Energy Materials

Review

Optimization strategies for high-performance aqueous zinc-sulfur batteries: challenges and future perspectives

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Abstract

Aqueous zinc-sulfur batteries (AZSBs) have emerged as promising candidates for high-energy density, cost-effective, and environmentally sustainable energy storage systems. Despite their potential, several challenges hinder the realization of high-performance AZSBs, including sluggish reaction kinetics, disproportionation reactions of ZnS in water, low conductivity and volume expansion of the sulfur cathode, poor wetting properties, and dendrite growth issues of the zinc anode. This review comprehensively summarizes optimization strategies for overcoming these challenges. We discuss cathode modification approaches, such as sulfur/carbon composites, sulfide composites, and catalytic sulfur matrices, which address low conductivity and volume expansion while enhancing sulfur conversion reaction kinetics. Additionally, electrolyte engineering strategies, including the use of iodide-based additives and co-solvent modifications, are examined for their effectiveness in improving reaction kinetics and wetting properties. Despite these advancements, AZSBs still face issues with long-cycle stability. Therefore, this review proposes future perspectives for the development of AZSBs. We aim to provide valuable insights into sulfur-based cathode materials and advance the achievement of high-performance AZSBs.

**Keywords:** Aqueous zinc-sulfur batteries, sulfur cathode, electrolyte additive, sulfur redox chemistry

INTRODUCTION

Energy stands as one of the most critical challenges humanity faces in the 21st century[1]. For sustainable development, the utilization of renewable natural energy is imperative. However, sources such as solar, wind, and hydrogen energy are spatially localized and temporally intermittent, posing challenges in consistently meeting energy demands. Among the various solutions, electrochemical systems have become among the most viable approaches for achieving efficient energy storage[2-4]. Primary batteries suffer from several drawbacks, including limited usage time, non-renewability, and environmental unfriendliness[5]. In contrast, rechargeable batteries offer greater operational flexibility and are a cornerstone technology for grid-scale energy storage applications[6]. At present, lithium-ion batteries (LIBs) lead the energy storage realm in light of their excellent energy density[7,8]. Yet, the extensive use of organic solvents and active lithium metal in LIBs introduces significant safety concerns, impeding their development[9]. Addressing the issues associated with LIBs and identifying a green, high-capacity, safe, and cost-effective battery energy storage system is crucial for future advancements in this field.

Recently, aqueous batteries have attracted growing interest because of their enhanced safety, affordability, and eco-friendliness, positioning them as strong contenders for sustainable development technologies[10]. The use of aqueous electrolytes reduces the flammability issues associated with organic electrolytes, thereby improving safety[11,12]. In the field of aqueous batteries, zinc has become the favored option for the anode electrode in aqueous zinc-ion batteries (AZIBs) for various reasons: (1) Zinc, the 24th most common element on Earth, making it economically feasible at around \$2 per kilogram with a crustal abundance of 75 ppm[13-15]; (2) Compared to other commonly used metals in batteries, such as cadmium, magnesium, and lithium, zinc is harmless and reliable. Additionally, its redox potential of -0.763 V [*vs.* Standard Hydrogen Electrode (SHE)] makes it suitable for use with aqueous electrolytes[16,17]; and (3) Zinc is non-toxic and environmentally friendly, producing minimal pollution during recycling[18]. This characteristic has spurred extensive research into AZIBs[19].

In 2012, Xu *et al.* discovered that MnO_2 could serve as a cathode for the reversible insertion/extraction of Zn^{2+}[20]. This pivotal finding spurred extensive research into cathode materials for AZIBs. Over the years, various materials have been explored as cathodes for AZIBs, comprising vanadium-based oxides[21-23], manganese-based oxides[24-26], Prussian blue analogs (PBAs)[27,28], iodine-containing compounds[29-32], and organic compounds[33-35]. Each of these materials presents distinct advantages and challenges, as summarized in Figure 1A. The radar chart illustrates the key characteristics of different types of cathode materials, highlighting their respective strengths and limitations[36]. For instance, vanadium-based oxides offer high discharge capacity but suffer from low operating voltage; Mn-based oxides are prone to capacity loss due to Mn^{2+} dissolution; PBAs deliver high output voltage (exceeding 1.7 V) but exhibit low capacity; iodine electrodes face severe shuttle effects and poor Zn reversibility; and organic electrodes, while environmentally friendly, typically provide low capacity[35,37]. Among these cathode materials, sulfur-based materials may have certain limitations in terms of cycle life and operating voltage; however, they exhibit a significantly higher areal capacity, underscoring their potential for practical applications in high-energy-density battery systems. Researchers share a common goal of developing cathode materials that offer high capacity, high energy density, affordability, safety, and environmental sustainability.

Sulfur has been widely applied in lithium-sulfur batteries (LSBs) due to its involvement in multi-electron transfer processes, giving rise to a theoretical specific capacity proximate to 1,675 mA h g^{-1}[38-41]. Consequently, sulfur has also sparked the interest of researchers studying aqueous batteries. In 2020, Zhao *et al.* were the first to apply sulfur as a cathode in AZIBs, demonstrating remarkable performance[42].
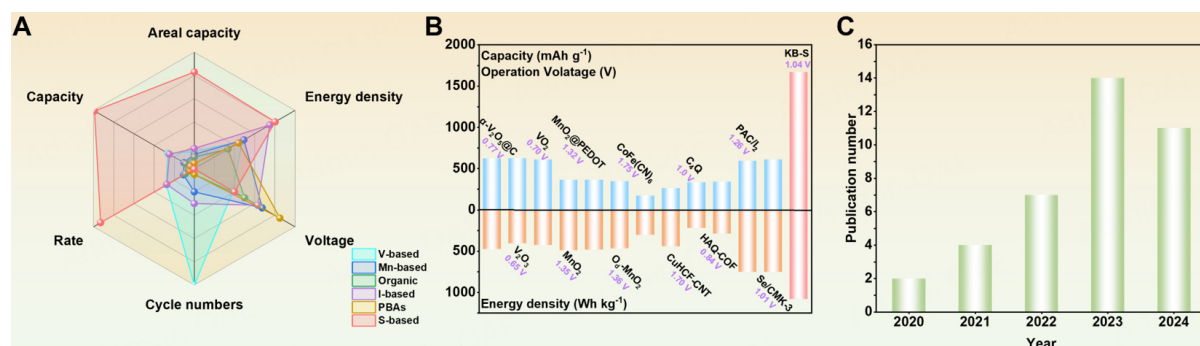
Figure 1. (A) Radar graph of various types of cathode materials for AZIBs. (B) Performance evaluation among various kinds of cathode materials. (C) Number of publications on AZSBs over the past five years.

Compared to other cathode materials, sulfur-based cathode materials offer excellent performance, particularly in achieving higher capacity and energy density [Figure 1B]. As a result, aqueous zinc-sulfur batteries (AZSBs) have captured considerable concentration, with researchers considering them a promising avenue for overcoming energy storage challenges. Consequently, a series of studies have focused on addressing the issues inherent in AZSBs[43,44]. We have also summarized the number of publications on AZSBs in recent years [Figure 1C], revealing a clear upward trend in research activity in this field. Compared to other aqueous battery technologies, such as zinc-air batteries and redox flow batteries[45], AZSBs demonstrate superior energy density due to high theoretical capacity of sulfur, while still offering the safety and environmental benefits of aqueous systems[46].

A typical AZSB device configuration is shown in Figure 2A. The battery assembly includes a sulfur-based cathode, a zinc foil anode, a separator, and an aqueous electrolyte[47]. Figure 2B has shown a standard Galvanostatic charge-discharge (GCD) curve of AZSBs; the working mechanism can be summarized as follows: during discharge, sulfur (S_8) gains electrons and is converted to zinc sulfide (ZnS), and during charging, ZnS loses electrons and reverts to S_8[43,48-50]. Overall, in contrast to the multi-step reactions and multi-electron transfers in LSBs, AZSBs involve a single-step solid-solid conversion[41,49]. However, as marked in the GCD curves in Figure 2B, the electrochemical process of AZSBs faces several challenges including:

i. The primary issue with AZSBs is their sluggish reaction kinetics, which arises from the solid-solid conversion mechanism[51]. As observed from the charge-discharge curve [Figure 2B], the discharge voltage is typically below 0.4 V, and the oxidation of ZnS during charging is accompanied by a high energy barrier[43,52,53]. This results in high overpotential and significant polarization, ultimately leading to poor rate performance and low energy utilization efficiency.

ii. During charging, ZnS undergoes a disproportionation reaction in water, forming SO_4^{2-}, leading to capacity deterioration, depletion of active material, and reduced Coulombic efficiency[5,36,49,54].

iii. Similar to issues observed in LSBs, the volume expansion of the sulfur cathode leads to mechanical damage of the electrode, further worsening cycle stability. Due to the inherently inferior conductivity of sulfur (5×10^{-28}-10^{-30} S cm^{-1}) and ZnS (10^{-12}-10^{-14} S cm^{-1}), AZSBs typically exhibit slow redox reaction kinetics and poor cycle stability, hindering practical applications[43,49].
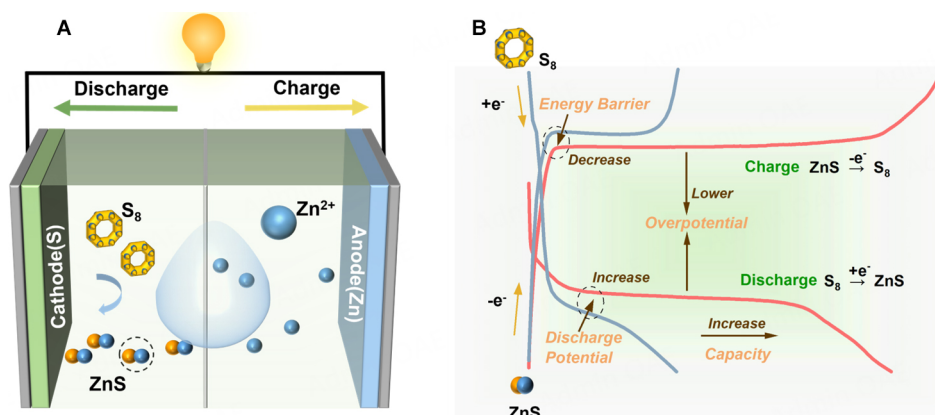
Figure 2. (A) Schematic diagram of the working system of AZSBs. (B) Typical schematic diagram of GCD.

iv. The inadequate wetting of the sulfur electrode by the aqueous medium impedes the transfer of Zn^{2+} within the cathode, triggering significant polarization[50,55].

v. Furthermore, the gradual growth of Zn dendrites accelerates Zn corrosion and can even lead to zinc degradation, causing inferior Coulombic efficiency and truncated cycle life. Due to the standard electrode potential of the Zn/Zn^{2+} electrode being -0.76 V relative to SHE, it allows for the stripping and plating of Zn metal in aqueous electrolytes while keeping the hydrogen evolution reaction at a minimal level[56-58].

Based on the above discussion, sulfur-based cathode materials show great potential for achieving high-capacity and excellent energy density AZSBs. However, the sluggish electrochemical processes, along with other challenges, have hindered the realization of high-performance AZSBs. So far, a few articles have reported on the current progress in research on AZSBs. Feng *et al.* discussed the cathode materials, reaction mechanisms, and electrochemical performance improvements of AZSBs, focusing on challenges such as zinc dendrite growth and active material decomposition[59]. Recent reviews by other researchers have also explored various aspects of AZSBs, including electrolyte modification and cathode design strategies[47,59]. These reviews have provided valuable insights into the challenges and optimization strategies for AZSBs. However, there is a lack of a dedicated review that comprehensively summarizes and discusses both the fundamental mechanisms and the practical challenges of AZSBs, including issues related to cathode modification, electrolyte engineering, and large-scale pouch cell applications. We provide a comprehensive summary of optimization strategies for AZSBs, highlighting the current challenges and offering detailed insights into the pressing issues that require resolution. In this review, as shown in Figure 3, we begin with the cathode modification process, introducing three types of sulfur confinement strategies: sulfur@carbon composites, sulfide composites, and catalytic sulfur matrices. Following this, we summarize the latest developments in electrolyte engineering, including effective additives, co-solvent modifications, and eutectic electrolytes. Additionally, we highlight innovations in battery configuration, particularly decoupled batteries, and explore attempts to fabricate flexible and stretchable batteries. Finally, we discuss how these strategies address existing challenges and offer rational future perspectives. As research on AZSBs is still in its early stages, studies on the anode are limited, and the number of related research articles is insufficient. Therefore, our review primarily focuses on the optimization of the cathode and electrolyte. We hope this review provides a valuable overview of sulfur-based cathode materials and advances the achievement of high-performance AZSBs.
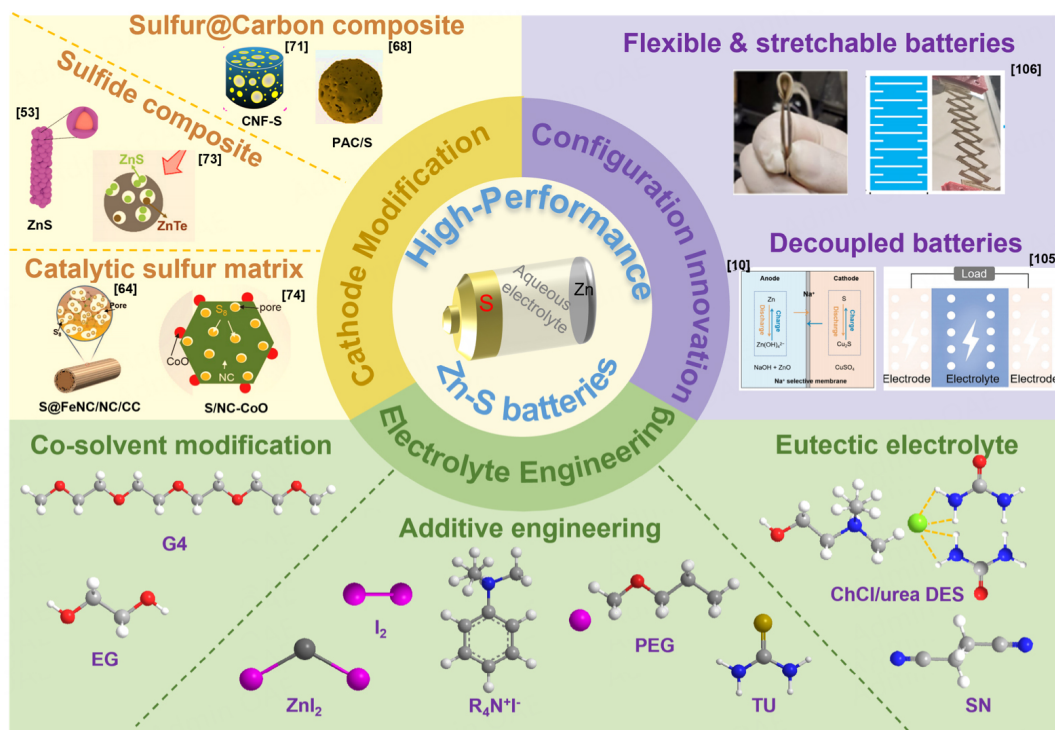
Figure 3. Overview of research strategies for high-performance AZSBs.

STRATEGIES FOR IMPROVEMENT

In the development of AZSBs, researchers have implemented various strategies to gradually enhance their performance. Firstly, in the optimization of the sulfur cathode, varieties of sulfur-based composites, such as sulfur@carbon composites and sulfide composites, have been developed to strengthen its conductivity and cycling durability. Meanwhile, the introduction of catalytic sulfur matrices has effectively enhanced reaction kinetics, accelerating the sulfur conversion reactions. In terms of electrolyte modification, researchers have successfully inhibited the dissolution and migration of polysulfides by introducing specific electrolyte additives, co-solvent systems, and eutectic solvents, thereby significantly improving the coulombic efficiency and cycle life of batteries. Additionally, many attempts have been undertaken for device innovation; the development of stretchable flexible zinc-sulfur batteries has opened up new applications in portable and wearable devices, while the design of decoupled batteries has further optimized the stability of the battery and energy density. In summary, these multifaceted progress strategies have established a firm basis for the development of AZSBs and provided strong support for their practical application. Thus, in Table 1, we systematically summarize the key advancements and findings from various studies, aiming to visually present the research trends and technological breakthroughs in different areas of AZSBs.

Cathode modification

Cathode materials within aqueous AZSBs are pivotal in defining the system's performance and efficiency. Researchers have concentrated on numerous strategies for modifying cathodes. Incorporating conductive carbon materials can significantly optimize the electronic conductivity of sulfur cathodes[36,43,62]. Moreover, nanostructuring sulfur or forming sulfur-carbon composites can effectively address challenges related to poor conductivity and mechanical instability. Then, incorporating catalytic sulfur matrices into the sulfur can significantly accelerate the redox reactions, further boosting the overall electrochemical performance of the sulfur cathodes. Overall, the development of effective sulfur cathodes for AZSBs involves a delicate

Table 1. comparison of electrochemical performance of different research

Cathode material	Loading (mg/cm^2)	Electrolyte	Voltage windows (V)	Additive	Max capacity (mAh g^{-1}@A g^{-1})	Retention (% of no. cycle)	Energy density (Wh kg$^{-1}_{cathode}$)	Ref
PLSD	4.0	1 M Zn(TFSI)$_2$	0.1-2.3	/	1,146/0.3	53.7/700 at 1 A g^{-1}	724.7	[42]
S@CNTs-50 (S@CNTs-50:AB:PTFE = 8:1:1)	3-5	1 M Zn(OAc)$_2$	0.05-1.6	0.05 wt% I$_2$	1,105/0.1	65.9/225 at 2 A g^{-1}	502	[43]
SeS$_2$@PCS (SeS$_2$@PCS:CB:PTFE = 8:1:1)	1.8-3.0	1 MZnSO$_4$	0.1-1.3	0.1 wt%	1,107/0.1	85/1,000 at 5 A g^{-1}	772	[60]
KB-S (KB-S:KB:Sodium alginate = 7:2:1)	3.9-8.3	1 M ZnCl$_2$	0.1-1.5	/	1,668/0.01	80.1	1,083.3	[5]
S@C (S@C:KB:PVDF) = 8:1:1	1.0-1.5	DES	0-2.4	AN	846/0.5	94.58 after 72 h	259	[61]
S@Fe-PANi (S@Fe-PANi:nanotube:PTFE = 8.5:1:0.5)	1.8	2 M ZnSO$_4$	0.1-1.6	/	1,205/0.2	54/200 at 0.5 A g^{-1}	720	[52]
S@CNTs-50 (S@CNTs-50:super P:PVDF = 8:1:1)	1.5-2.5	1 M Zn(OAc)$_2$	0.05-1.6	PEG-400	1,116/0.1	81.7/300 at 1 A g^{-1}	/	[62]
ZnS@CF (ZnS@CF:KB:PTFE = 8:1:1)	1.5-3	3 M ZnSO$_4$	0.1-1.4	1 wt% TUI	465/0.1	65.5/300 at 2 A g^{-1}	274	[53]
CMK-3@S (CMK-3@S:AB:PVDF = 8:1:1)	1-2	3 M Zn(OTF)$_2$	0.05-1.75	0.1 wt% I$_2$	1,174/0.2	90/200 at 1 A g^{-1}	/	[63]
HCS/S-53.7 (HCS/S-53.7:CB:guar gum = 7:1.5:1.5)	1.2-1.6	Zn(OTF)$_2$	0.05-1.6	0.15 wt% I$_2$ and 40% G4	1,140/0.5	70/600 at 4 Ag^{-1}	/	[49]
S@KB (S@KB:KB:PTFE = 8:1:1)	1	2 M ZnSO$_4$	0.2-1.7	TU	1,785.1/1	67.0/300 at 5 A g^{-1}	803.3	[36]
FeNC/NC/CC	2.0-2.6	2 M ZnSO$_4$	0.1-1.6	/	1,143/0.2	57.7/300 at 0.5 A g^{-1}	/	[64]
S@NPC (S@NPC:super-P:PTFE = 8:1:1)	3	2 M Zn(OTF)$_2$	0.05-1.6	50 mM ZnI$_2$	1,435/0.1	70/250 at 3 A g^{-1}	730	[65]
HMCs-n@S (HMCs-n@S:CB:PVDF = 8:1:1)	1-2	3 M Zn (OTF)$_2$	0.1-1.6	/	768/0.1	90.2/100 at 1 A g^{-1}	307	[66]
S@Ti$_3$C$_2$T$_x$ (S@Ti$_3$C$_2$T$_x$:CB:PVDF = 8:1:1)	0.8-5.0	1 M Zn(OAc)$_2$	0.1-1.6	30% P123 0.2 wt% I$_2$	772.7/0.3	92.8/300 at 0.5 A g^{-1}	363.16	[54]
S/C (S/C:KB:CMC = 8:1:1)	2	0.1 M Zn(OAc)$_2$	0.1-1.7	/	700/0.25	90/800 at 3 A g^{-1}	2,543	[67]
PAC/S-60.33% (PAC/S-60.33%:Super P:Guar gum = 7:1.5:1.5)	1.4-1.8	2 M Zn(OTF)$_2$	0.1-1.6	0.15 wt% I$_2$	633.5/0.5	68.6/400 at 5 A g^{-1}	297.5	[68]
S/KB (S/KB:sodium alginate = 9:1)	3	1 M Zn(OAc)$_2$	0.2-1.5	0.25 M Me$_3$PhN$^+$I$^-$	1,659/0.1	71.1/50 at 3 A g^{-1}	349	[69]
AJPC/S (AJPC/S:AB:PVDF = 8:1:1)	1-2	1 M Zn(OTF)$_2$	0.05-1.6	0.05 wt% I$_2$	1,167/0.2	47.6/200 at 1 A g^{-1}	502	[70]

CNF-S	3-7	$Zn(OAc)_2$	0.1-1.4	0.1 wt% I_2	667/0.5	39.7/300 at 1 A g^{-1}	283	[71]
S@KB-MI	2-26.6	0.5 M $CuSO_4$; 3 M NaOH + 0.3 M ZnO	0-0.4	/	3,150/1	62/300 at 2 A g^{-1}	3,988	[10]
KB/S (KB/S:guar gum:Super P = 8:1:1)	1.4-1.6	3 M $ZnSO_4$	0.15-1.4	0.05 M ZnI_2	1,580/0.5	100,0/550 at 5 A g^{-1}	742	[72]
Te_1S_7/C (Te_1S_7/C:Super P:PTFE = 7:2:1)	1-6	1 M ZnSO4	0.1-1.7	/	1,335/0.1	/	934.6	[73]
S/CoO-NC (S/CoO-NC:CN:PTFE = 8:1:1)	2	2 M $ZnSO_4$	0.1-1.8	/	1,172/0.2	71.6/500 at 0.5 A g^{-1}	585	[74]
S@MMPC-Co (S@MMPC-Co:Super P:CMC = 7:1.5:1.5)	1-1.2	2 M $Zn(OTF)_2$	0.05-1.6	0.15 wt% I_2	1,245/1	110.0/500 at 4 A g^{-1}	/	[75]
S@VC (S@VC:PVDF = 9:1)	/	1 M $Zn(OAc)_2$	0-1.7	10% EG 0.05 wt% I_2	1,210/0.075	91/250 at 1 C	605	[76]
$ZnS_{1-x}Se_x$	2.5	2 M $ZnSO_4$	0.2-1.7	50 mM ZnI	1,518.6/0.1	52/200 at 2 A g^{-1}		[77]
S/CSs (S/CSs:AB:PVDF = 8:1:1)	2	8 M $Zn(ClO_4)_2$	0.05-2.1	/	1,284/0.1	85.7/500 at 2 A g^{-1}	527	[44]
ZnS:KB:PTFE = 7:2:1 KB:S:PTFE = 8:1:1	2.5/2.5	2 M $ZnSO_4$ + ZnI	0.2-1.4	U/TU/AA/TAA	1,478/0.1	53.3/300 at 2 A g^{-1}	/	[78]

AB: Acetylene black; PTFE: polytetrafluoroethylene binder; PVDF: polyvinylidene fluoride; KB: ketjen black; TUI: iodinated thiourea; G4: tetraglyme; TU: thiourea; CB: carbon black; EG: ethylene glycol; U: urea; AA: acetamide; TAA: thioacetamide; CMC: carboxymethyl cellulose; AN: acetonitrile.

balance of material engineering, structural design, and electrolyte optimization to tackle the inherent challenges and fully exploit the potential of this promising energy storage technology[79].

Sulfur@Carbon composite

During battery operation, owing to the low conductivity of its material and the discharge product ZnS, the cathode endures significant internal resistance and polarization. To address this issue, enhancing the conductivity of sulfur cathode through electrode modification is essential[80]. One widely adopted strategy involves using conductive carbon as a substrate material for S_8, effectively encapsulating sulfur within various carbon structures to render it electrochemical activity[81]. However, the effectiveness of this approach varies depending on the type of carbon material used, as different carbon materials can enhance the performance of AZSBs to varying extents. Recent studies have shown that functional carbon hosts can significantly enhance the discharge capacity and conductivity of these cathodes[43,49]. Carbon nanotubes (CNTs), by providing high conductivity, large surface area, and structural support, significantly enhanced the electrochemical performance, stability, and overall energy density of the sulfur cathode. Li *et al.* developed economical AZSBs that achieved ultrahigh energy density by using sulfur supported on carbon nanotubes (S@CNTs-50) as the cathode[43]. Subsequent studies reported an enhancement in sulfur cathode conductivity by infiltrating elemental sulfur into Ketjen Black[5]. Then, $Ti_3C_2T_x$ MXene was used to modify sulfur, forming the composite $S@Ti_3C_2T_x$. As a conductive confinement material, MXene improves the electrochemical performance of the cathode by enhancing sulfur utilization,

accelerating redox reactions, and promoting ion diffusion[54].

The above research indicates that the addition of conductive carbon materials is beneficial, leading to the exploration of more diverse carbon materials to further enhance performance. Wang *et al.* reported a cathode material that was prepared by encapsulating sulfur powder within a three-dimensional amorphous carbon structure derived from coal tar pitch[68], followed by heat treatment and activation using K_2CO_3 [Figure 4A]. An expanded specific surface area enhances sulfur loading and electrolyte accessibility in the cathode, thereby improving its electrochemical performance. The sulfur content in the cathode ranged from 60.33% to 76.40%, with sulfur uniformly distributed within the micropores of the carbon matrix. The use of K_2CO_3 as an activating agent created a suitable microporous structure in the carbon host, promoting efficient electrolyte interaction. However, the overall performance was not ideal, with the capacity remaining below 300 mAh g^{-1} [Figure 4B].

Improving the cathode fabrication technique to enhance performance is also a viable strategy. Amiri *et al.* employed an electrostatic spray coating to uniformly deposit S_8 onto the highly porous carbon nanofibers[71], effectively filling micro- and mesopores, achieving a sulfur loading of up to 60 wt% while maintaining the structural integrity and conductivity of fibers [Figure 4C]. They investigated the coupling effects between electrochemical energy storage and mechanical performance. Their findings demonstrated that these AZSBs exhibit excellent stability under multiple mechanical and electrochemical cycles [Figure 4D], combining high energy density with superior mechanical properties, making an intriguing attempt in the realm of structural energy storage.

The porous carbon matrix can overcome the electrical insulation, buffer the mechanical damage during the cycle, and boost the battery performance. Therefore, most of the cathodic electrode materials in AZSBs will add conductive carbon additives, such as Ketjen black, acetylene black[5,36], carbon fibers (CFs)[71], CNTs[43], and graphene[82-84]. However, most of the raw materials come from non-renewable fossil fuels, which limits the sustainable development of sulfur-based cathodes to a certain extent, and brings environmental and resource problems[85,86]. Sustainability has always been a central theme in development, and in recent years, biomass-derived carbon has gradually become a research hotspot. Inspired by the seaweed Enteromorpha, Liu *et al.* were the first to use Enteromorpha as a precursor to synthesize nitrogen-doped carbon material with a superior specific surface area and rich micro-porous structure, addressing the challenges of conductivity and volume expansion in sulfur-based cathode materials[66]. Patel *et al.* utilized low-cost jackfruit peel to prepare porous carbon material for sulfur loading, which enhanced the electrode's conductivity and reaction kinetics, sign-ificantly enhancing the battery's capacity and cycling durability[70]. The use of renewable biomass resources to produce battery cathode materials not only reduces costs but also minimizes environmental impact, aligning with the trend of sustainable development.

Benefiting from this, Zhao *et al.* utilized mangosteen peel as a precursor to synthesize single-atom cobalt-doped porous carbon material (MMPC-Co) through a multistep heat treatment process, and used it as cathode material in AZSBs [Figure 4E][75]. The abundant pore structure of MMPC-Co not only limits sulfur decline but expedites zinc ion transport, while its large pore volume helps diminish the stress effect resulting from ZnS volume expansion at the time of charge and discharge cycles, hence keeping the stability of the electrode structure. The introduction of single-atom cobalt into the carbon material significantly enhances the interfacial charge transfer rate of the sulfur electrode, promotes the rapid kinetics of the sulfur reduction reaction, enables fast solid-solid conversion from sulfur to ZnS, and reduces the overpotential [Figure 4F][75]. This was a successful attempt, providing a novel approach for future exploration of carbon-based functional hosts.
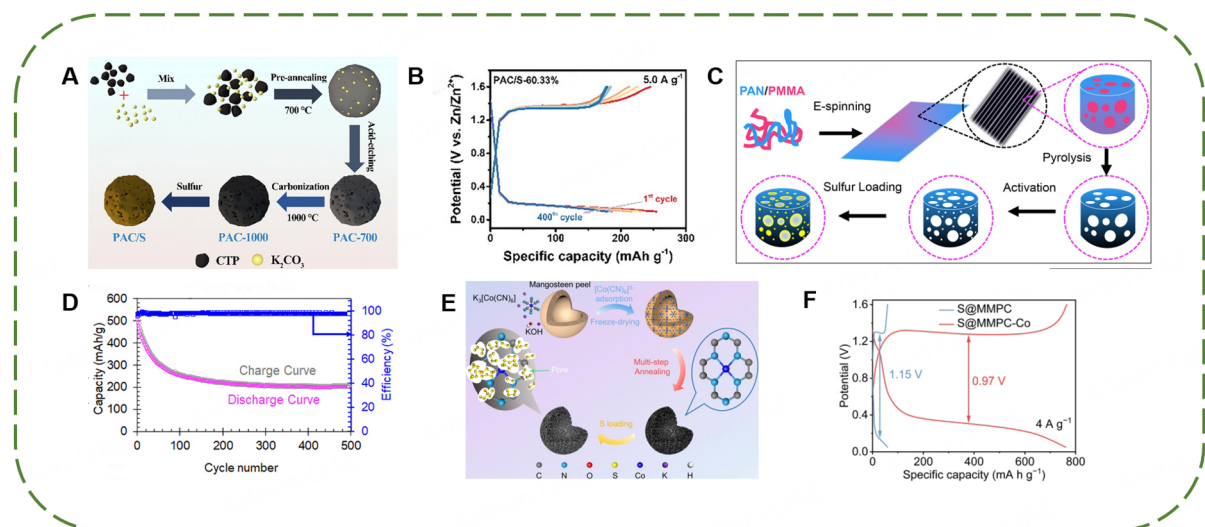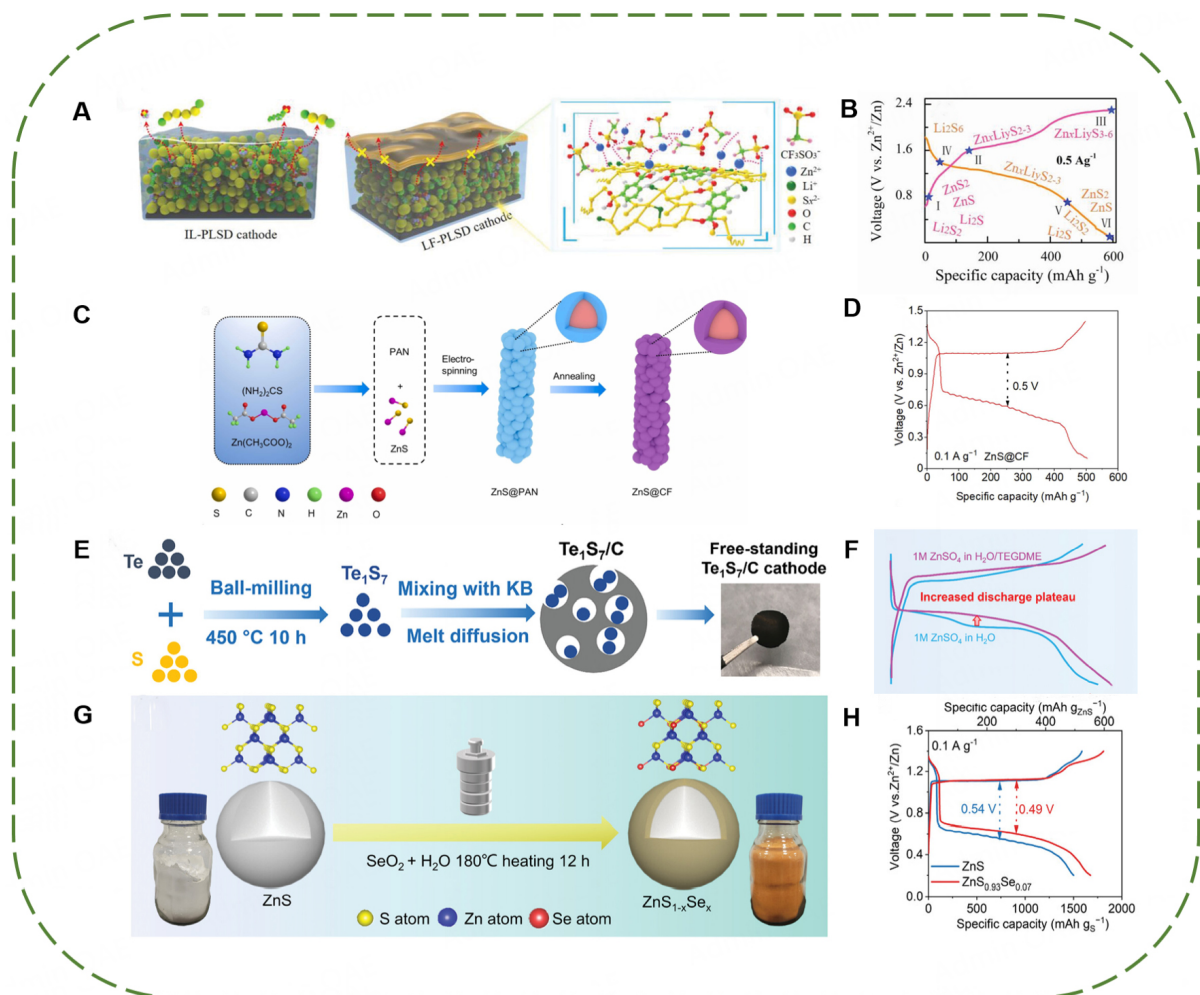
Figure 4. (A) Experimental preparation process and (B) GCD curves of PAC@S. (A and B) were cited with permission from Wang *et al.*[68] Reproduction rights 2023, Springer Nature. (C) Experimental preparation process of CNF-S cathode. (D) The GCD curves of the AZSBs at 1 A g⁻¹.(C and D) were cited with permission from Amiri *et al.*[71] Reproduction rights 2022, American Chemical Society. (E) Schematic representation of the preparation procedure of S@MMPC-Co. (F) The GCD graphs of S@MMPC as well as S@MMPC-Co. (E and F) were cited with permission from Zhao *et al.*[75] Reproduction rights 2024, Elsevier.

Compared to traditional carbon materials, biomass resources are abundant and widely available, including agricultural waste, wood residues, and by-products from food processing. These materials can be converted into high-performance carbon materials through simple pyrolysis or chemical activation processes, significantly reducing production costs. However, despite the lower production costs, ensuring consistency and controllability in large-scale production remains a critical challenge. Additionally, the diversity of biomass feedstocks may lead to fluctuations in material performance, posing challenges for standardization and industrial applications[87]. In summary, although biomass-derived carbon materials have clear advantages in terms of cost and environmental impact, achieving large-scale application will require further research into optimizing material performance, ensuring process stability, and validating applications.

Sulfide composite

The challenge of slow reaction kinetics in sulfur cathodes, which leads to rapid capacity decay and significant volume expansion (~53 vol%) during the charge-discharge process, has been addressed through innovative strategies[88,89]. The combination or doping of chalcogenide elements will be an efficacious strategy to solve the slow kinetics of AZSBs and improve the capacity and stability of batteries. Zhao *et al.* reported the first reversible AZSBs by introducing ionic liquids into a polymer framework[42], achieving stable cycling and addressing the polysulfide shuttle effect common in traditional LSBs [Figure 5A]. A "liquid film" structure was designed, encapsulating the ionic liquid within a polymer network, which not only provided Zn^{2+} transport channels but also enhanced the structural stability of the polysulfide cathode. This innovation led to exceptional electrochemical performance and long cycle life during charge and discharge processes. As displayed in Figure 5B, the sulfur cathode undergoes multi-electron conversion, forming polysulfides and releasing high capacity, indicating that sulfur compounds were a promising choice for enhancing cathode performance[42].

Organic sulfides as cathodes present a range of challenges, prompting researchers to shift their focus to inorganic sulfides, particularly chalcogenides, to enhance battery performance. Consequently, Li *et al.* used phosphorus-doped carbon sheets (PCS) as a substrate material, combining them with SeS_2 to construct a

Figure 5. (A) Schematic diagram of the function of the IL and LF-PLSD cathode. (B) The GCD plots of PLSD. (A and B) were cited with permission from Zhao *et al.*[42] Reproduction rights 2020, Wiley. (C) Experimental preparation process of ZnS@CF cathode. (D) The GCD plots of ZnS@CF. (C and D) were cited with permission from Liu *et al.*[53] Reproduction rights 2022, Elsevier. (E) Preparation scheme of Te_1S_7/C cathodes. (F) The working mechanism in Zn-Te_1S_7 batteries. (E and F) were cited with permission from Zhang *et al.*[73] Reproduction rights 2024, Wiley. (G) Experimental preparation process of $ZnS_{1-x}Se_x$ cathode. (H) The GCD profiles of batteries with ZnS and $ZnS_{0.93}Se_{0.07}$. (G and H) were cited with permission from Ren *et al.*[77] Reproduction rights 2024, Wiley.

high-performance aqueous Zn-SeS_2 battery cathode[60]. The study revealed the reversible conversion mechanism of SeS_2 during charge and discharge processes, where SeS_2 was successfully converted to ZnSe and ZnS, and regenerated as SeS_2 during charging, demonstrating brilliant cycling stability and outstanding energy efficiency. To further validate the optimization effect of sulfides, Liu *et al.* synthesized nanoscale ZnS particles and encapsulated them within CFs to form a ZnS@CF composite structure [Figure 5C][53]. The nanoscale ZnS particles notably enhance the contact area with the electrolyte and shorten the diffusion paths for ions and electrons, thereby enhancing the electrochemical reaction kinetics. The CFs not only provide efficient electron transport channels but also serve as a mechanical framework, enhancing the structural durability of the electrode and preventing damage resulting from the volumetric changes of ZnS during charge and discharge cycles. The ZnS@CF electrode exhibits lower overpotential and voltage hysteresis, substantially extending the cycle life and rate performance of batteries [Figure 5D].

Through the introduction of highly conductive dopant elements, the overall conductivity of the material can be significantly enhanced, improving the transport efficiency of charges and ions. Dopant elements can also provide additional active sites or alter surface properties, thereby accelerating reaction kinetics and improving catalytic efficiency or electrochemical performance. With the appropriate choice of dopant, the physical, chemical, or mechanical properties of the material can be precisely tailored to meet specific application needs[90].

Leveraging these advantages, Zhang *et al.* doped tellurium (Te) into the sulfur cathode[73], demonstrating for the first time the dual function of Te in Zn-S batteries: not only did it accelerate the S and ZnS electrochemical conversion, but it also increased the total discharge capacity through the formation of ZnTe [Figure 5E]. The cathode was designed using polytetrafluoroethylene (PTFE) as a binder, combined with a carbon matrix to create a self-supporting electrode without the need for traditional adhesives. This design not only simplified the electrode fabrication process but also allowed for higher active material loading, enhancing general performance of the battery. Consequently, the Te_1S_7/C electrode exhibited better structural stability and lower polarization during charge and discharge cycles, ensuring long cycle life and excellent rate performance [Figure 5F][73].

To address the inherent issues of large volume expansion and poor conductivity in sulfur-based cathodes, which hinder their practical application, Ren *et al.* enhanced the reaction kinetics and stability through selenium (Se) doping[77]. Se-doped ZnS ($ZnS_{1-x}Se_x$) was synthesized using a one-step hydrothermal method [Figure 5G]. Various doping ratios of Se were explored to optimize performance. Se doping reduced the band gap of ZnS from 1.86 to 1.40 eV, significantly enhancing its intrinsic conductivity. Notably, the $ZnS_{0.93}Se_{0.07}$ cathode presented a higher reversible capacity of 1,656 mAh g_S^{-1} and a lower polarization of 0.49 V compared to ZnS at 0.1 A g^{-1} (1,500 mAh g_S^{-1}, 0.54 V), owing to its increased reaction kinetics [Figure 5H].

Sulfides as cathode materials for AZSBs have displayed significant promise in enhancing battery performance. Their unique chemical properties can effectively promote sulfur conversion reactions and improve the electrochemical reaction kinetics of the battery. Additionally, sulfides possess good conductivity and stability, helping to overcome the poor conductivity and short cycle life caused by polysulfide dissolution in traditional sulfur-based cathode materials. Through rational design and optimization of sulfide structures, the energy density and cycle stability of AZSBs can be further enhanced. However, in the current application of sulfides, most of the reported capacities are calculated based on the active material sulfur, with actual capacities still below 600 mAh g^{-1}, which is an issue that needs attention. Furthermore, challenges such as performance degradation at high rates and long-term stability must still be addressed. Overall, sulfides as cathode materials for zinc-sulfur batteries hold great promise for future development and lay a crucial cornerstone for the practical employment of zinc-sulfur batteries.

Catalytic sulfur matrix
The excellent porosity and conductivity of carbon hosts markedly elevate the electronic conductivity of the composite sulfur cathode and accommodate volumetric changes during the (de)zincification process. However, the non-polar characteristics of carbon materials were insufficient to regulate sulfur redox kinetics[64]. Therefore, the use of composites such as metal oxides[91], redox mediators[52], and metal sulfides[92] became an effective strategy to accelerate sulfur conversion reaction kinetics. Catalysts can lower activation energy, improve reaction efficiency, and be reused, making them highly promising for accelerating the redox kinetics of sulfur[93]. However, currently reported catalytic substrates often catalyze only one half-reaction, ultimately leading to the accumulation of by-products and reduced battery efficiency. Therefore,

developing a bifunctional electrocatalytic cathode with multiple catalytic centers to facilitate complete sulfur redox reactions and reduce the reoxidation barrier of ZnS is a promising area to explore.

Zhang *et al.* were the first to introduce $Fe(CN)_6^{4-}$-doped polyaniline (Fe-PANi) as a catalyst in AZSBs, effectively promoting sulfur reduction kinetics, significantly reducing voltage hysteresis, and enhancing the capacity and cycle life of batteries[52]. The previously designed material utilized a single matrix, but to further improve the catalytic mechanism, Wang *et al.* developed a bifunctional electrocatalytic cathode that simultaneously hastens sulfur reduction and ZnS oxidation [Figure 6A][74]. This innovation effectively addresses the issues of lacking sulfur reduction and high ZnS reoxidation energy barriers in traditional Zn-S batteries. The cathode material is synthesized by carbonizing ZIF-8 to form N-doped carbon, absorbing cobalt ions, activating to form CoO-decorated carbon, and encapsulating sulfur via a melting-diffusion method [Figure 6B][74]. Compared to the control cathodes (S/C and S/NC), the S/NC-CoO cathode exhibits higher discharge capacity, lower polarization, and better sulfur utilization, as shown in Figure 6C. This also confirms the feasibility of bifunctional catalysts.

Besides cobalt, iron is also a common catalytic element. Zhang *et al.* utilized single-atom catalytic centers with Fe-N_4 coordination structures[64], which both effectively promoted the reduction of sulfur and significantly reduced the reoxidation barrier of ZnS [Figure 6D]. This resulted in lower voltage hysteresis and higher reversible capacity during battery charge and discharge cycles. The atomically dispersed iron sites enabled complete sulfur conversion, achieving high specific capacity [Figure 6E]. Through these innovative catalytic strategies, researchers have successfully improved the energy efficiency and cycle durability of batteries, advancing the potential of AZSBs for superior-performance energy storage applications.

In summary, the design principles of the cathode in AZSBs, as demonstrated in previous examples, involve strategic doping, catalyst incorporation, and optimization of the carbon matrix to enhance redox reaction kinetics. Despite these advancements, AZSBs are still in their early developmental stages, and the fundamental reaction mechanisms need further investigation. Future research should prioritize addressing the inherent challenges of these batteries and advancing their practical applications. Key areas of focus should include advanced doping techniques, catalyst integration, and carbon matrix design.

Progress of electrolytes
Electrolytes play an imperative role in AZSBs, acting as a medium for ion transport between the cathode and anode and facilitating the redox reactions necessary for energy storage and release. An ideal electrolyte for AZSBs should meet several key criteria: high ionic conductivity, a wide electrochemical stability window, compatibility with sulfur cathodes and zinc anodes, and the ability to inhibit side reactions[94]. Aqueous electrolytes, composed of water and dissolved zinc salts, offer high ionic conductivity, safety, and low cost, making them a promising alternative for battery electrolytes[95]. However, aqueous electrolytes face several challenges: hydrogen evolution competes with the desired redox reactions, resulting in gas generation and reduced efficiency[96]. During cycling, zinc dendrites form, leading to short circuits and potential battery failures[97]. Ensuring the long-term stability of the electrolyte without decomposition, especially at high voltages, remains a significant challenge. Developing electrolytes that are compatible with both sulfur cathodes and zinc anodes is crucial, as incompatibility can degrade battery performance.

Addressing these challenges requires a comprehensive understanding of electrolyte chemistry and its interactions with electrode materials. Ongoing research focuses on developing advanced electrolyte formulations, involving the use of electrolyte additives, co-solvents, and the development of novel solvents
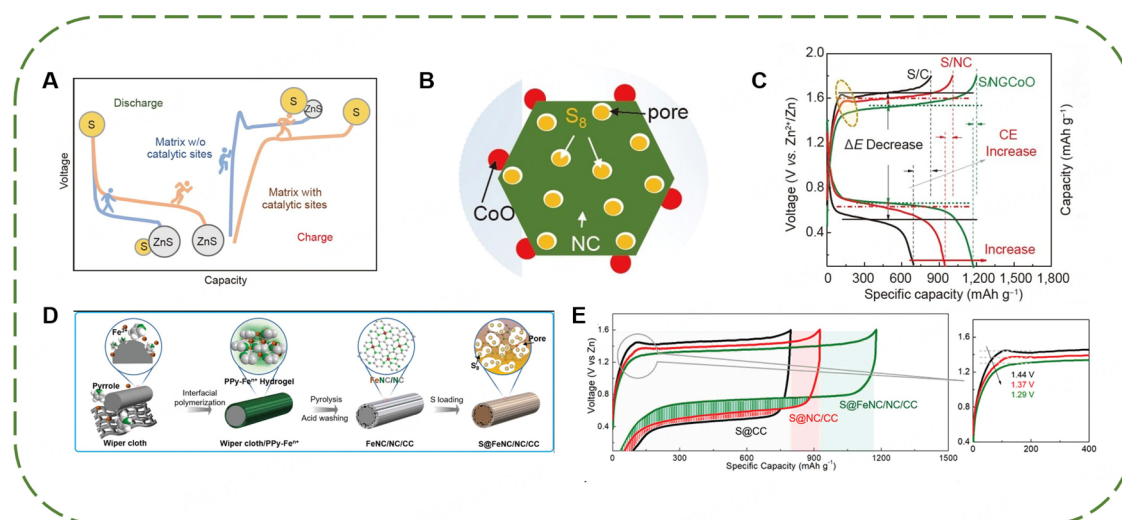
Figure 6. (A) Redox mechanism of sulfur in the catalytic matrix. (B) schematic diagram of S/NC-CoO. (C) The GCD plots of various cathodes. (A-C) were cited with permission from Wang *et al.*[74] Reproduction rights 2024, Springer Nature. (D) Experimental preparation process of S@FeNC/NC/CC cathode. (E) Voltage profiles of various cathodes at 0.2 A g^{-1}. (D and E) were cited with permission from Zhang *et al.*[64] Reproduction rights 2023, Wiley.

to enhance overall battery performance[98]. By overcoming these obstacles, the potential of AZSBs for high-performance, sustainable energy storage can be fully realized. Therefore, an ideal electrolyte design can form a solvation structure with zinc ions to accelerate transport, weaken Zn-S bonds to reduce reactivation energy barriers, mitigate side reactions, and minimize the formation of by-products.

Additive engineering

Beyond cathode modifications, addressing various battery challenges can also be achieved through electrolyte regulation. For example, electrolyte additives can reduce electrolyte reactivity to minimize dendrite formation, enhance the wetting property between the electrode and electrolyte, and improve electrolyte stability[76]. This approach can be particularly beneficial for AZSBs, thereby increasing their potential for practical applications. Recent studies indicate that incorporating redox-active electrolyte additives is an impactful strategy for improving the performance of AZSBs. These additives deliver significant improvements in the sulfur redox reaction kinetics[72]. The primary focus of research is to gain a deeper understanding of the reaction mechanisms and specific functions of these additives within the battery system.

To reduce the energy barrier, enhance redox kinetics, and stabilize zinc stripping and plating, Li *et al.* introduced 0.05 wt% iodine as an electrolyte additive[43]. The iodine additive acts as a Zn^{2+} ion carrier, reducing voltage hysteresis and improving the discharge efficiency of the sulfur cathode, thereby significantly enhancing the comprehensive performance of the battery. Iodine can be added to other zinc salts. Xu *et al.* introduced a high-concentration $Zn(OTF)_2$ electrolyte in AZSBs, which significantly improved the capacity retention and cycling performance by suppressing side reactions, reducing Zn corrosion, and expanding the electrochemical window[63].

This improvement was attributed to I_2 acting as a redox mediator, which enhanced kinetics and reduced the reaction barrier. Unfortunately, the introduction of I_2 resulted in the formation of highly soluble polyiodides (I^{3-}), which led to a severe shuttle effect, which further exacerbated the corrosion and degradation of the zinc anode[50]. Therefore, when selecting additives, it is crucial to consider system compatibility to optimize

overall performance. The poor solubility of non-polar I_2 in aqueous solvent (typically around 0.05-0.1 wt%) presents challenges for studying its catalytic effects[50]. Therefore, Hei *et al.* introduced highly soluble ZnI_2 as an electrolyte additive[72], discovering that iodide ions (I^-) strongly interact with the discharge product ZnS, significantly promoting the electrochemical oxidation of ZnS [Figure 7A]. With the help of the *in situ* spectroscopy, electrochemical studies, and theoretical simulations, the mechanism of I^- in catalyzing ZnS oxidation was revealed, showing that I^- induces rearrangement of the ZnS crystal structure and weakens Zn-S bonds, thereby promoting the efficient conversion of ZnS back to sulfur [Figure 7B][72]. Additionally, it has been reported that the introduction of tetramethylphenylammonium iodide ($Me_3PhN^+I^-$) as a dual mediator transformed the sulfur reduction pathway in AZSBs from solid-solid to solid-liquid-solid [Figure 7C], effectively enhancing reaction kinetics and battery performance[69]. This approach achieved a near-theoretical high capacity of 1,659 mAh g^{-1} and a decreased overpotential of 0.34 V, while demonstrating excellent cycling stability under copious sulfur loading and limited electrolyte conditions [Figure 7D].

Inhibiting the formation of by-product sulfate ions through electrolyte additives was identified as a promising approach. Chang *et al.* unveiled the bifunctional electrolyte additive thiourea (TU), which provides additional capacity through reversible redox reactions and significantly improves the reaction kinetics of the sulfur cathode [Figure 7E][36]. TU effectively suppresses the formation of by-product SO_4^{2-} during discharge, reducing internal side reactions and thereby improving the cycling stability of AZSBs [Figure 7F and G]. The addition of TU offers a new perspective on the use of organic additives in battery systems. Zhou *et al.* presented polyethylene glycol (PEG-400) into the electrolyte of AZSBs[62], which significantly reduced electrode polarization by regulating the uniform nucleation of ZnS [Figure 7H]. In Figure 7I, the two ^1H shifts corresponded to H_2O, and an additional signal appeared with the introduction of PEG[62]. Figure 7J shows the charge and discharge curves of the battery with S@CNTs-50 as the cathode at different current densities[62]. It highlights the performance under various conditions, with a polarization voltage of only 0.47 V and a discharge capacity of 1,116 mAh g^{-1} at a current density of 0.1 A g^{-1}. The battery starts with a relatively low capacity but gradually stabilizes, reaching around 645 mAh g^{-1} after 300 cycles, demonstrating good cycling stability and efficiency [Figure 7K][62].

Co-solvent modification

Whether adding iodine or other additives, these approaches focus solely on the introduction of catalysts and/or the optimization of zinc electrolyte salts, absent fully considering the compatibility and variability of the entire system. This makes achieving electrode reversibility in zinc aqueous solutions more challenging[49]. A co-solvent is an auxiliary solvent used in combination with the primary solvent to enhance the solution's solubility, stability, or reactivity. By introducing a co-solvent, certain characteristics of the primary solvent system, such as solubility, viscosity, conductivity, or reaction rate, can be improved. These co-solvents typically have similar polarity or functional groups to the primary solvent, allowing them to mix well with the primary solvent[99].

Yang *et al.* introduced the synergistic effect of tetraethylene glycol (G4) and iodine (I_2) in AZSBs [Figure 8A], which significantly enhanced the reaction kinetics of the S_8 cathode and the stability of the Zn anode by optimizing the electrolyte environment[49]. G4 enhanced the wettability of the electrolyte on the surface of the sulfur cathode, reducing water interference and promoting efficient solid-solid conversion of sulfur. The shift observed in the chemical peaks in the ^1H nuclear magnetic resonance (NMR) spectroscopy further confirms a strong interaction between the G4 co-solvent and iodine additive. This interaction is critical as it facilitates the conversion reactions of sulfur within the battery, thereby improving both the reversibility and efficiency of the sulfur redox processes [Figure 8B][49]. The Z/G/I/W electrolyte system
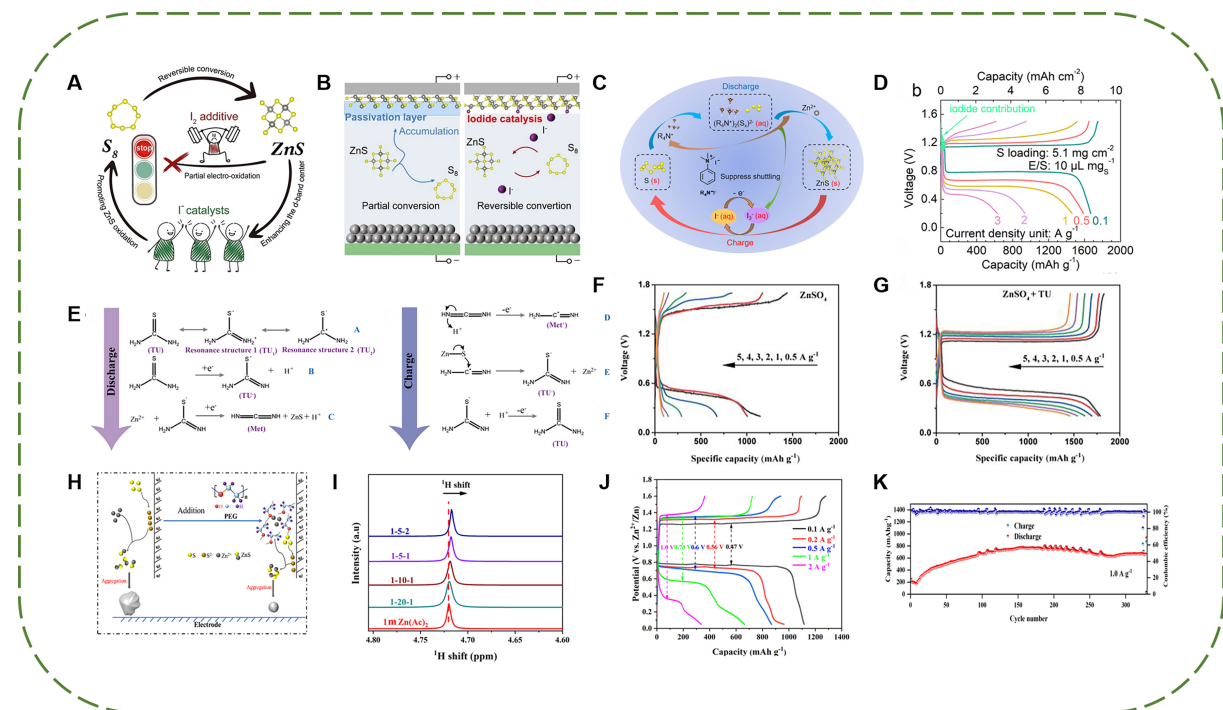
Figure 7. (A) Diagram illustration of ZnS function (B) Illustration of the catalytic mechanism of iodide ions. (A and B) were cited with permission from Hei *et al.*[72] Reproduction rights 2024, Wiley. (C) Reaction mechanism of sulfur in the R4N+I-. (D) GCD tests of AZSBs with Zn(CH₃COO)₂/Me₃PhN+I- electrolyte. (C and D) were cited with permission from Wu *et al.*[69] Reproduction rights 2023, Royal Society of Chemistry. (E) Redox mechanism of TU during discharging and charging. (F and G) The GCD plots (F) without TU. (G) in TU. (E-G) were cited with permission from Chang *et al.*[36] Reproduction rights 2022, Elsevier. (H) Mechanism of PEG's influence. (I) ¹H NMR spectra of various electrolytes. (J) GCD curves. (K) Long-cycle performance of the AZSBs at 1 A g⁻¹. (H-K) were cited with permission from Zhou *et al.*[62] Reproduction rights 2022, Elsevier.

demonstrates superior electrochemical behavior, maintaining clearly distinguishable plateaus even under higher current densities. This indicates the electrolyte's ability to reduce polarization and support stable charge-discharge processes [Figure 8C][49]. This "cocktail-optimized" electrolyte strategy not only performed exceptionally well in G4 but also showed broad applicability in other ether-based co-solvents.

Ethylene glycol (EG) has a low melting point and a high boiling point, and it can mix with water in any proportion. The melting point of the resulting mixture is significantly reduced, making it suitable for use as an antifreeze, and also making it a promising candidate as a co-solvent. Guo *et al.* reported that using EG as a co-solvent, combined with ZnI₂ as an additive[65], significantly suppressed side reactions at the sulfur cathode and dendrite growth at the Zn anode, thereby reducing polarization [Figure 8D]. As shown in Figure 8E and F, S²⁻ tends to coordinate with EG; specifically, the two hydroxyl groups of EG coordinate with S²⁻ in a bidentate way, increasing the binding energy[65]. Due to the presence of intermolecular hydrogen bonds, EG reduces water activity, thereby inhibiting the occurrence of side reactions. Additionally, Mehta *et al.* utilized EG and I₂ as additives in an aqueous zinc acetate [Zn(OAc)₂] electrolyte to stabilize the performance of AZSBs[76].

Eutectic solvent
Deep eutectic solvents (DESs) are a type of solvent system formed via mixing two or more compounds in a specific molar ratio, typically consisting of a hydrogen bond donor and a hydrogen bond acceptor. The melting point of DESs is lower compared with their individual components due to the hydrogen bond
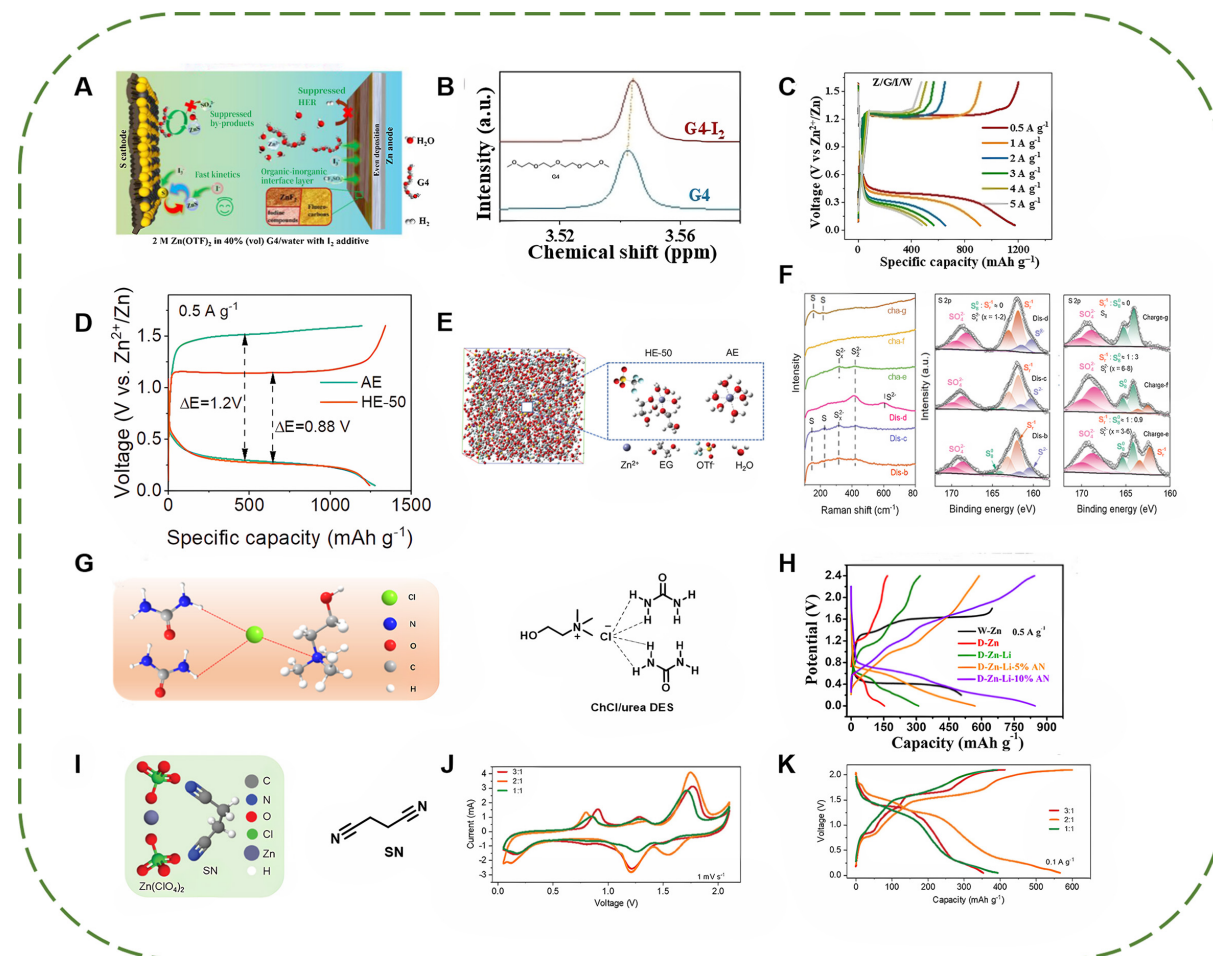
Figure 8. (A) Illustration of AZSBs: 2 M $Zn(OTF)_2$ in 40% G4 including I_2 additive. (B) ^1H NMR spectroscopy with G4 and G4-I_2 electrolytes. (C) GCD curves of the AZSBs. (A-C) were cited with permission from Yang *et al.*[49] Reproduction rights 2022, Wiley. (D) Zn^{2+} solvation structure in HE-50 and AE using MD simulation cell. (E) The GCD profile of Zn/50-S@NPC at 500 mA g^{-1}. (F) Raman and XPS spectra of 50-S@NPC. (D-F) were cited with permission from Guo *et al.*[65] Reproduction rights 2023, Wiley. (G) The molecular structural formula of the ChCl/urea DES. (H) GCD curves of AZSBs in various electrolytes. (G and H) were cited with permission from Cui *et al.*[61] Reproduction rights 2021, American Chemical Society. (I) Molecular structural formula of $Zn(ClO_4)_2$ and SN. (J) CV curves and (K) GCD curves of the AZSBs with eutectic electrolytes. (I-K) were cited with permission from Chen *et al.*[44] Reproduction rights 2024, Wiley.

network between the components, which weakens the lattice energy. Traditional organic solvents have high flammability, are toxic to humans, and are difficult to biodegrade, posing significant safety and environmental risks during use. Additionally, they are costly, unstable, and have limited electrochemical windows in high-voltage systems, making them prone to decomposition[100]. Compared to traditional organic solvents, DESs offer advantages such as low cost, easy preparation, low toxicity, and good biodegradability, giving them broad application prospects. They remain liquid at low temperatures and exhibit excellent solubility and chemical stability. Due to these unique characteristics, DESs are considered a promising alternative solvent in green chemistry[101-103].

Therefore, Cui *et al.* proposed a low-cost DES consisting of choline chloride and urea for use in AZSBs, providing a more stable electrochemical environment [Figure 8G][61]. To provide a clearer understanding, the corresponding molecular structures were also shown. It effectively suppressed side reactions in aqueous electrolytes by optimizing the solvation environment, thereby improving battery stability. The DES

electrolyte enabled the AZSBs to achieve a capacity of 846 mAh g⁻¹ [Figure 8H] then effectively resolving the common issue of zinc dendrites in traditional AZSBs[61].

Although sulfur can exist in multiple valence states, successful electrochemical oxidation of sulfur to a positive valence in AZSBs has not been achieved. To address this, Chen *et al.* adopted a succinonitrile (SN)-based eutectic electrolyte that effectively suppressed the dissolution of positive-valence sulfur compounds, enhancing both conversion activity and cycling stability (Figure 8I, with the chemical structures of SN shown on the right)[44]. Zn-S cells were constructed to examine the electrochemical performance of these eutectic electrolytes. The SZ-2:1 cell demonstrated a multistep conversion process, featuring three distinct cathodic peaks at 1.54, 1.21, and 0.18 V [Figure 8J][44]. In the GCD curves, the SZ-2:1 cell showed three discharge plateaus at 1.54, 1.24, and 0.26 V, achieving a discharge capacity of 572 mAh g⁻¹, which was a notable improvement over the SZ-3:1 and SZ-1:1 cells [Figure 8K]. The higher discharge voltage suggested an improved positive-valence sulfur conversion reaction in the eutectic electrolyte, likely due to better compatibility between the sulfur cathode and the eutectic electrolyte compared to aqueous systems. This approach to electrolyte design, aimed at enhancing multivalent sulfur conversion activity, could be paired with various metal anodes to create high-energy and reversible sulfur-based batteries.

Configuration innovation
Decoupled batteries
Decoupled batteries represent an emerging technology that optimizes performance by separating the reaction environments of the cathode and anode. This approach typically involves using different electrolytes, allowing each electrode to operate under its ideal conditions, thereby increasing energy density and extending cycle life. For example, in an acid-alkaline hybrid electrolyte system, the cathode and anode are placed in acidic and alkaline environments, respectively, which reduces side reactions and enhances electrochemical reaction kinetics. This technology shows great potential for future high-performance energy storage systems, especially in applications that demand long life, high-energy density, and enhanced safety.

Cai *et al.* proposed a mixed electrolyte design in AZSBs, utilizing an acidic sulfur cathode and an alkaline zinc anode, effectively separating the electrode reaction environments and optimizing electrochemical conditions, thereby achieving higher battery voltage and energy density[67]. Admittedly, in a strongly acidic reaction system, the Zn anode is prone to corrosion resulting from the acidic electrolyte, along with rigorous hydrogen evolution reactions[104]. Therefore, He *et al.* tackled the two main issues with Cu-S electrochemistry to unlock its potential for achieving high-energy aqueous batteries[105]. As depicted in Figure 9A, the S cathode converted to Cu_2S during discharge. Subsequently, the Cu^{2+} in the electrolyte is further discharged by depositing Cu on the cathode surface. This synergistic energy storage mechanism, involving both the cathode and the electrolyte, significantly enhanced the capacity of Zn-S decoupled cells. As shown in Figure 9B and C, the Zn-S alkaline-acid decoupled cell utilized an alkaline anolyte [6 M KOH + 0.3 M $Zn(Ac)_2$] and a bipolar exchange membrane (BPM).

Decoupled batteries can also enhance performance through cathode modification. Recently, Zhang *et al.* proposed a zinc-sulfur decoupled battery based on Cu-S electrochemistry [Figure 9D][10]. By constructing nanoscale hollow carbon spheres (HCS) as carriers for the sulfur cathode, they reached a high capacity of 2,250 mAh g⁻¹ and superb cycling stability, exceeding 2,500 cycles [Figure 9E and F]. They also introduced an electrode-electrolyte co-energy storage mechanism to compensate for the energy density loss caused by the additional electrolyte in decoupled batteries, resulting in a fivefold increase in battery capacity.
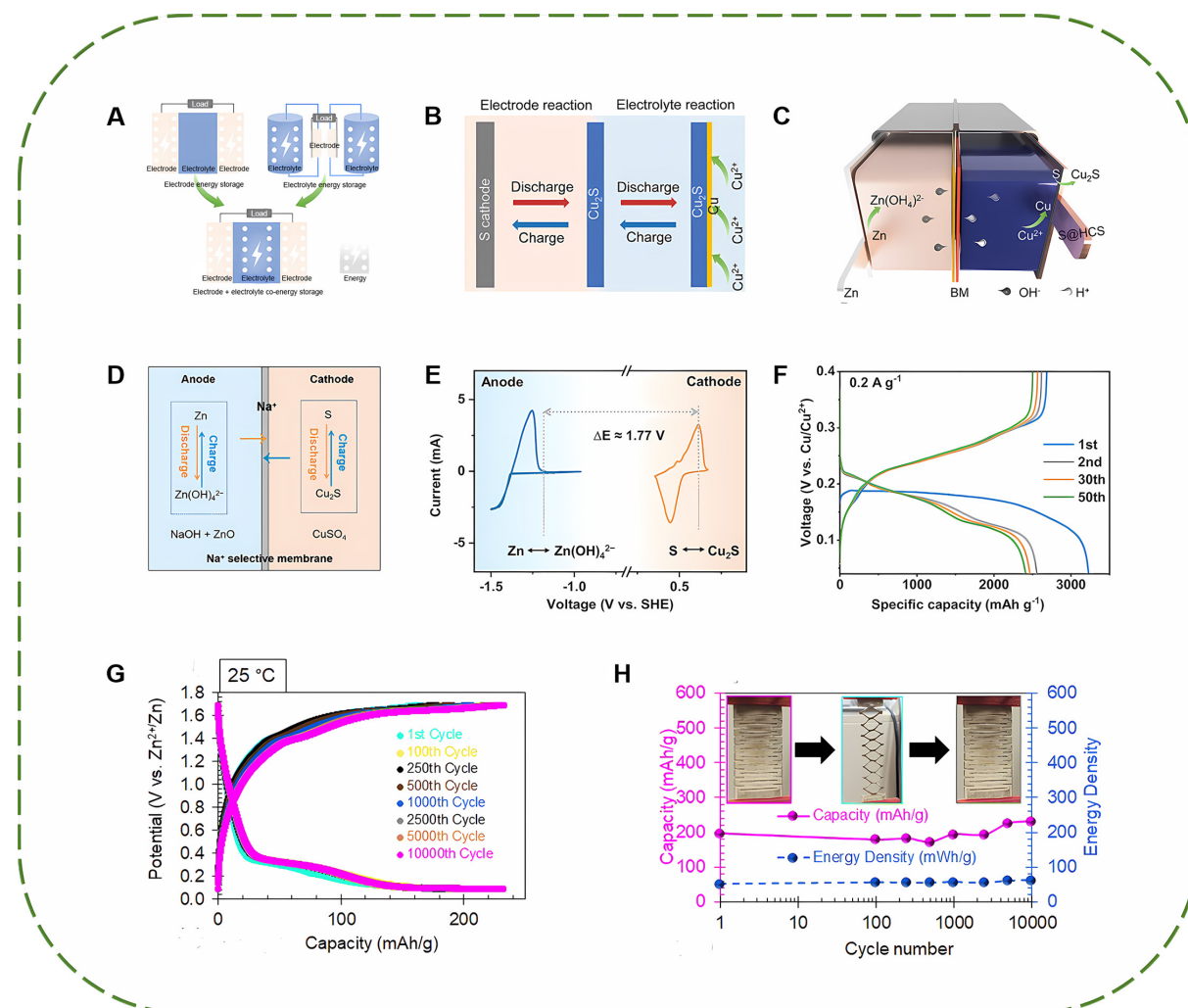
Figure 9. (A) Energy storage paradigms of various battery technologies. (B) Schematic illustration of the reaction processes in an electrode-electrolyte co-energy storage cell. (C) Schematic illustration of the Zn//S@HCS alkaline-acid decoupled cell. (A-C) were cited with permission from He *et al.*[105] Reproduction rights 2024, Wiley. (D) Reaction mechanism of the decoupled battery. (E) CV curves of S/Cu_2S and $Zn/Zn(OH)_4^{2-}$. (F) The GCD plots of the S@KB cathode. (D-F) were cited with permission from Zhang *et al.*[10] Reproduction rights 2023, Wiley. (G) The GCD charts of the AZSBs. (H) Electrochemical properties of the Zn-S battery. (G and H) were cited with permission from Amiri *et al.*[106] Reproduction rights 2023, Royal Society of Chemistry.

Aqueous zinc-sulfur decoupled batteries, as an innovative energy storage technology, demonstrate potential in enhancing energy density and cycle stability through their unique design, which separates the electrodes from the electrolyte. This design optimizes the independent performance of each component, enabling more effective control of the reaction processes and significantly reducing the impact of polysulfide migration and other side reactions on battery performance, thereby improving overall efficiency and lifespan. However, zinc-sulfur decoupled batteries still face several challenges, including structural complexity, interface stability, and material selection. Additionally, achieving higher energy density and long-term cycle stability imposes greater demands on material development and battery management. Nonetheless, as a hopeful direction for the future generation of energy storage technologies, aqueous zinc-sulfur decoupled batteries offer broad research prospects and provide important technical foundations for future alternatives to LIBs.

Flexible & stretchable batteries

Flexible batteries are energy storage devices that can bend, fold, or stretch, specifically designed to meet the demands of wearable devices, flexible electronics, and smart textiles[107]. These batteries not only possess excellent mechanical flexibility but also maintain stable electrochemical performance under various deformation conditions. Zhang *et al.* demonstrated the excellent mechanical flexibility of the flexible Zn-S battery in a solid-state configuration[64]. The battery not only operated stably under bending, stretching, and other deformation conditions but also maintained stable electrochemical performance after repeated mechanical deformations, showing great potential for applications in wearable devices and flexible electronics. Amiri *et al.* proposed a micro-sized zinc-sulfur battery design inspired by kirigami, masterfully balancing exceptional compactness with remarkable stretchability and flexibility[106]. This groundbreaking design showcased remarkable durability, retaining stable performance even after enduring 10,000 charging-discharging cycles [Figure 9G]. Furthermore, it was astonished by maintaining substantial capacity and energy density amidst varying degrees of stretching, demonstrating unparalleled resilience and adaptability [Figure 9H].

As an emerging energy storage technology, stretchable flexible zinc-sulfur batteries have gained significant attention for their potential applications in flexible electronics and wearable devices. These batteries can maintain steady electrochemical performance under different deformation conditions, including bending and stretching, by optimizing electrode materials and electrolytes to achieve a combination of superior energy density and excellent mechanical flexibility. The use of solid or gel electrolytes further enhances their stability and safety. However, despite the promising prospects of stretchable flexible zinc-sulfur batteries, they still face challenges in large-scale production, long-term stability, and cost control. Future research should focus on material optimization, process improvement, and technology integration. Therefore, from a practical application perspective, there is still a substantial distance to go in optimizing the performance of stretchable flexible zinc-sulfur batteries.

CONCLUSION AND OUTLOOK

Here, we provide a thorough review of the challenges and advances in the field of Aqueous Zinc-Sulfur Batteries (AZSBs), which have garnered significant attention as promising candidates for high-energy density, cost-effective, and environmentally sustainable energy storage systems. Despite their potential, AZSBs face numerous challenges that hinder their performance and large-scale commercial application. Several key issues include: (i) sluggish reaction kinetics; (ii) the disproportionation reaction of ZnS in water; (iii) low conductivity and volume expansion of the sulfur cathode; (iv) significant polarization due to the poor wetting properties of sulfur in aqueous electrolytes; and (v) zinc dendrite growth on the anode.

To address these challenges, a variety of optimization strategies have been proposed and explored. Cathode modification strategies, such as constructing sulfur/carbon composites, sulfide composites, and catalytic sulfur matrices, aim to improve conductivity and reduce volume expansion of the sulfur cathode. Furthermore, incorporating catalytic sites has shown promise in accelerating the sulfur conversion reaction, thereby addressing the sluggish kinetics issue. In terms of electrolyte engineering, iodide-based additives have demonstrated effective catalytic action by serving as redox intermediates, which help mitigate the slow reaction kinetics. Additionally, co-solvent strategies, involving the introduction of organic solvents to create hybrid electrolytes, have proven effective in improving the wetting properties of sulfur in aqueous systems. These strategies have collectively advanced the performance of AZSBs by mitigating the aforementioned key obstacles.

Challenges for practical application

Despite these advances, AZSBs are still in the early stages of development, and many issues persist when scaling the technology for practical applications, particularly in large-size pouch cells. Several critical challenges remain unsolved:

(1) Long-cycle stability: Despite recent advancements, the long-cycle stability of AZSBs remains a major obstacle. The battery's capacity and efficiency tend to degrade rapidly after 100-200 cycles, primarily due to sulfur cathode degradation. This degradation is especially problematic for practical applications such as grid-scale energy storage and electric vehicles, where battery life needs to extend over thousands of cycles. Achieving long-term stability requires more robust cathode designs and strategies to improve the stability of sulfur cathodes.

(2) Zinc dendrite formation: Zinc dendrite growth presents a significant barrier to the commercialization of AZSBs, particularly in larger cells where uneven current distribution and high-rate cycling exacerbate dendrite formation. This leads to short circuits, reduced battery lifespan, and safety concerns. For large-scale applications such as electric vehicles or grid storage systems, developing effective strategies to suppress dendrite growth is critical. Approaches such as protective coatings, solid-state electrolytes, and advanced electrolyte additives are essential to ensure the safe and reliable operation of AZSBs.

(3) Scaling to large-size pouch cells: When transitioning from lab-scale prototypes to large-size pouch cells, several technical challenges arise. One key issue is the uniform distribution of active materials and current across large cells. Inhomogeneities in material dispersion or current densities can lead to localized hotspots, accelerated material degradation, and reduced overall cell efficiency. Additionally, the expansion of sulfur during charge-discharge cycles (~53% volume change) poses significant mechanical challenges in large cells, causing structural damage over time. Designing large cells that can accommodate these mechanical stresses without compromising performance is a major hurdle that must be overcome.

Perspectives for future development

For the future development of AZSBs and their practical application, several critical research areas need to be addressed:

(1) In-depth exploration of charge-discharge mechanisms

Understanding sulfur redox pathways: The precise reaction mechanisms of sulfur reduction in aqueous electrolytes remain unclear, particularly the role of redox intermediates such as polysulfides. Unraveling the sulfur evolution pathways during charge-discharge processes is essential for optimizing material designs and improving long-cycle stability.

Advanced characterization techniques: Employing *in-situ* tools such as *in-situ* X-ray diffraction (XRD), Raman spectroscopy, and electron paramagnetic resonance (EPR) can provide real-time insights into sulfur conversion, intermediate formation, and zinc anode behavior. These techniques will assist in designing more efficient and stable materials by observing the dynamic behavior of sulfur and zinc during operation.

(2) Development of high-performance electrolytes

Iodine-based additives and co-solvents: Iodide additives have shown potential as redox mediators, improving reaction kinetics. Exploring new iodine-based additives and co-solvent systems could enhance the sulfur reduction process and stabilize the zinc plating/stripping mechanism, minimizing the energy barrier and improving long-term cycling.

Compatibility with both electrodes: Future electrolytes must exhibit high compatibility with both sulfur cathodes and zinc anodes to improve overall performance. The sluggish reaction kinetics and overpotential issues caused by electrolyte-electrode interface must be addressed to enhance battery efficiency.

Solid-state electrolytes: Solid-state or quasi-solid-state electrolytes offer enhanced safety, high ionic conductivity, and improved stability. Developing these electrolytes will help address issues such as zinc dendrite growth and enhance the overall performance of AZSBs.

(3) Precise design of sulfur cathode modifications

Sulfur/carbon composites: While sulfur/carbon composites have shown success in addressing conductivity and volume expansion, advanced designs are needed to further improve sulfur utilization. Incorporating high surface area carbons can enhance the reaction kinetics and sulfur loading, reducing volume expansion during cycling.

Chemical confinement via organic conductive frameworks: Introducing organic conductive polymers or covalent organic frameworks (COFs) as chemical confinements for sulfur could provide enhanced electron transport pathways and stabilize sulfur during cycling. These materials can also be tailored to improve structural stability, conductivity, and long-cycle performance.

Catalytic matrices: Catalytic sulfur matrices, such as metal sulfides and oxides, can accelerate sulfur redox reactions, lower activation barriers, and improve cycle life. These catalytic systems need to be further explored to enhance the reaction kinetics and minimize capacity fade over time.

(4) Zinc dendrite suppression and anode protection

Dendrite inhibition strategies: Zinc dendrite formation remains a critical challenge, particularly for long-term cycling stability and safety. Potential approaches include developing solid or hybrid electrolytes that inhibit dendrite growth, engineering artificial solid-electrolyte interfaces (SEI) to regulate zinc ion deposition, and employing electrolyte additives to control zinc nucleation and growth.

Zinc anode stabilization: Enhancing the stability of the zinc anode through surface coatings, novel additives, and optimized electrolyte formulations can significantly improve long-term performance by stabilizing zinc stripping and plating processes.

By addressing these critical research areas, AZSBs can overcome the technical barriers currently limiting their practical application. Continued progress in these fields will be crucial to realizing the full potential of AZSBs as a competitive energy storage technology for various applications, including electric vehicles, grid storage, and portable electronics.

DECLARATIONS

Availability of data and materials

Not applicable.

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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