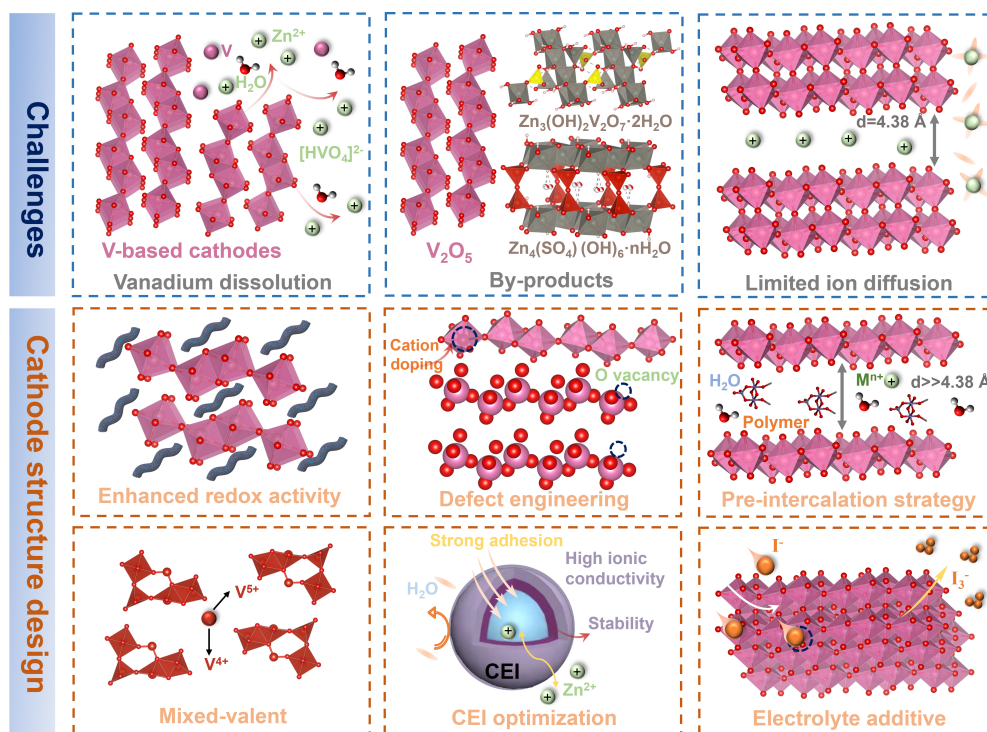
### Vanadium-based cathodes with the V<sup>5+</sup>/V<sup>3+</sup> reaction

V-based oxides are another promising cathode material due to their low cost, high theoretical specific capacity (+3  $\rightleftharpoons$  +5 for V<sub>2</sub>O<sub>5</sub>, 589 mAh g<sup>-1</sup>)<sup>[73,74]</sup>, and reversible cycling stability<sup>[75]</sup>. However, the practical application of Zn-V batteries faces great challenges of inferior cycling stability, low capacity, and poor rate capability caused by the dissolution of active substances, poor conductivity, and sluggish Zn<sup>2+</sup> diffusion kinetics. Therefore, enhancing the redox activity of V-based cathode materials is essential for high-rate and high-energy AZBs. Based on these, this section summarizes the ways to solve the above issues, including modifying V-based materials and the electrolyte optimization strategy [Figure 3].

#### Improved V<sup>5+</sup>/V<sup>3+</sup> reaction activity

One common issue with V-based cathode materials is the serve capacity fading caused by the low conductivity and active material dissolution during the battery cycling test. Incorporating conductive materials such as MXene (the family of two-dimensional transition metal carbides), nitrides, and carbonitrides<sup>[76,77]</sup>, graphene oxide (GO)<sup>[78]</sup>, reduced GO (rGO)<sup>[79-82]</sup>, and carbon nanotubes (CNTs)<sup>[83]</sup> into V-based composite cathode materials significantly enhances redox activity with the restrained vanadium dissolution and byproduct formation. Besides, carbon-based materials also act as conductive additives into V-based hosts via merely physical mixing with active substances. Such direct compositing with V-based materials can significantly enhance the conductivity and stability for the improved energy density of Zn-V devices. The dissolution of vanadium and formation of byproducts can be effectively inhibited by coating carbon materials onto the surface of V-based cathodes. Wan *et al.* developed a KV<sub>3</sub>O<sub>8</sub>·0.75H<sub>2</sub>O (KVO) material coated with single-walled CNTs (SWCNTs) to obtain an independent KVO/SWCNTs cathode film, which displayed high capacity (379 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>), excellent rate performance (92 mAh g<sup>-1</sup> at 5 A g<sup>-1</sup>), and remarkable capacity retention rate of 91% over 10,000 cycles<sup>[11]</sup>. Therefore, introducing conductive carbon materials is effective for the enhanced reaction activity of V-based hosts in high-performance Zn batteries.

V-based cathodes often exhibit layered and tunneling characteristics, limiting the Zn<sup>2+</sup> diffusion kinetics caused by the electronegative O atoms<sup>[84]</sup>. Hence, ion doping and organic intercalation as the modified strategies have been explored to enhance the rate capability and stability of Zn-V batteries<sup>[85,86]</sup>. For instance, free-standing Ca-doped V<sub>2</sub>O<sub>5</sub> (a-Ca-V<sub>2</sub>O<sub>5</sub>) with high utilization of the abundant active sites exhibits fast reaction kinetics and improved discharge capacity even at large current densities<sup>[12]</sup>. Density functional calculations (DFT) revealed that doped Ca atoms yielded lower adsorption energy for inserted Zn<sup>2+</sup> ions, thereby facilitating rapid reaction kinetics and achieving exceptional rate performance during the Zn<sup>2+</sup> insertion/extraction process. Besides ion doping, Song *et al.* utilized p-aminophenol (pAP) pre-intercalated into layered V-based oxides of V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O, increasing the V-O layer spacing to improve rate performance and cycle life<sup>[13]</sup>. The pAP intercalated-V<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O hybrid cathode exhibits double electron transfer, demonstrating remarkable reversible specific capacity (386.7 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup>) at the high mass loading of 6.5 mg cm<sup>-2</sup><sup>[13]</sup>. Recently, Ma *et al.* successfully developed an organic-inorganic hybrid cathode by combining the high capacity of VO with the high working voltage of ethylenediamine (EDA), resulting in a remarkable working voltage of up to 0.82 V and ultra-long lifespan of VO-EDA cathodes<sup>[87]</sup>. Furthermore, the incorporation of EDA molecules also improved ion diffusion ability, achieving higher capacity (382.6 mAh g<sup>-1</sup> at 0.5 A g<sup>-1</sup>) and extended cycle life (10,000 cycles)<sup>[87]</sup>. Therefore, the intercalation modification strategies offer insights for exploring high-energy V-based cathode materials. Furthermore, intercalating ions such as K<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup>, Li<sup>+</sup>, and Zn<sup>2+</sup> can also significantly improve the structural stability and cycling performance of Zn-V devices<sup>[86,88-91]</sup>. For instance, Wang *et al.* reported a novel cathode of Mg<sup>2+</sup> pre-intercalated V-based oxide (designed as MgV<sub>2</sub>O<sub>6</sub>·1.7H<sub>2</sub>O), enhancing the V-O layer distance for high redox kinetics and cathode integrity<sup>[92]</sup>. These above-mentioned modification strategies for cathodes have significantly enhanced the capacity, discharge platform, and rate performance of VO cathodes, thereby constructing advanced Zn-V systems for practical applications.



**Figure 3.** Graphic depiction of challenges and design strategies for constructing high-performance vanadium-based cathodes with more than two-electron transfer mechanism.

### Improved CEI and additional redox couples

Optimizing the electrolyte is another critical strategy for developing high-performance Zn-V batteries. V-based cathodes generally suffer from the dissolution of V elements and irreversible structure collapses in conventional aqueous electrolytes, such as  $\text{ZnSO}_4$  and  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ . In light of this, the formation of CEI on the cathode surface prevents the side reactions and harmful substance exchange between the V-based cathode and the electrolyte, such as interlayer water shuttling effect and V-based compound dissolution. Among various options, using high concentration electrolytes enhances the cycling stability of the V-based cathodes. However, it still faces the challenges of water molecular interaction and the inferior rate capability of V-based cathodes during battery cycling. Hence, forming a reliable and stable CEI is crucial for zinc-vanadium batteries with high energy density, particularly during the long cycling test. To lower the cost of the high concentration electrolyte, Wang *et al.* introduced an ultra-low water activity electrolyte addition of trimethyl phosphate (TMP) to improve the stability and capacity of Zn- $\text{V}_6\text{O}_{13}$  batteries, significantly suppressing vanadium dissolution and side reactions at the cathode interface<sup>[14]</sup>. Therefore, the Zn- $\text{V}_6\text{O}_{13}$  battery with the innovative electrolyte addition exhibits an exceptional cycle life of up to 30,000. In light of these findings, the electrolyte modification strategy not only provides a more stable CEI interface but also inhibits vanadium dissolution to minimize byproduct deposition.

Additionally, functional electrolyte additives, such as  $\text{I}_2/\text{I}^-$ , can provide additional discharge capacity by participating in the energy storage process. Considering the higher redox potential of  $\text{I}_2/\text{I}^-$  than that of  $\text{V}^{5+}/\text{V}^{3+}$ , many researchers have attracted much attention to this modification strategy to construct high-energy Zn-V batteries. Recently, Yang *et al.* proposed an ethylene glycol solution of  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  and  $\text{ZnI}_2$  for a dual-functional cathode of  $\text{NH}_4\text{V}_4\text{O}_{10}$  and porous active carbon (AC) to realize the synergistic effect of  $\text{Zn}^{2+}$  insertion/extraction and electrolyte-assisted  $\text{I}_2/\text{I}^-$  conversion reaction mechanism<sup>[93]</sup>. During the cycles,



three-electron transfers (one-electron transfer for halogen ion) were realized, which obtained higher discharge medium voltage (0.96 V) and capacity retention rate (0.032%/cycle) at 0.2 A g<sup>-1</sup>[93]. The unique electrolyte modification method has deeply explored the compatibility of halogen redox and Zn<sup>2+</sup> insertion/extraction, improving the cycle stability and energy density of aqueous Zn-V batteries. Therefore, improving the redox activity of V<sup>5+</sup>/V<sup>3+</sup> chemistry along with additional redox couples is the future developing direction for high-energy and long-life Zn-V batteries.

### Halogen-based cathodes with multi-electron transfer chemistry

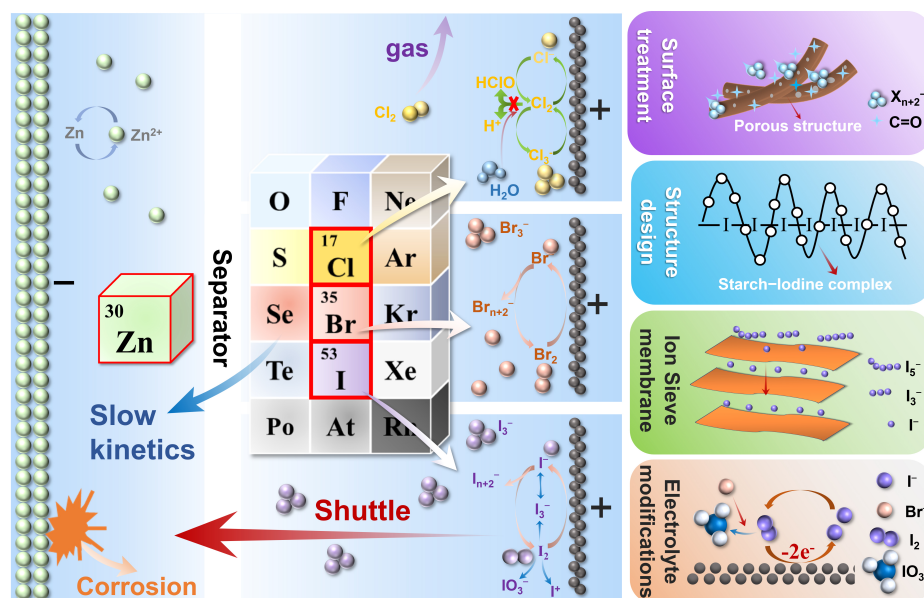
In contrast to conventional Zn batteries based on the ion insertion/extraction mechanism, Zn-halogen batteries (Zn-X<sub>2</sub>, X=Cl, Br, and I) exhibit a distinct energy storage chemistry through the conversion reaction between halogen and their ions. The conversion mechanism of halogen cathodes can avoid the issues of lattice distortion, sluggish Zn<sup>2+</sup> diffusion, and poor conductivity in V- and Mn-based cathodes. Besides, the rich valence states of halogen atoms can achieve multi-electron transfer under certain conditions, thereby constructing long-life and high-energy AZBs [Figure 4]<sup>[94,95]</sup>. When halogen hosts directly act as the cathodes, conductive and porous carbon materials are generally utilized as stabilizers to fix the halogen atoms, which is highly related to the electrochemical performance and lifespan of the Zn-halogen batteries<sup>[96]</sup>. Yet, the mass loading of the halogen host is limited by the conductive carbon-based additions, resulting in inferior areal capacity and rate capability for the AZBs.

In the case of the conversion energy storage mechanism, it is also possible to prepare a cathode-free battery system by introducing halogen ions into the electrolyte, such as the electrolytic Zn-chlorine<sup>[97]</sup>, Zn-bromine<sup>[98]</sup>, and Zn-iodine electrodes<sup>[99]</sup>. Moreover, Zn-halogen devices are cost-effective compared to other cathode materials due to the abundance of halogen elements in the ocean. The multiple valence states of halogen elements (-1, 0, +1, +3, +5, and +7) make halogen hosts highly promising for high-energy AZBs. The reversible conversion reaction based on X<sub>2</sub>/2X<sup>-</sup> involves a two-electron transfer chemistry, leading to the harmful polyhalides through the reactions between X<sub>2</sub> and X<sup>-</sup>. Furthermore, it is interesting to note that three, four or even six-electron transfer reactions can also be triggered under the influence of other halogen ions in the electrolyte, thereby achieving the ultra-high energy density of 200 Wh kg<sup>-1</sup>[17,100]. Therefore, high-energy and low-cost Zn-halogen devices exhibit application prospects to replace commercial lead-acid batteries with strong acid electrolytes and heavy metal lead pollution<sup>[101,102]</sup>. The early-stage challenges of Zn-halogen batteries primarily include polyhalides shuttling effect and low energy conversion efficiency, leading to serious Zn corrosion, slow reaction kinetics, and poor lifespan. The following section mainly focuses on constructing high-performance Zn-halogen batteries through the modified methods of optimizing cathode material structures, incorporating functional electrolytes, and adjusting separator types.

### Cl-based batteries with multi-electron transfer reactions

The chloride redox reaction (ClRR) in Cl-based batteries, known for its cost-effectiveness, high redox potential of 1.36 V (*vs.* SHE), and excellent theoretical capacity (756 mAh g<sup>-1</sup> for two-electron Cl-based reaction), has gained prominence for producing high-energy AZBs<sup>[103,104]</sup>. However, the gas-liquid two-phase conversion reaction of ClRR faces the challenges of redox irreversibility and inferior cycling stability caused by the inadequate fixation of chlorine and electrolyte decomposition. These issues significantly influence the practicality of Zn-Cl<sub>2</sub> batteries<sup>[97,105]</sup>. Enhancing chlorine fixation is vital for developing effective Cl-based devices, especially for the activation of multi-electron transfer chemistry. Recent efforts have focused on immobilizing oxidized chlorine in carbon-based host materials, including AC, graphite, CNTs, and porous carbon spheres<sup>[16,106]</sup>. Wang *et al.* developed a graphite cathode for accommodating the electrochemical generation of bromine and chlorine, demonstrating an increased average discharge voltage of 1.71 V and a capacity reaching up to 257 mAh g<sup>-1</sup> based on double halogen redox reactions involving two-electron transfers (Br<sup>0</sup>/Br<sup>-</sup> and Cl<sup>0</sup>/Cl<sup>-</sup>)<sup>[18]</sup>. However, physical adsorption on carbon-based materials cannot fully





**Figure 4.** Schematic illustration of the energy storage mechanisms, issues, and modified strategies for Zn- $X_2$  batteries ( $X = \text{Cl}, \text{Br}, \text{I}$ ,  $n = 1, 3, 5$ ).

prevent  $\text{Cl}_2$  precipitation,  $\text{Cl}_3^-$  dissolution, and  $\text{Cl}_2$  decomposition reaction, affecting the coulometric efficiency and cycling stability of Cl-based batteries<sup>[107]</sup>.

Compared to carbon materials, a cathode that can form stable chemical adsorption via the chemical bonds with chloride species is required for reversible ClRR. A novel approach by Chen *et al.* involved diphenyl diselenide (di-Ph-Se) as a cathode material to activate the Se-halogen synergistic chemistry for efficient chlorine fixation<sup>[17]</sup>. This resulted in a highly reversible ClRR with low  $\text{Cl}_2$  emission and a significantly elevated discharge voltage (1.87 V vs.  $\text{Zn}^{2+}/\text{Zn}$ ). Each Ph-Se in the cathode can facilitate the fixation of two oxidized  $\text{Cl}^0$  and enable the polyvalent conversion of Se, thereby triggering a six-electron transfer reaction for an ultra-high energy density of  $665 \text{ Wh Kg}^{-1}$  with a high average voltage and coulombic efficiency (CE) of 1.51 V and 99.3%, respectively. Furthermore, the packaged Zn//Ph-Se/Cl exhibits a notable area capacity of  $6.87 \text{ mAh cm}^{-2}$  and exceptional self-discharge performance, demonstrating the practical application potential. The chemical reaction of Se and Cl synergism provides a novel approach for achieving reversible and efficient halogen redox reactions.

In addition to the rational design of cathode materials for achieving effective adsorption of chloride species, employing the redox reaction of active substances in the electrolyte represents a novel strategy for promoted Cl fixation. Similarly, the catalytic effect of metal ions is also evident in Zn- $\text{Cl}_2$  batteries. Chen *et al.* introduced trace amounts of  $\text{Mn}^{2+}$  ions into the electrolyte, forming an *in situ*  $\text{MnO}_2$  redox adsorbent to aid in  $\text{Cl}_2$  adsorption during the charging process<sup>[108]</sup>. The resulting Zn- $\text{Cl}_2$ @ $\text{MnO}_2$  battery based on a multi-electron transfer mechanism exhibits a high voltage of 2.0 V at  $2.5 \text{ mA cm}^{-2}$  and exceptional cycling stability over 1,000 cycles with an average CE of 91.6%<sup>[108]</sup>. These above-mentioned approaches present a promising direction for advancing viable aqueous Cl-based batteries.

### Br-based batteries with multi-electron transfer reactions

Compared to Cl-based batteries, Zn-bromine ( $\text{Br}_2$ ) batteries with lower volatility and toxicity have seen practical advancements, including commercial demonstrations at the  $\text{kW/kW h}^{-1}$  level<sup>[109]</sup>. In 1980, the

Zn-Br<sub>2</sub> battery introduced by Eustace *et al.* was a groundbreaking milestone, offering a high voltage of 1.85 V, a theoretical capacity of 335 mAh g<sub>Br</sub><sup>-1</sup>, and a theoretical energy density of 440 Wh kg<sup>-1</sup><sup>[110,111]</sup>. However, challenges of the corrosiveness of Br<sub>2</sub> and the diffusion of soluble polybromine anions (Br<sub>3</sub><sup>-</sup>, Br<sub>5</sub><sup>-</sup>, etc.) can cause Zn anode corrosion and low CE, preventing further progress in Zn-Br<sub>2</sub> systems<sup>[112-115]</sup>.

Early single-chamber Zn-Br<sub>2</sub> batteries utilized high-density Br<sub>2</sub> and low water absorption for physical separation, offering a cost-effective storage solution. Yet, this system still faces the volatilization of Br<sub>2</sub> gas<sup>[102]</sup>. To address this issue, electrode materials, particularly conventional carbon materials such as porous carbon, are used for their conductivity, large surface area, and stability. They provide active sites for bromine ion adsorption but require enhanced catalysis and Br storage capacity<sup>[116-119]</sup>. Building upon this foundation, Xiang *et al.* utilized N-doped carbon materials as adsorbents to enhance the capacity with high reversibility, although some Br species still escaped<sup>[116]</sup>. Wang *et al.* designed a novel cage-like porous carbon material (CPC) with tailored pore sizes according to the molecular size of Br<sup>-</sup> ions and bromine complexes (MEP<sup>+</sup> and MEPBR<sub>3</sub>)<sup>[118]</sup>. The optimized CPC can successfully fix Br<sub>2</sub> within their porous structures, effectively preventing Br<sub>2</sub> gas leakage for stable Br-based cathodes over 300 cycles<sup>[118]</sup>. With advancements in anode, cathode, and electrolyte modifications, zinc-bromine batteries with multi-electron transfer capability and high discharge voltage are now commercially viable. Continuing research focuses on enhancing CE and energy efficiency for further improvements.

Xu *et al.* constructed a practical water-based Zn-Br<sub>2</sub> static battery based on continuous Br<sup>-</sup>/Br<sup>0</sup>/Br<sup>+</sup> redox reactions, which solved the shuttle and hydrolysis problems of polybromides (Br<sub>3</sub><sup>-</sup> and BrCl<sub>2</sub><sup>-</sup>) by synergizing pyridine complexation chemistry and the salting-out effect of ZnSO<sub>4</sub> water-based electrolyte<sup>[120]</sup>. Pyridinium-polybromide complexes (HPY Br) can be used both as a complexing agent and active material and show excellent binding strength with polybromides. Additionally, 3 M ZnSO<sub>4</sub> causes a strong salting-out effect through SO<sub>4</sub><sup>2-</sup>, which is beneficial to the dissociation of complexes. Benefiting from these advantages, the two-electron Zn-Br static battery exhibited good cycling stability (88.5% retention after 1,000 cycles), a high CE of 99.8%, and an energy efficiency of 89.9%<sup>[120]</sup>. This type of Zn-Br<sub>2</sub> battery shows great potential for expanded applications, and its cost in production is expected to be quite cheap. It provides a promising sustainable power source of high-performance and low-cost Zn-Br<sub>2</sub> batteries for large-scale energy storage.

### I-based batteries with multi-electron transfer reactions

Iodine (I<sub>2</sub>) stands out among halogen batteries for its low toxicity and corrosion, plus the practicality of solid I<sub>2</sub> for large-scale energy storage, making it one of the fastest-developing Zn-halogen batteries based on the I<sub>2</sub>/2I<sup>-</sup> chemistry<sup>[109]</sup>. However, challenges such as the polyiodide shuttle effect, Zn corrosion, and low CE severely limit the development of Zn-I<sub>2</sub> devices<sup>[121]</sup>. Recent advancements in pinning I<sub>2</sub> hosts have focused on porous carbon materials<sup>[122,123]</sup>, single-atom metal-nitrogen carbon materials<sup>[124]</sup>, metal complexes<sup>[125]</sup>, and conductive polymers<sup>[126]</sup>. The shuttle problem of polyiodide ions can be fundamentally solved by improving the reaction kinetics and reducing the production of polyiodide ions<sup>[127]</sup>. Zhang *et al.* developed a starch-iodine complex as the cathode material to limit the polyiodide shuttle effect, enhancing the lifespan of up to 50,000 cycles in the modified Zn-I<sub>2</sub> battery<sup>[119]</sup>. Additionally, novel electrolytes and functionalized membranes are crucial in effectively preventing the polyiodide shuttle during battery working<sup>[128-130]</sup>. For instance, Chen *et al.* designed a vermiculite nanosheet (VS) suspension electrolyte, which can efficiently anchor polyiodides and improve the cycling stability<sup>[131]</sup>. This study demonstrated that the Si-O bond between the primary intermediate I<sub>3</sub><sup>-</sup> and VS possesses high binding energy, enabling efficient anchoring of dissolved polyiodides on the VS surface<sup>[131]</sup>.

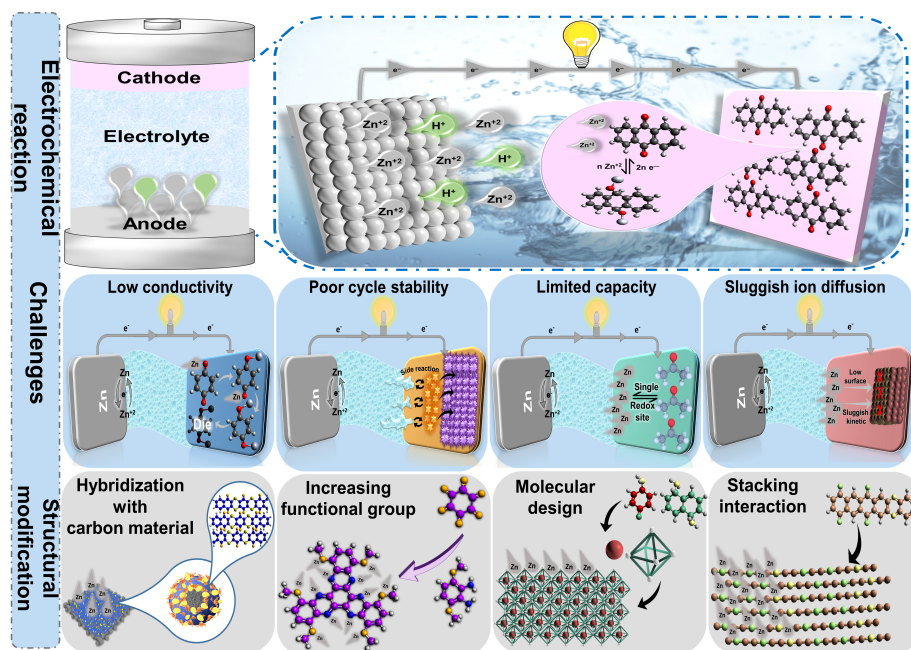
To achieve high specific energy Zn-I<sub>2</sub> batteries, the characteristics of iodine elements with variable valence states are utilized to stimulate new redox couples with enhanced electron transfer numbers and higher reaction potential. Zou *et al.* introduced an aqueous zinc-iodine battery with a four-electron transfer, leveraging the redox couple of I<sup>+</sup>/I<sub>2</sub> (1.83 V vs. Zn<sup>2+</sup>/Zn) and I<sub>2</sub>/I<sup>-</sup> (1.29 V vs. Zn<sup>2+</sup>/Zn) with ZnCl<sub>2</sub> electrolyte. This approach resulted in an increased specific capacity of 594 mAh g<sup>-1</sup> and an energy density of 750 Wh kg<sup>-1</sup> over 6,000 cycles<sup>[15]</sup>. Earlier attempts to use iodine oxides of IO<sub>4</sub><sup>-</sup>/IO<sub>3</sub><sup>-</sup> in an acidic electrolyte for multi-electron transfer face issues such as HER and Zn corrosion<sup>[132-134]</sup>. A recent breakthrough with a six-electron transfer redox couple of IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> achieved impressive capacities of 1,200 mAh g<sup>-1</sup> and energy densities of 1,357 Wh kg<sup>-1</sup> by employing halogen interchange chemistry with Br<sup>-</sup><sup>[100]</sup>. This cycling process happened through halogen interchange chemistry between I<sub>2</sub> (in the electrode) and Br<sup>-</sup> (in the acidic electrolyte). Specifically, the polar IBr halogen interchange intermediate formed undergoes nucleophilic reaction with H<sub>2</sub>O to form IO<sub>3</sub><sup>-</sup> during the charging process. During discharge, Br<sup>-</sup> acts as a catalyst for the dissociation of IO<sub>3</sub><sup>-</sup> and reduces it to IBr and Br<sub>2</sub>. Therefore, iodine-based devices offer significant potential for high-energy and fast-charging Zn batteries with a long lifespan.

Based on previously mentioned Zn-halogen batteries with multiple electron transfer mechanisms, Zn-I<sub>2</sub> devices have induced great attention for high-energy AZBs with the twelve-electron transfer reaction. However, the lighter molar mass of Br and Cl is positive for further improving the battery energy density. Therefore, preventing the gas formation of Cl<sub>2</sub> and Br<sub>2</sub> and the shuttle effect for the inferior CE and lifespan are urgent for developing high-performance Zn-halogen batteries.

### Organic cathodes with multi-redox centers

Compared to inorganic cathode materials, organic cathodes with low mass, flexible molecular chains, and multiple redox groups generally offer improved structural stability, better rate performance, and the potential for higher energy densities<sup>[135-138]</sup>. Besides, the organic cathode in Zn batteries prevents Zn dendrite formation and extends battery life by creating a chemical barrier<sup>[139,140]</sup>. The energy storage mechanism in aqueous Zn-organic batteries (AZOBs) is driven by the insertion of Zn<sup>2+</sup> or H<sup>+</sup> ions combined with multiple active sites in the organic cathode materials during the discharge process<sup>[141-143]</sup>. As illustrated in Figure 5, electron transfer at the cathode often involves conjugated structures and delocalized electrons to facilitate ion and electron transfer kinetics<sup>[144-146]</sup>. Despite these advantages, organic cathodes face challenges such as low actual capacity, poor cycle stability, and inadequate rate performance, primarily due to low electronic conductivity and unstable organic intermediates<sup>[20,147]</sup>. Organic cathodes with redox-active centers such as C=O and C=N can improve electron transfer numbers by providing more reaction sites and faster electron transfer kinetics, increasing energy density and stability<sup>[140,148,149]</sup>. For example, quinone compounds and their derivatives including 6,8,15,17-tetraaza-heptacene-5,7,9,14,16,18-hexaone (TAHQ), 9,10-phenanthraquinone (PQ), tetracyanoquinodimethane (TCNQ), pyrene-4,5,9,10-tetraone (PTO), and 8,21-dihydronaphtho[2,3-a]naphtho[2',3':7,8]quinoxalino[2,3-i]phenazine-5,11,16,22-tetraone (DADB) exhibit multi-functional groups for boosting multiple electron transfer reactions for achieving advanced AZOBs<sup>[143,148-150]</sup>. Therefore, the rational design of organic molecular structures is the primary method for boosting their battery performance.

The selection of organic cathode materials for activating multi-electron transfer reactions is a complex decision involving a thorough evaluation of various factors to determine the optimal option for a specific application. The C=O (carbonyl) group is generally preferred over the C=N (imine) group due to its higher reduction potential, better stability, and stronger interaction with zinc ions, enhancing its electrochemical performance. However, some C=N and C≡N compounds have shown excellent electrochemical performance, depending on their specific molecular structures, electrolyte composition, and battery operating conditions<sup>[139,141,146,149,151-153]</sup>. To tackle the concerns mentioned above, it is imperative to modify the



**Figure 5.** Diagrammatic representation of the energy storage mechanism, challenges, and structural modification strategies for high-performance Zn-organic batteries with multiple electron transfer reactions.

organic cathode structure to enable multi-electron transfer reactions for the enhanced battery performance. Recent strategies include modifying and rearranging the organic structures in various ways that further nudge the organic cathode to the subsequent multi-electron transfer<sup>[154-157]</sup>. The primary causes of the low conductivity of the organic cathodes are caused by the molecular structure of organic compounds with wide highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gap values<sup>[158-161]</sup>. For instance, Zhao *et al.* fabricated a carbon-based poly(meta-aminophenol, 3-AP)/poly(para-aminophenol, 4-AP) hybrid cathode for four-electron transfer AZOBs with a high capacity of 347 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup><sup>[21]</sup>.

Addressing the high solubility and weak molecular bonding of organic cathodes requires increased active sites with high stability<sup>[21,152-154,162,163]</sup>. Peng *et al.* described the benzo[a]benzo[7,8]quinoxalino[2,3-i]phenazine-8,17-dione (BBQPH) cathode with reversible multi-electron transferred by the Zn<sup>2+</sup>/H<sup>+</sup> co-insertion mechanism, exhibiting a superior capacity reservation of 380 mAh g<sup>-1</sup> after 1,000 cycles at 5 A g<sup>-1</sup> and an excellent energy density of 355 Wh Kg<sup>-1</sup><sup>[39]</sup>. Challenges such as sluggish ion diffusion are addressed by improving the morphology and electrical conductivity of organic molecules in cathode materials. For example, Zhao *et al.* sequentially deposited poly(1,5-naphthalenediamine, NAPD) and poly(para-aminophenol, pAP) onto porous carbon to fabricate the C@multi-layer polymer cathode with an enhanced capacity of 348 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup><sup>[164]</sup>. The intrinsic electrical conductivity in conjugated organic cathodes generally exhibits the rapid diffusion pathway of Zn<sup>2+</sup> ions for improved rate capability of AZOBs<sup>[165-167]</sup>. By utilizing electroactive phenazine, Ye *et al.* prepared a liner  $\pi$ -conjugated poly(phenazine-alt-pyromellitic anhydride) (PPPA) cathode material with both C=O and C=N groups<sup>[22]</sup>. Quinone-based PPPA cathodes provide a remarkable capacity retention of 140 mAh g<sup>-1</sup> and ultra-high lifespan over 20,000 cycles at 5 A g<sup>-1</sup>, evaluating promising applications in Zn//PPPA devices<sup>[22]</sup>.



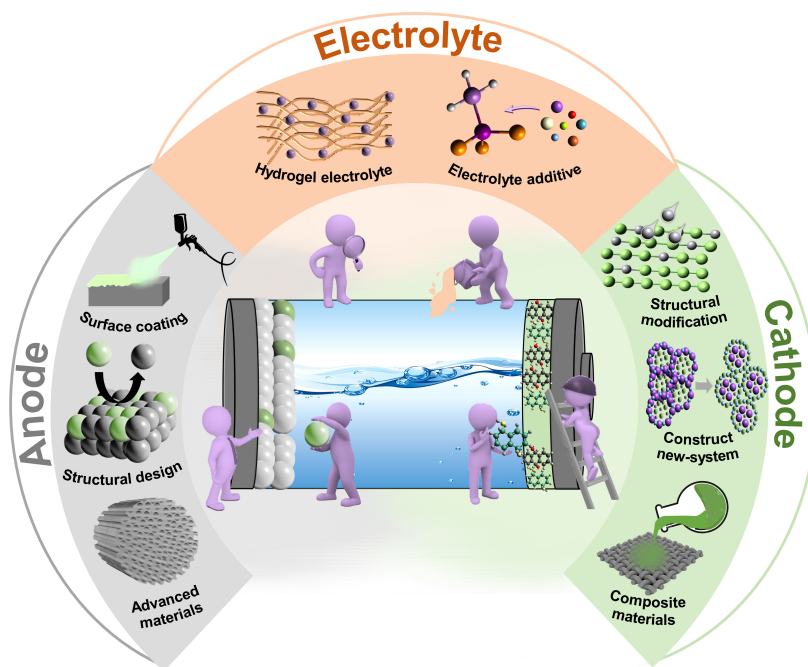
In addition to increased redox activity, introducing multiple redox elements of halogen, sulfide, and selenium has been drawing great attention to enhance electron transfer reactions of high-performance AZOBs<sup>[23,148,168-170]</sup>. For example, Chen *et al.* developed dual-ion Zn-triphenylphosphine selenide (Zn/TP-Se) batteries with a high-potential triphenylphosphine selenide organic cathode, achieving excellent cycling performance and remarkable discharge capacity after 4,300 cycles with a flat discharge plateau at 1.96 V<sup>[170]</sup>. Attention to selenium-based cathodes is growing due to their potential for fast charging and improved long-term cycling performance<sup>[148,171-174]</sup>. Recently, Zhang *et al.* utilized polyaniline (PANI) as the catalytic cathode material to trigger the dual-redox mechanism of Zn<sup>2+</sup> insertion and I/I<sub>3</sub><sup>-</sup>, thereby achieving a high areal capacity of ~1.0 mAh cm<sup>-2</sup> after 200 cycles<sup>[175]</sup>. Therefore, evaluating and assessing multi-functional organic cathodes matched with multiple redox couples is essential for developing high-performance Zn-organic batteries. Covalent organic frameworks (COFs) have emerged as a promising approach for enhancing the electron transfer kinetics and redox potential of AZOBs. For example, the COF (Tp-PTO-COF) with numerous carbonyl active sites exhibits a high pair of redox peaks at 1.53 V/1.54 V caused by the anti-aromatic effect<sup>[44]</sup>. Moreover, a high capacity of 208 mAh g<sup>-1</sup> and stable cycling over 1,000 cycles demonstrate the contribution of dual-redox sites (C=O and C=N) in the Tetraamino-p-benzoquinone-Benzoquinone (TAQ-BQ) COF cathode host<sup>[176,177]</sup>.

## SUMMARY AND PERSPECTIVES

AZBs with cost-effectiveness and intrinsic safety have emerged as promising candidates for the large-scale energy storage systems. However, several challenges impede their widespread adoption including limitations in the energy density and battery lifespan. This paper comprehensively reviews multi-electron transfer cathode designs, including Mn-based oxides, V-based oxides, halogens, and organic compounds. To further enhance the performance of zinc-based devices, it is imperative to explore new modifications and designs in cathode structures. The selection of the optimal cathode material is crucial for battery performance, necessitating a thorough evaluation of the specific requirements for different cathode hosts. Remarkable cathode materials significantly enhance the overall efficiency and energy density of the battery. The goal of current research in this area is to facilitate multiple redox reactions within a confined voltage range to achieve the high energy density and long lifespan. Pursuing alternative structural modification strategies for these common multi-electron transfer cathode materials is essential, such as metal oxide nanostructure doping agents, redox mediators (RMs) for halogen-based cathodes, and ion storage mechanism optimization for organic hosts. These strategies aim to amplify their inherent multi-electron transfer capabilities while preventing the dissolution of active materials during multi-step redox processes.

Furthermore, exploring novel cathode materials is crucial for developing innovative battery systems. In designing cathodes, principles based on light element multi-electron reactions are employed to achieve high-energy and long-life AZBs, such as transitioning from V<sub>2</sub>O<sub>5</sub> to VO<sub>2</sub>, and iodine to chlorine or sulfur elements. It is also important to note that cathode-free systems can still achieve high surface capacity and long cycle life by constructing Zn batteries with active substances present in the electrolyte. Additionally, exploring more redox couples that facilitate synergistic oxidation/reduction processes involving both cations and anions could further advance AZB technology. For Mn-based, V-based compounds, organics and halogens, incorporating specific redox couples not only inhibits the generation of deactivated matter for enhanced cycle life but also increases the redox activity for boosted energy density. Therefore, the coupling or mutual excitation of multiple redox reactions between the cathode and the electrolyte, resulting in multiple electron transfers, is the future research trend of Zn batteries. In addition, artificial intelligence (AI) can be used to predict electrode material functions and design structures to efficiently build high-energy density and durable cathode materials. For example, AI can calculate to predict the physical/chemical properties of MnO<sub>2</sub> cathodes doped with different transition metals, thereby quickly choosing optimal combination for superior cathode materials with the sensitized MnO<sub>2</sub>/Mn<sup>2+</sup> redox reaction.





**Figure 6.** Perspectives of the high-energy aqueous Zn batteries enabled by multi-electron transfer reactions.

AZBs hold the potential to revolutionize the energy storage landscape, offering solutions that address safety concerns, leverage abundant resources, and stand at the forefront of emerging battery technologies. To achieve this potential, however, advanced electrode materials, electrolytes, and cell designs are necessary to be integrated into full zinc-ion battery systems, along with the comprehensive optimization and testing. This process ensures the AZB system meets safety, efficiency, and durability standards, achieving high-energy and long-life Zn batteries based on light-element hosts and multi-electron reactions. Moreover, exploring more redox couples that facilitate synergistic oxidation/reduction processes involving cations and anions could greatly boost the further advancements in AZBs. Besides developing novel cathode materials matched with the optimized electrolyte, understanding the battery degradation mechanisms and operating condition optimization is essential for constructing advanced AZBs. Meanwhile, strategic optimization of battery design is required with targeted modifications to both the Zn anodes and electrolytes, as shown in [Figure 6](#). To mitigate common issues associated with Zn anodes, such as dendritic growth, hydrogen evolution, and corrosion, several strategies can be employed. These include surface coatings or treatments, structural modifications, and the use of advanced materials or anode-free Zn battery systems. Each of these approaches aims to enhance the stability and longevity of the anodes, thereby improving the overall battery performance. Similarly, electrolyte modifications play a critical role in enhancing battery efficiency. Electrolyte additives, regulating pH buffers, temperature control, and redox couples, are pivotal for improving Zn stability, CE, and energy density of Zn batteries. For example, the addition of pH buffers can not only protect the Zn anode from corrosion but also inhibit the side reactions of the cathode for the high reaction efficiency. Therefore, creating a more conducive working environment can greatly optimize the battery performance of AZBs.

The successful commercialization and integration of AZBs into our existing energy infrastructure hinge on thorough integration and compatibility studies. These batteries have a wide range of potential applications, from small-scale portable electronics to large electric grids, each with unique requirements and challenges. To this end, scientists and engineers are actively engaged in exploring how Zn battery technology can be

seamlessly incorporated into current energy systems, with a vision to foster a more sustainable and energy-efficient future. This review aims to offer insightful perspectives and recommendations for ongoing research in multi-electron transfer AZBs, with the additional goal of stimulating further innovation in this field. The ultimate objective is to realize the full potential of Zn devices, delivering energy storage solutions to meet the diverse needs of modern and future energy demands. By continuing to push the boundaries of this technology, AZBs with multiple electron transfer reactions could play a pivotal role in shaping the energy storage landscape and contribute significantly to global sustainability efforts.

## DECLARATIONS

### Authors' contributions

Performed an extensive literature search and information gathering, and subsequently composed the paper:

Li Q, Abdalla KK

Managed copyright aspects and associated picture legend: Song Z, Liu M

Revised and modified paper: Xiong J, Wang Y, Zhao Y, Fan Y

Acquired the funding and supervised the entire process: Zhao Y, Sun XM

### Availability of data and materials

Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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## REFERENCES

1. Han L, Wu Y, Fang K, et al. The splanchnic mesenchyme is the tissue of origin for pancreatic fibroblasts during homeostasis and tumorigenesis. *Nat Commun* 2023;14:1. [DOI](#) [PubMed](#) [PMC](#)
2. Hou D, Xia D, Gabriel E, et al. Spatial and temporal analysis of sodium-ion batteries. *ACS Energy Lett* 2021;6:4023-54. [DOI](#) [PubMed](#) [PMC](#)
3. Xiong P, Lin C, Wei Y, et al. Charge-transfer complex-based artificial layers for stable and efficient Zn metal anodes. *ACS Energy Lett* 2023;8:2718-27. [DOI](#)
4. Xiao D, Lv X, Fan J, Li Q, Chen Z. Zn-based batteries for energy storage. *Energy Mater* 2023;3:300007. [DOI](#)
5. Bruce PG, Freunberger SA, Hardwick LJ, Tarascon JM. Li-O<sub>2</sub> and Li-S batteries with high energy storage. *Nat Mater* 2011;11:19-29. [DOI](#) [PubMed](#)
6. Xia X, Zhao Y, Zhao Y, Xu M, Liu W, Sun X. Mo doping provokes two electron reaction in MnO<sub>2</sub> with ultrahigh capacity for aqueous zinc ion batteries. *Nano Res* 2023;16:2511-8. [DOI](#)

7. Zhong Y, Xu X, Veder JP, Shao Z. Self-recovery chemistry and cobalt-catalyzed electrochemical deposition of cathode for boosting performance of aqueous zinc-ion batteries. *iScience* 2020;23:100943. DOI PubMed PMC
8. Liu Y, Wang K, Yang X, Liu J, Liu XX, Sun X. Enhancing two-electron reaction contribution in MnO<sub>2</sub> cathode material by structural engineering for stable cycling in aqueous Zn batteries. *ACS Nano* 2023;17:14792-9. DOI
9. Zhao Y, Xia X, Li Q, et al. Activating the redox chemistry of MnO<sub>2</sub>/Mn<sup>2+</sup> in aqueous Zn batteries based on multi-ions doping regulation. *Energy Storage Mater* 2024;67:103268. DOI
10. Ma Y, Xu M, Liu R, et al. Molecular tailoring of MnO<sub>2</sub> by bismuth doping to achieve aqueous zinc-ion battery with capacitor-level durability. *Energy Storage Mater* 2022;48:212-22. DOI
11. Wan F, Huang S, Cao H, Niu Z. Freestanding potassium vanadate/carbon nanotube films for ultralong-life aqueous zinc-ion batteries. *ACS Nano* 2020;14:6752-60. DOI PubMed
12. Guo J, He B, Gong W, et al. Emerging amorphous to crystalline conversion chemistry in Ca-Doped VO<sub>2</sub> cathodes for high-capacity and long-term wearable aqueous zinc-ion batteries. *Adv Mater* 2024;36:e2303906. DOI
13. Song Z, Zhao Y, Zhou A, et al. Organic intercalation induced kinetic enhancement of vanadium oxide cathodes for ultrahigh-loading aqueous zinc-ion batteries. *Small* 2024;20:e2305030. DOI
14. Wang W, Yang C, Chi X, Liu J, Wen B, Liu Y. Ultralow-water-activity electrolyte endows vanadium-based zinc-ion batteries with durable lifespan exceeding 30 000 cycles. *Energy Storage Mater* 2022;53:774-82. DOI
15. Zou Y, Liu T, Du Q, et al. A four-electron Zn-I<sub>2</sub> aqueous battery enabled by reversible I<sup>-</sup>/I<sub>2</sub><sup>+</sup> conversion. *Nat Commun* 2021;12:170. DOI PubMed PMC
16. Liu H, Chen CY, Yang H, et al. A zinc-dual-halogen battery with a molten hydrate electrolyte. *Adv Mater* 2020;32:e2004553. DOI
17. Chen Z, Hou Y, Wang Y, et al. Selenium-anchored chlorine redox chemistry in aqueous zinc dual-ion batteries. *Adv Mater* 2024;36:e2309330. DOI
18. Wang C, Lai Q, Xu P, Zheng D, Li X, Zhang H. Cage-like porous carbon with superhigh activity and Br<sub>2</sub>-complex-entrapping capability for bromine-based flow batteries. *Adv Mater* 2017;29:1605815. DOI
19. Zhang SJ, Hao J, Li H, et al. Polyiodide confinement by starch enables shuttle-free Zn-iodine batteries. *Adv Mater* 2022;34:e2201716. DOI
20. Peng C, Ning G, Su J, et al. Reversible multi-electron redox chemistry of  $\pi$ -conjugated N-containing heteroaromatic molecule-based organic cathodes. *Nat Energy* 2017;2:17074. DOI
21. Zhao Y, Huang Y, Chen R, Wu F, Li L. Tailoring double-layer aromatic polymers with multi-active sites towards high performance aqueous Zn-organic batteries. *Mater Horiz* 2021;8:3124-32. DOI
22. Ye F, Liu Q, Dong H, et al. Organic zinc-ion battery: planar,  $\pi$ -conjugated quinone-based polymer endows ultrafast ion diffusion kinetics. *Angew Chem Int Ed* 2022;61:e202214244. DOI
23. Lu Y, Cai Y, Zhang Q, Chen J. Structure-performance relationships of covalent organic framework electrode materials in metal-ion batteries. *J Phys Chem Lett* 2021;12:8061-71. DOI
24. Kumankuma-Sarpong J, Tang S, Guo W, Fu Y. Naphthoquinone-based composite cathodes for aqueous rechargeable zinc-ion batteries. *ACS Appl Mater Interfaces* 2021;13:4084-92. DOI PubMed
25. Li Q, Zhao Y, Wang Y, Khasraw AK, Zhao Y, Sun X. Rational design of nanostructured MnO<sub>2</sub> cathode for high-performance aqueous zinc ion batteries. *Chem Res Chin Univ* 2023;39:599-611. DOI
26. Zhao Y, Zhang P, Liang J, et al. Uncovering sulfur doping effect in MnO<sub>2</sub> nanosheets as an efficient cathode for aqueous zinc ion battery. *Energy Storage Mater* 2022;47:424-33. DOI
27. Dai H, Zhou R, Zhang Z, Zhou J, Sun G. Design of manganese dioxide for supercapacitors and zinc-ion batteries: similarities and differences. *Energy Mater* 2022;2:200040. DOI
28. Dong H, Li J, Guo J, et al. Insights on flexible zinc-ion batteries from lab research to commercialization. *Adv Mater* 2021;33:e2007548. DOI
29. Wang M, Tang Y. A review on the features and progress of dual-ion batteries. *Adv Energy Mater* 2018;8:1703320. DOI
30. Wang S, Hu N, Huang Y, Deng W. Charge-transfer complex promotes energy storage performance of single-moiety organic electrode materials in aqueous zinc-ion battery at low temperatures. *Appl Surf Sci* 2023;619:156725. DOI
31. Xiong P, Kang Y, Yao N, et al. Zn-ion transporting, *in situ* formed robust solid electrolyte interphase for stable zinc metal anodes over a wide temperature range. *ACS Energy Lett* 2023;8:1613-25. DOI
32. Wang M, Zheng X, Zhang X, et al. Opportunities of aqueous manganese-based batteries with deposition and stripping chemistry. *Adv Energy Mater* 2021;11:2002904. DOI
33. Ruan P, Liang S, Lu B, Fan HJ, Zhou J. Design strategies for high-energy-density aqueous zinc batteries. *Angew Chem Int Ed* 2022;61:e202200598. DOI
34. Li Y, Liu L, Lu Y, et al. High-energy-density quinone-based electrodes with [Al(OTf)]<sup>2+</sup> storage mechanism for rechargeable aqueous aluminum batteries. *Adv Funct Mater* 2021;31:2102063. DOI
35. Xu Y, Xu X, Guo M, Zhang G, Wang Y. Research progresses and challenges of flexible zinc battery. *Front Chem* 2022;10:827563. DOI PubMed PMC
36. Chen H, Wang C, Dai Y, et al. Rational design of cathode structure for high rate performance lithium-sulfur batteries. *Nano Lett* 2015;15:5443-8. DOI
37. Xu Y, Xie C, Li T, Li X. A high energy density bromine-based flow battery with two-electron transfer. *ACS Energy Lett*

- 2022;7:1034-9. DOI
38. Ge G, Zhang C, Li X. Multi-electron transfer electrode materials for high-energy-density flow batteries. *Next Energy* 2023;1:100043. DOI
39. Zhao Y, Wang Y, Zhao Z, et al. Achieving high capacity and long life of aqueous rechargeable zinc battery by using nanoporous-carbon-supported poly(1,5-naphthalenediamine) nanorods as cathode. *Energy Storage Mater* 2020;28:64-72. DOI
40. Huang YX, Wu F, Chen RJ. Thermodynamic analysis and kinetic optimization of high-energy batteries based on multi-electron reactions. *Natl Sci Rev* 2020;7:1367-86. DOI PubMed PMC
41. Gao X, Yang H. Multi-electron reaction materials for high energy density batteries. *Energy Environ Sci* 2010;3:174-89. DOI
42. Chen R, Luo R, Huang Y, Wu F, Li L. Advanced high energy density secondary batteries with multi-electron reaction materials. *Adv Sci* 2016;3:1600051. DOI PubMed PMC
43. Whittingham MS, Siu C, Ding J. Can multielectron intercalation reactions be the basis of next generation batteries? *ACC Chem Res* 2018;51:258-64. DOI PubMed
44. Guo RQ, Wu F, Wang XR, Wu C, Bai Y. Multi-electron reaction-boosted high energy density batteries: material and system innovation. *J Electrochem* 2022;28:2219011. DOI
45. Chen W, Li G, Pei A, et al. A manganese-hydrogen battery with potential for grid-scale energy storage. *Nat Energy* 2018;3:428-35. DOI
46. Chao D, Zhou W, Ye C, et al. An electrolytic Zn-MnO<sub>2</sub> battery for high-voltage and scalable energy storage. *Angew Chem Int Ed* 2019;58:7823-8. DOI
47. Pan H, Shao Y, Yan P, et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. *Nat Energy* 2016;1:16039. DOI
48. Xie C, Li T, Deng C, Song Y, Zhang H, Li X. A highly reversible neutral zinc/manganese battery for stationary energy storage. *Energy Environ Sci* 2020;13:135-43. DOI
49. Fu Y, Wei Q, Zhang G, et al. High-performance reversible aqueous Zn-ion battery based on porous MnO<sub>x</sub> nanorods coated by MOF-derived N-doped carbon. *Adv Energy Mater* 2018;8:1801445. DOI
50. Radha AV, Forbes TZ, Killian CE, Gilbert PU, Navrotsky A. Transformation and crystallization energetics of synthetic and biogenic amorphous calcium carbonate. *Proc Natl Acad Sci USA* 2010;107:16438-43. DOI PubMed PMC
51. Huang J, Zeng J, Zhu K, Zhang R, Liu J. High-performance aqueous zinc-manganese battery with reversible Mn<sup>2+</sup>/Mn<sup>4+</sup> double redox achieved by carbon coated MnO<sub>x</sub> nanoparticles. *Nanomicro Lett* 2020;12:110. DOI PubMed PMC
52. Moon H, Ha KH, Park Y, et al. Direct proof of the reversible dissolution/deposition of Mn<sup>2+</sup>/Mn<sup>4+</sup> for mild-acid Zn-MnO<sub>2</sub> batteries with porous carbon interlayers. *Adv Sci* 2021;8:2003714. DOI PubMed PMC
53. Yang H, Zhang T, Chen D, et al. Protocol in evaluating capacity of Zn-Mn aqueous batteries: a clue of pH. *Adv Mater* 2023;35:e2300053. DOI
54. Yang H, Zhou W, Chen D, et al. The origin of capacity fluctuation and rescue of dead Mn-based Zn-ion batteries: a Mn-based competitive capacity evolution protocol. *Energy Environ Sci* 2022;15:1106-18. DOI
55. Xu Y, Huang W, Liu J, et al. Promoting the reversibility of electrolytic MnO<sub>2</sub>-Zn battery with high areal capacity by VOSO<sub>4</sub> mediator. *Energy Mater* 2024;4:400005. DOI
56. Ma D, Zhao H, Cao F, et al. A carbonyl-rich covalent organic framework as a high-performance cathode material for aqueous rechargeable zinc-ion batteries. *Chem Sci* 2022;13:2385-90. DOI PubMed PMC
57. Rubio-garcia J, Kucernak A, Zhao D, et al. Hydrogen/manganese hybrid redox flow battery. *J Phys Energy* 2019;1:015006. DOI
58. Liu Z, Yang Y, Lu B, Liang S, Fan HJ, Zhou J. Insights into complexing effects in acetate-based Zn-MnO<sub>2</sub> batteries and performance enhancement by all-round strategies. *Energy Storage Mater* 2022;52:104-10. DOI
59. Ye X, Han D, Jiang G, et al. Unraveling the deposition/dissolution chemistry of MnO<sub>2</sub> for high-energy aqueous batteries. *Energy Environ Sci* 2023;16:1016-23. DOI
60. Wu J, Huang J, Chi X, Yang J, Liu Y. Mn<sup>2+</sup>/I<sup>-</sup> hybrid cathode with superior conversion efficiency for ultrahigh-areal-capacity aqueous zinc batteries. *ACS Appl Mater Interfaces* 2022;14:53627-35. DOI
61. Lei J, Yao Y, Wang Z, Lu Y. Towards high-areal-capacity aqueous zinc-manganese batteries: promoting MnO<sub>2</sub> dissolution by redox mediators. *Energy Environ Sci* 2021;14:4418-26. DOI
62. Chuai M, Yang J, Wang M, et al. High-performance Zn battery with transition metal ions co-regulated electrolytic MnO<sub>2</sub>. *eScience* 2021;1:178-85. DOI
63. Li G, Chen W, Zhang H, et al. Membrane-free Zn/MnO<sub>2</sub> flow battery for large-scale energy storage. *Adv Energy Mater* 2020;10:1902085. DOI
64. Tang H, Yin Y, Huang Y, et al. Battery-everywhere design based on a cathodeless configuration with high sustainability and energy density. *ACS Energy Lett* 2021;6:1859-68. DOI
65. Alfuruqi MH, Mathew V, Gim J, et al. Electrochemically induced structural transformation in a γ-MnO<sub>2</sub> cathode of a high capacity zinc-ion battery system. *Chem Mater* 2015;27:3609-20. DOI
66. Lee B, Seo HR, Lee HR, et al. Critical role of pH evolution of electrolyte in the reaction mechanism for rechargeable zinc batteries. *ChemSusChem* 2016;9:2948-56. DOI
67. Liu W, Zhang X, Huang Y, et al. β-MnO<sub>2</sub> with proton conversion mechanism in rechargeable zinc ion battery. *J Energy Chem* 2021;56:365-73. DOI

68. Fitz O, Bischoff C, Bauer M, et al. Electrolyte study with in operando pH tracking providing insight into the reaction mechanism of aqueous acidic Zn/MnO<sub>2</sub> batteries. *ChemElectroChem* 2021;8:3553-66. DOI
69. Wu D, Housel LM, Kim SJ, et al. Quantitative temporally and spatially resolved X-ray fluorescence microprobe characterization of the manganese dissolution-deposition mechanism in aqueous Zn/ $\alpha$ -MnO<sub>2</sub> batteries. *Energy Environ Sci* 2020;13:4322-33. DOI
70. Kim SJ, Wu D, Sadique N, et al. Unraveling the dissolution-mediated reaction mechanism of  $\alpha$ -MnO<sub>2</sub> cathodes for aqueous Zn-ion batteries. *Small* 2020;16:e2005406. DOI
71. Chen H, Dai C, Xiao F, et al. Reunderstanding the reaction mechanism of aqueous Zn-Mn batteries with sulfate electrolytes: role of the zinc sulfate hydroxide. *Adv Mater* 2022;34:e2109092. DOI
72. Guo S, Liang S, Zhang B, Fang G, Ma D, Zhou J. Cathode interfacial layer formation via in situ electrochemically charging in aqueous zinc-ion battery. *ACS Nano* 2019;13:13456-64. DOI
73. Jiang W, Zhu K, Yang W. Critical issues of vanadium-based cathodes towards practical aqueous Zn-ion batteries. *Chemistry* 2023;29:e202301769. DOI
74. Hu Z, Miao Z, Xu Z, et al. Carbon felt electrode modified by lotus seed shells for high-performance vanadium redox flow battery. *Chem Eng J* 2022;450:138377. DOI
75. Jiang H, Chen GF, Hai G, et al. A nitrogen battery electrode involving eight-electron transfer per nitrogen for energy storage. *Angew Chem Int Ed* 2023;62:e202305695. DOI
76. Venkatkarthick R, Rodthongkum N, Zhang X, et al. Vanadium-based oxide on two-dimensional vanadium carbide MXene (V<sub>2</sub>O<sub>x</sub>@V<sub>2</sub>CT<sub>x</sub>) as cathode for rechargeable aqueous zinc-ion batteries. *ACS Appl Energy Mater* 2020;3:4677-89. DOI
77. Zhu X, Wang W, Cao Z, et al. Zn<sup>2+</sup>-intercalated V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O derived from V<sub>2</sub>CT<sub>x</sub> MXene for hyper-stable zinc-ion storage. *J Mater Chem A* 2021;9:17994-8005. DOI
78. Wu S, Liu S, Hu L, Chen S. Constructing electron pathways by graphene oxide for V<sub>2</sub>O<sub>5</sub> nanoparticles in ultrahigh-performance and fast charging aqueous zinc ion batteries. *J Alloys Compd* 2021;878:160324. DOI
79. Wang X, Li Y, Das P, Zheng S, Zhou F, Wu Z. Layer-by-layer stacked amorphous V<sub>2</sub>O<sub>5</sub>/Graphene 2D heterostructures with strong-coupling effect for high-capacity aqueous zinc-ion batteries with ultra-long cycle life. *Energy Storage Mater* 2020;31:156-63. DOI
80. Cui F, Wang D, Hu F, et al. Deficiency and surface engineering boosting electronic and ionic kinetics in NH<sub>4</sub>V<sub>4</sub>O<sub>10</sub> for high-performance aqueous zinc-ion battery. *Energy Storage Mater* 2022;44:197-205. DOI
81. Narayanasamy M, Hu L, Kirubasankar B, Liu Z, Angaiah S, Yan C. Nanohybrid engineering of the vertically confined marigold structure of rGO-VSe<sub>2</sub> as an advanced cathode material for aqueous zinc-ion battery. *J Alloys Compd* 2021;882:160704. DOI
82. Deka Boruah B, Mathieson A, Park SK, et al. Vanadium dioxide cathodes for high-rate photo-rechargeable zinc-ion batteries. *Adv Energy Mater* 2021;11:2100115. DOI
83. Kong D, Li X, Zhang Y, et al. Encapsulating V<sub>2</sub>O<sub>5</sub> into carbon nanotubes enables the synthesis of flexible high-performance lithium ion batteries. *Energy Environ Sci* 2016;9:906-11. DOI
84. Wan F, Niu Z. Design strategies for vanadium-based aqueous zinc-ion batteries. *Angew Chem Int Ed* 2019;58:16358-67. DOI PubMed
85. Guo C, Yi S, Si R, et al. Advances on defect engineering of vanadium-based compounds for high-energy aqueous zinc-ion batteries. *Adv Energy Mater* 2022;12:2202039. DOI
86. Deng S, Jiang Y, Huang D, et al. Driving intercalation kinetic through hydrated Na<sup>+</sup> insertion in V<sub>2</sub>O<sub>5</sub> for high rate performance aqueous zinc ion batteries. *J Alloys Compd* 2022;891:161946. DOI
87. Ma X, Cao X, Yao M, et al. Organic-inorganic hybrid cathode with dual energy-storage mechanism for ultrahigh-rate and ultralong-life aqueous zinc-ion batteries. *Adv Mater* 2022;34:e2105452. DOI
88. Islam S, Alfaruqi MH, Putro DY, et al. K<sup>+</sup> intercalated V<sub>2</sub>O<sub>5</sub> nanorods with exposed facets as advanced cathodes for high energy and high rate zinc-ion batteries. *J Mater Chem A* 2019;7:20335-47. DOI
89. Sambandam B, Soundharrajan V, Kim S, et al. K<sub>2</sub>V<sub>6</sub>O<sub>16</sub>·2.7H<sub>2</sub>O nanorod cathode: an advanced intercalation system for high energy aqueous rechargeable Zn-ion batteries. *J Mater Chem A* 2018;6:15530-9. DOI
90. He P, Quan Y, Xu X, et al. High-performance aqueous zinc-ion battery based on layered H<sub>2</sub>V<sub>3</sub>O<sub>8</sub> nanowire cathode. *Small* 2017;13:1702551. DOI
91. Peng B, Zhang H, Shao H, et al. Chemical intuition for high thermoelectric performance in monolayer black phosphorus,  $\alpha$ -arsenene and aW-antimonene. *J Mater Chem A* 2018;6:2018-33. DOI
92. Wang X, Zhang Z, Xiong S, et al. A high-rate and ultrastable aqueous zinc-ion battery with a novel MgV<sub>2</sub>O<sub>6</sub>·1.7H<sub>2</sub>O nanobelt cathode. *Small* 2021;17:e2100318. DOI
93. Yang Y, Guo S, Pan Y, Lu B, Liang S, Zhou J. Dual mechanism of ion (de)intercalation and iodine redox towards advanced zinc batteries. *Energy Environ Sci* 2023;16:2358-67. DOI
94. Liang G, Liang B, Chen A, et al. Development of rechargeable high-energy hybrid zinc-iodine aqueous batteries exploiting reversible chlorine-based redox reaction. *Nat Commun* 2023;14:1856. DOI PubMed PMC
95. Wang H, Chen S, Fu C, et al. Recent advances in conversion-type electrode materials for post lithium-ion batteries. *ACS Mater Lett* 2021;3:956-77. DOI
96. Kang J, Zhao Z, Li H, Meng Y, Hu B, Lu H. An overview of aqueous zinc-ion batteries based on conversion-type cathodes. *Energy Mater* 2022;2:200009. DOI
97. Kralik D, Jorne J. Hydrogen evolution and zinc nodular growth in the zinc chloride battery. *J Electrochem Soc* 1980;127:2335-40.



## DOI

98. Gao L, Li Z, Zou Y, et al. A high-performance aqueous zinc-bromine static battery. *iScience* 2020;23:101348. DOI PubMed PMC
99. Li Y, Liu L, Li H, Cheng F, Chen J. Rechargeable aqueous zinc-iodine batteries: pore confining mechanism and flexible device application. *Chem Commun* 2018;54:6792-5. DOI
100. Ma W, Liu T, Xu C, et al. A twelve-electron conversion iodine cathode enabled by interhalogen chemistry in aqueous solution. *Nat Commun* 2023;14:5508. DOI PubMed PMC
101. Darling RM, Gallagher KG, Kowalski JA, Ha S, Brushett FR. Pathways to low-cost electrochemical energy storage: a comparison of aqueous and nonaqueous flow batteries. *Energy Environ Sci* 2014;7:3459-77. DOI
102. Biswas S, Senju A, Mohr R, et al. Minimal architecture zinc-bromine battery for low cost electrochemical energy storage. *Energy Environ Sci* 2017;10:114-20. DOI
103. Zhu G, Tian X, Tai HC, et al. Rechargeable Na/Cl<sub>2</sub> and Li/Cl<sub>2</sub> batteries. *Nature* 2021;596:525-30. DOI
104. Yang C, Chen J, Ji X, et al. Aqueous Li-ion battery enabled by halogen conversion-intercalation chemistry in graphite. *Nature* 2019;569:245-50. DOI
105. Kim JT, Jorné J. The kinetics of a chlorine graphite electrode in the zinc-chlorine battery. *J Electrochem Soc* 1977;124:1473-7. DOI
106. Fan X, Huang K, Chen L, et al. High power- and energy-density supercapacitors through the chlorine respiration mechanism. *Angew Chem Int Ed* 2023;62:e202215342. DOI
107. Holleck GL. The reduction of chlorine on carbon in AlCl<sub>3</sub>-KCl-NaCl melts. *J Electrochem Soc* 1972;119:1158. DOI
108. Chen N, Wang W, Ma Y, et al. Aqueous zinc-chlorine battery modulated by a MnO<sub>2</sub> redox adsorbent. *Small Methods* 2023:e2201553. DOI
109. Lin D, Li Y. Recent advances of aqueous rechargeable zinc-iodine batteries: challenges, solutions, and prospects. *Adv Mater* 2022;34:e2108856. DOI
110. Eustace DJ. Bromine complexation in zinc-bromine circulating batteries. *J Electrochem Soc* 1980;127:528-32. DOI
111. Jameson A, Gyenge E. Halogens as positive electrode active species for flow batteries and regenerative fuel cells. *Electrochem Energy Rev* 2020;3:431-65. DOI
112. Pei Z, Zhu Z, Sun D, et al. Review of the I<sub>3</sub><sup>-</sup> redox chemistry in Zn-iodine redox flow batteries. *Mater Res Bull* 2021;141:111347. DOI
113. Miao L, Guo Z, Jiao L. Insights into the design of mildly acidic aqueous electrolytes for improved stability of Zn anode performance in zinc-ion batteries. *Energy Mater* 2023;3:300014. DOI
114. Yin Y, Yuan Z, Li X. Rechargeable aqueous zinc-bromine batteries: an overview and future perspectives. *Phys Chem Chem Phys* 2021;23:26070-84. DOI
115. Mahmood A, Zheng Z, Chen Y. Zinc-bromine batteries: challenges, prospective solutions, and future. *Adv Sci* 2024;11:e2305561. DOI PubMed PMC
116. Xiang HX, Tan AD, Piao JH, Fu ZY, Liang ZX. Efficient nitrogen-doped carbon for zinc-bromine flow battery. *Small* 2019;15:e1901848. DOI PubMed
117. Wang C, Li X, Xi X, Xu P, Lai Q, Zhang H. Relationship between activity and structure of carbon materials for Br<sub>2</sub>/Br<sup>-</sup> in zinc bromine flow batteries. *RSC Adv* 2016;6:40169-74. DOI
118. Suresh S, Ulaganathan M, Venkatesan N, Periasamy P, Ragupathy P. High performance zinc-bromine redox flow batteries: role of various carbon felts and cell configurations. *J Energy Storage* 2018;20:134-9. DOI
119. Suresh S, Ulaganathan M, Aswathy R, Ragupathy P. Enhancement of bromine reversibility using chemically modified electrodes and their applications in zinc bromine hybrid redox flow batteries. *ChemElectroChem* 2018;5:3411-8. DOI
120. Xu C, Lei C, Jiang P, et al. Practical high-energy aqueous zinc-bromine static batteries enabled by synergistic exclusion-complexation chemistry. *Joule* 2024;8:461-81. DOI
121. Park H, Bera RK, Ryoo R. Microporous 3D graphene-like carbon as iodine host for zinc-based battery-supercapacitor hybrid energy storage with ultrahigh energy and power densities. *Adv Energy Sustain Res* 2021;2:2100076. DOI
122. Liu T, Wang H, Lei C, et al. Recognition of the catalytic activities of graphitic N for zinc-iodine batteries. *Energy Storage Mater* 2022;53:544-51. DOI
123. Bai C, Cai F, Wang L, Guo S, Liu X, Yuan Z. A sustainable aqueous Zn-I<sub>2</sub> battery. *Nano Res* 2018;11:3548-54. DOI
124. Liu M, Chen Q, Cao X, Tan D, Ma J, Zhang J. Physicochemical confinement effect enables high-performing zinc-iodine batteries. *J Am Chem Soc* 2022;144:21683-91. DOI
125. Tan Y, Tao Z, Zhu Y, et al. Anchoring I<sub>3</sub><sup>-</sup> via charge-transfer interaction by a coordination supramolecular network cathode for a high-performance aqueous dual-ion battery. *ACS Appl Mater Interfaces* 2022;14:47716-24. DOI
126. Zeng X, Meng X, Jiang W, et al. Anchoring polyiodide to conductive polymers as cathode for high-performance aqueous zinc-iodine batteries. *ACS Sustain Chem Eng* 2020;8:14280-5. DOI
127. Chen M, Zhu W, Guo H, et al. Tightly confined iodine in surface-oxidized carbon matrix toward dual-mechanism zinc-iodine batteries. *Energy Storage Mater* 2023;59:102760. DOI
128. Yang H, Qiao Y, Chang Z, Deng H, He P, Zhou H. A metal-organic framework as a multifunctional ionic sieve membrane for long-life aqueous zinc-iodide batteries. *Adv Mater* 2020;32:e2004240. DOI
129. Shang W, Zhu J, Liu Y, et al. Establishing high-performance quasi-solid Zn/I<sub>2</sub> batteries with alginate-based hydrogel electrolytes. *ACS Appl Mater Interfaces* 2021;13:24756-64. DOI

130. Sonigara KK, Zhao J, Machhi HK, Cui G, Soni SS. Self-assembled solid-state gel catholyte combating iodide diffusion and self-discharge for a stable flexible aqueous Zn-I<sub>2</sub> Battery. *Adv Energy Mater* 2020;10:2001997. DOI
131. Chen G, Kang Y, Yang H, et al. Toward forty thousand-cycle aqueous zinc-iodine battery: simultaneously inhibiting polyiodides shuttle and stabilizing zinc anode through a suspension electrolyte. *Adv Funct Mater* 2023;33:2300656. DOI
132. Wang Z, Meng X, Chen K, Mitra S. Development of high-capacity periodate battery with three-dimensional-printed casing accommodating replaceable flexible electrodes. *ACS Appl Mater Interfaces* 2018;10:30257-64. DOI
133. Wang A, Gyenge EL. Borohydride electro-oxidation in a molten alkali hydroxide eutectic mixture and a novel borohydride-periodate battery. *J Power Sources* 2015;282:169-73. DOI
134. Wang Z, Meng X, Chen K, Mitra S. High capacity aqueous periodate batteries featuring a nine-electron transfer process. *Energy Storage Mater* 2019;19:206-11. DOI PubMed PMC
135. Shi Y, Chen Y, Shi L, et al. An overview and future perspectives of rechargeable zinc batteries. *Small* 2020;16:e2000730. DOI
136. Grignon E, Battaglia AM, Schon TB, Seferos DS. Aqueous zinc batteries: design principles toward organic cathodes for grid applications. *iScience* 2022;25:104204. DOI PubMed PMC
137. Yan Y, Li P, Wang Y, et al. Molecular engineering of N-heteroaromatic organic cathode for high-voltage and highly stable zinc batteries. *Adv Funct Mater* 2024;2312332. DOI
138. Chen W, Chen T, Fu J. Pivotal role of organic materials in aqueous zinc-based batteries: regulating cathode, anode, electrolyte, and separator. *Adv Funct Mater* 2024;34:2308015. DOI
139. Zhang X, Zhang L, Jia X, Song W, Liu Y. Design strategies for aqueous zinc metal batteries with high zinc utilization: from metal anodes to anode-free structures. *Nanomicro Lett* 2024;16:75. DOI PubMed PMC
140. Cui H, Ma L, Huang Z, Chen Z, Zhi C. Organic materials-based cathode for zinc ion battery. *SmartMat* 2022;3:565-81. DOI
141. Huang L, Li J, Wang J, et al. Organic compound as a cathode for aqueous zinc-ion batteries with improved electrochemical performance via multiple active centers. *ACS Appl Energy Mater* 2022;5:15780-7. DOI
142. Abdalla KK, Wang Y, Abdalla KK, et al. Rational design and prospects for advanced aqueous Zn-organic batteries enabled by multielectron redox reactions. *Sci China Mater* 2024;67:1367-78. DOI
143. Yang B, Ma Y, Bin D, Lu H, Xia Y. Ultralong-life cathode for aqueous zinc-organic batteries via pouring 9,10-phenanthraquinone into active carbon. *ACS Appl Mater Interfaces* 2021;13:58818-26. DOI
144. Yan L, Zhang Y, Ni Z, et al. Chemically self-charging aqueous zinc-organic battery. *J Am Chem Soc* 2021;143:15369-77. DOI
145. Li Z, Tan J, Wang Y, et al. Building better aqueous Zn-organic batteries. *Energy Environ Sci* 2023;16:2398-431. DOI
146. Wang Y, Li Q, Li Q, et al. Design strategies and challenges of next generation aqueous Zn-organic batteries. *Next Energy* 2023;1:100061. DOI
147. Li W, Xu H, Zhang H, et al. Tuning electron delocalization of hydrogen-bonded organic framework cathode for high-performance zinc-organic batteries. *Nat Commun* 2023;14:5235. DOI PubMed PMC
148. Lee M, Hong J, Lee B, et al. Multi-electron redox phenazine for ready-to-charge organic batteries. *Green Chem* 2017;19:2980-5. DOI
149. Lin Q, Li H, Chen L, He X. Naphthalenediimide-carbonylpyridiniums: stable six electron acceptors for organic cathodes. *Mater Chem Front* 2023;7:3747-53. DOI
150. Zhao Y, Zhang S, Zhang Y, et al. Vacancy-rich Al-doped MnO<sub>2</sub> cathodes break the trade-off between kinetics and stability for high-performance aqueous Zn-ion batteries. *Energy Environ Sci* 2024;17:1279-90. DOI
151. Zhong Y, Li Y, Meng J, et al. Boosting the cyclability of tetracyanoquinodimethane (TCNQ) as cathode material in aqueous battery with high valent cation. *Energy Storage Mater* 2021;43:492-8. DOI
152. Cheng M, Zheng S, Sun T, et al. A solubility limited pyrene-4,5,9,10-tetraone-based covalent organic framework for high-performance aqueous zinc-organic batteries. *Nano Res* 2024;17:5095-103. DOI
153. Zuo S, Xu X, Ji S, Wang Z, Liu Z, Liu J. Cathodes for aqueous Zn-ion batteries: materials, mechanisms, and kinetics. *Chemistry* 2021;27:830-60. DOI
154. Ji W, Du D, Liang J, et al. Aqueous Zn-organic batteries: electrochemistry and design strategies. *Battery Energy* 2023;2:20230020. DOI
155. Sun T, Yi Z, Zhang W, Nian Q, Fan HJ, Tao Z. Dynamic balance of partial charge for small organic compound in aqueous zinc-organic battery. *Adv Funct Mater* 2023;33:2306675. DOI
156. Gong Y, Wang B, Ren H, et al. Recent advances in structural optimization and surface modification on current collectors for high-performance zinc anode: principles, strategies, and challenges. *Nanomicro Lett* 2023;15:208. DOI PubMed PMC
157. Li J, Huang L, Lv H, et al. Novel organic cathode with conjugated N-heteroaromatic structures for high-performance aqueous zinc-ion batteries. *ACS Appl Mater Interfaces* 2022;14:38844-53. DOI
158. Wang Y, Wang C, Ni Z, et al. Binding zinc ions by carboxyl groups from adjacent molecules toward long-life aqueous zinc-organic batteries. *Adv Mater* 2020;32:e2000338. DOI
159. Lin Z, Shi HY, Lin L, Yang X, Wu W, Sun X. A high capacity small molecule quinone cathode for rechargeable aqueous zinc-organic batteries. *Nat Commun* 2021;12:4424. DOI PubMed PMC
160. Zheng S, Wang Q, Hou Y, Li L, Tao Z. Recent progress and strategies toward high performance zinc-organic batteries. *J Energy Chem* 2021;63:87-112. DOI
161. Chen Y, Fan K, Gao Y, Wang C. Challenges and perspectives of organic multivalent metal-ion batteries. *Adv Mater*

- 2022;34:e2200662. DOI
162. Peng H, Xiao J, Wu Z, et al. *N*-heterocycles extended  $\pi$ -conjugation enables ultrahigh capacity, long-lived, and fast-charging organic cathodes for aqueous zinc batteries. *CCS Chem* 2023;5:1789-801. DOI
  163. Zhang M, Ding C, Li C, et al. Bioactive small-molecule-based aqueous zinc-organic battery enables long-life and fast-charge performance. *Sci China Mater* 2023;66:3104-12. DOI
  164. Zhao Y, Huang Y, Wu F, Chen R, Li L. High-performance aqueous zinc batteries based on organic/organic cathodes integrating multiredox centers. *Adv Mater* 2021;33:e2106469. DOI
  165. Xu D, Zhang H, Cao Z, et al. High-rate aqueous zinc-ion batteries enabled by a polymer/graphene composite cathode involving reversible electrolyte anion doping/dedoping. *J Mater Chem A* 2021;9:10666-71. DOI
  166. Sun T, Fan HJ. Understanding cathode materials in aqueous zinc-organic batteries. *Curr Opin Electrochem* 2021;30:100799. DOI
  167. Song Z, Miao L, Duan H, et al. Anionic co-insertion charge storage in dinitrobenzene cathodes for high-performance aqueous zinc-organic batteries. *Angew Chem Int Ed* 2022;61:e202208821. DOI
  168. Shuai H, Liu R, Li W, et al. Recent advances of transition metal sulfides/selenides cathodes for aqueous zinc-ion batteries. *Adv Energy Mater* 2023;13:2202992. DOI
  169. Ye Z, Xie S, Cao Z, et al. High-rate aqueous zinc-organic battery achieved by lowering HOMO/LUMO of organic cathode. *Energy Storage Mater* 2021;37:378-86. DOI
  170. Chen X, Su H, Yang B, Yin G, Liu Q. Realizing high-rate aqueous zinc-ion batteries using organic cathode materials containing electron-withdrawing groups. *Sustain Energy Fuels* 2022;6:2523-31. DOI
  171. Chen Z, Cui H, Hou Y, et al. Anion chemistry enabled positive valence conversion to achieve a record high-voltage organic cathode for zinc batteries. *Chem* 2022;8:2204-16. DOI
  172. Bayaguud A, Luo X, Fu Y, Zhu C. Cationic surfactant-type electrolyte additive enables three-dimensional dendrite-free zinc anode for stable zinc-ion batteries. *ACS Energy Lett* 2020;5:3012-20. DOI
  173. Dai C, Hu L, Chen H, et al. Enabling fast-charging selenium-based aqueous batteries via conversion reaction with copper ions. *Nat Commun* 2022;13:1863. DOI PubMed PMC
  174. Cui F, Pan R, Su L, et al. Activating selenium cathode chemistry for aqueous zinc-ion batteries. *Adv Mater* 2023;35:e2306580. DOI
  175. Zhang Q, Ma Y, Lu Y, et al. Halogenated Zn<sup>2+</sup> solvation structure for reversible Zn metal batteries. *J Am Chem Soc* 2022;144:18435-43. DOI
  176. Lin Z, Lin L, Zhu J, Wu W, Yang X, Sun X. An anti-aromatic covalent organic framework cathode with dual-redox centers for rechargeable aqueous zinc batteries. *ACS Appl Mater Interfaces* 2022;14:38689-95. DOI
  177. Xiong P, Zhang Y, Zhang J, et al. Recent progress of artificial interfacial layers in aqueous Zn metal batteries. *EnergyChem* 2022;4:100076. DOI