

# The Promises and Challenges of Aqueous Zinc-Sulfur Batteries

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## Abstract

The aqueous Zinc-Sulfur (Zn-S) batteries hold significant promise for next-generation batteries due to their high theoretical specific capacity S (1,672 mA h g<sup>-1</sup>), their high safety, and the low price of sulfur. Nevertheless, the electrochemistry of the aqueous Zn-S batteries is still unclear, and their multifarious irreversible reactions also indicate their complexity. In this perspective, we have summarized the fundamental properties of and the current challenges for aqueous Zn-S batteries. Moreover, future opportunities for the development of aqueous Zn-S batteries are proposed.

**Key words:** Aqueous Zn-S batteries; Shuttle effect; Sulfur cathode; Zn anode.

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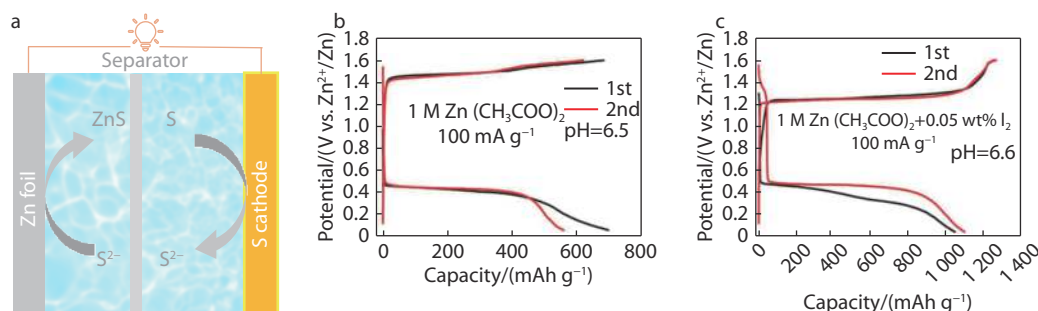
## Main text

Currently, metal-sulfur (M-S) batteries have shown significant promise for new emerging applications, including large-scale electrical grids and electric vehicles, because of their abundance and the high theoretical specific capacity of sulfur (1672 mA h g<sup>-1</sup>).<sup>[1,2]</sup> In recent decades, organic-electrolyte-based M-S batteries (such as Li-S batteries and Na-S batteries) have been widely investigated due to their satisfactory performance and mature industrial supply.<sup>[3–5]</sup> Nevertheless, these organic electrolytes are usually toxic and flammable, which may limit their applications.<sup>[6,7]</sup> Therefore, it is best to explore the aqueous electrolyte-based M-S batteries, which will possess the merits of the high capacity of sulfur and the safety and nonflammability of the aqueous electrolytes. Among these aqueous electrolyte-based batteries, Zn metal-based batteries hold great promise due to the fact that Zn metal has a high theoretical capacity (810 mA h g<sup>-1</sup>), and low cost (2 US\$ kg<sup>-1</sup>).<sup>[8,9]</sup> It is therefore a valuable project to devel-

op aqueous Zn-S batteries with high capacity, safety, and low cost.

Admittedly, the aqueous Zn-S batteries present challenges that have greatly obstructed their further application. For example, Zn can react with polysulfides, forming a passivating Zn sulfide (ZnS) film on the anode.<sup>[10]</sup> This passivating film will prevent further discharge.<sup>[11]</sup> In addition, the fundamental electrochemical mechanism of the sulfur in the aqueous electrolyte, including its kinetic and thermodynamic conversion reactions, is still unclear.<sup>[6]</sup> Therefore, developing a stable Zn electrode together with a compatible electrolyte to pair with the sulfur electrodes and achieving a profound understanding of their discharge-charge mechanism are urgently required.

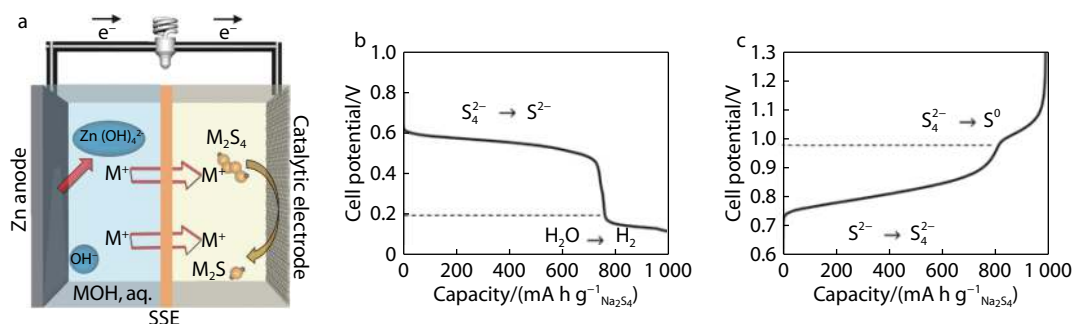
Figure 1 shows one of the two types of Zn-S batteries, the Zn-S battery, while the Zn-polysulfide battery is shown in Figure 2. The traditional half reactions of Zn-S batteries are as follows, where  $E^0$  is the standard electrode potential and SHE stands for standard hydrogen electrode:



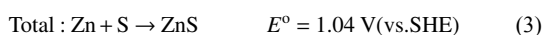
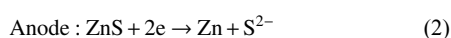
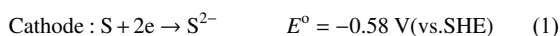
**Fig. 1** (a) Schematic representation of a Zn-S battery. Discharge/charge curves of Zn-S batteries in (b) 1 M Zn (CH<sub>3</sub>COO)<sub>2</sub> electrolyte, and (c) electrolyte consisting of 1 M Zn (CH<sub>3</sub>COO)<sub>2</sub> with 0.05 wt% I<sub>2</sub> as additive. Reproduced with permission.<sup>[12]</sup> Copyright 2020, Wiley-VCH.

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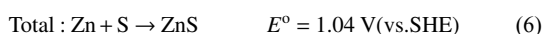
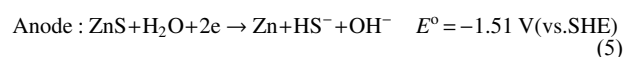
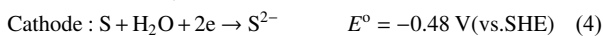
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**Fig. 2** (a) Schematic illustration of an aqueous Zn-polysulfide battery. (b) Discharge voltage profile and (c) charge voltage profile of an Zn-polysulfide battery in 0.5 M NaOH anolyte, Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> (NZSP) SSE, 0.1 M Na<sub>2</sub>S<sub>4</sub> + 0.1 M NaOH as catholyte, and a CoS catalytically active electrode. Reproduced with permission.<sup>[11]</sup> Copyright 2018, American Chemical Society.



The S<sup>2-</sup> will react with H<sub>2</sub>O to form HS<sup>-</sup> and OH<sup>-</sup>, however, and moreover, the acid dissociation constant to H<sub>2</sub>S is about 10<sup>-17</sup>, which could be neglected at ambient temperatures. Therefore, the aqueous electrolyte of Zn-S batteries may be better described by:

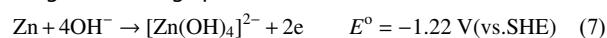


Based on the discharge production, the theoretical energy density of Zn-S batteries is 572 Wh kg<sup>-1</sup>.<sup>[12]</sup> The value of the theoretical energy density for the Zn-S battery is higher than those of many conventional aqueous cells, such as alkaline Zn-MnO<sub>2</sub> batteries (336 Wh kg<sup>-1</sup>), Zn-Ag batteries (447 Wh kg<sup>-1</sup>), Ni-Cd batteries (217 Wh kg<sup>-1</sup>), and Pd-acid batteries (170 Wh kg<sup>-1</sup>).<sup>[13]</sup>

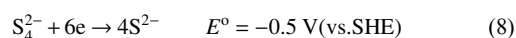
The typical discharge/charge curves of Zn-S batteries with 50 wt% sulfur, supported in carbon nanotubes in 1 M Zn (CH<sub>3</sub>COO)<sub>2</sub> electrolyte (pH = 6.5), are shown in Figure 1b.<sup>[12]</sup> This Zn-S cell exhibited an initial reversible capacity of 685 mAh g<sup>-1</sup> with an initial Coulombic efficiency (CE) of 98%. Its initial capacity is much lower than the theoretical capacity of sulfur, however, and the voltage hysteresis is 0.9 V. This performance is still far from being satisfactory. There are some efficient strategies that have been developed to reduce the voltage hysteresis and improve their capacity. For example, electrolyte additives can serve as the medium for Zn<sup>2+</sup> ions and thus reduce the voltage hysteresis. When employing 0.05 wt% I<sub>2</sub> as additive in 1 M Zn (CH<sub>3</sub>COO)<sub>2</sub> electrolyte, the Zn-S cell showed a high reversible capacity of 1105 mAh g<sup>-1</sup> at the current density of 100 mA g<sup>-1</sup> (Figure 1c). Its voltage hysteresis was reduced to 0.72 V, enhancing the kinetics. In addition, the I<sub>2</sub> additive in 1 M Zn (CH<sub>3</sub>COO)<sub>2</sub> electrolyte also can stabilize Zn stripping and plating during cycling, which can decrease the overpotential in Zn symmetrical cells.

Polysulfides also have attracted much attention as energy storage media, due to their solubility both in organic and aqueous solvents.<sup>[14,15]</sup> In addition, the short-chain sulfides usually show high solubility in water. This is quite different in

organic electrolyte, where the short-chain sulfides are usually insoluble. Therefore, if the cells contain very high molar values of polysulfides or short-chain sulfides, they do not require excess electrolyte for solid sulfur cathodes, which allows for a high energy density system. This concept of rechargeable Zn aqueous polysulfides batteries has been reported to consist of a Zn metal anode, an alkaline anolyte, an aqueous polysulfide catholyte, a catalytic electrode, and a mediator-ion solid-state electrolyte (SSE), as shown in Figure 2a.<sup>[11]</sup> During the discharge process, Zn will be oxidized to zincate ion:



As for the cathode, the dissolved S<sub>4</sub><sup>2-</sup> will be reduced into S<sup>2-</sup>:



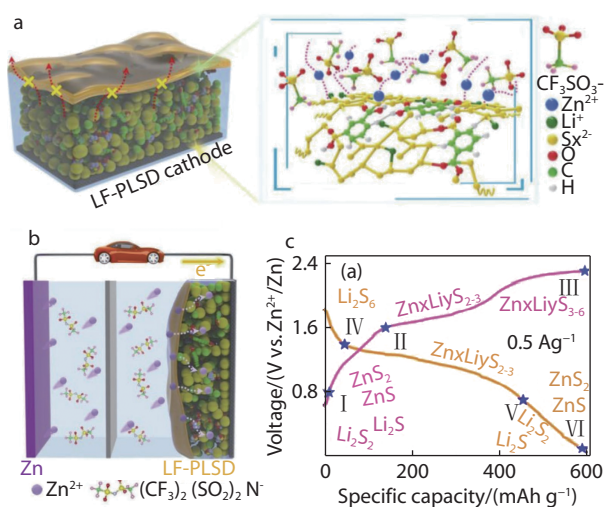
When the concentration of polysulfides become low, the reaction can be simplified:



The mediator ions Li<sup>+</sup> or Na<sup>+</sup> will shuttle from anolyte to catholyte to maintain the charge balance. During the charge process, the reverse reactions will occur. It should be noted that the dissolved sulfur in aqueous electrolyte will form a multitude of species, such as S<sup>2-</sup>, HS<sup>-</sup>, H<sub>2</sub>S, and polysulfides S<sub>x</sub><sup>2-</sup> (2 ≤ x ≤ 5); their concentration distribution is largely dependent on the pH of the solution. CoS electrocatalyst was employed to catalytic reduce polysulfides. On the basis of these conditions, the theoretical voltage of the Zn-polysulfide battery is about 0.74 V, as shown in Figure 2b and 2c. In addition, the SSE will effectively separate the Zn anode from the polysulfide catholyte, blocking the crossover of the polysulfides. Thus, this battery presents good electrochemical performance, maintaining a reversible discharge capacity of 822 mAh g<sup>-1</sup> after 50 cycles at the current density of 0.5 mA cm<sup>-2</sup>.

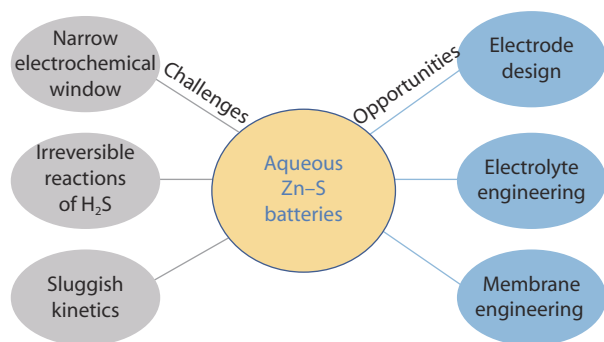
Immobilizing the polysulfides in the cathode is also an efficient strategy for constructing high-performance Zn-S batteries. For example, Li<sub>2</sub>S<sub>6</sub> was stored in 1,3-diisopropenylbenzene as a copolymer (PLSD), then activated by 4-(3-butyl-1-imidazolium)-1-butanethiolate triflate ionic liquid (IL), and confined by poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) in the form of a 'liquid film' (LF) to form a cathode (LF-PLSD) for Zn-polysulfide batteries in an aqueous electrolyte,<sup>[16]</sup> as shown in Figure 3a. This copolymer PLSD was cast onto carbon cloth, where it was held by chem-

ical bonding. This chemical bonding can trap PLSD, and thus there is no need for a binder or conductive agent in this PLSD cathode. In the ionic liquid (IL), there are large  $\text{CF}_3\text{SO}_3^-$  anions, which allow for Zn ion transfer (Figure 3a). In addition, the introduced PEDOT:PSS skeletons can maintain the cathode structure by the formation of a liquid film. This unique structure of LF-PLSD cathode ensures reversible Zn-polysulfide batteries. The full battery using Zn metal anode and LF-PLSD cathode in 1 M Zn (TFSI)<sub>2</sub> electrolyte (Figure 3b) presented an excellent capacity of 1148 mAh g<sup>-1</sup> and overwhelming energy density of 724.7 Wh kg<sup>-1</sup> at 0.3 A g<sup>-1</sup>. The discharge-charge profile of Zn/LF-PLSD batteries at 0.5 A g<sup>-1</sup> in the third cycle is shown in Figure 3c. It can be clearly seen that  $\text{S}_6^{2-}$  was mainly reduced to  $\text{S}^{2-}$  during the discharge process. When the cell was charged, the short-chain sulfides would be oxidized to long-chain  $\text{Zn}_x\text{Li}_y\text{S}_{3-6}$ .



**Fig. 3** (a) Schematic illustration of PLSD cathode coated with  $\text{Zn}^{2+}$ -conducting LF. (b) Schematic illustration of an aqueous Zn/LF-PLSD battery. (c) Discharge/charge profile at 0.5 A g<sup>-1</sup> based on data collected in the third cycle. Reproduced with permission.<sup>16</sup> Copyright 2020, Wiley-VCH.

Although progress has been made, there are still noteworthy issues of concern for aqueous Zn-S batteries (Figure 4):



**Fig. 4** Challenges and opportunities of aqueous Zn-S batteries.

(1) Narrow electrochemical window. The electrochemical window is usually lower than 1.23 V.<sup>[17]</sup> To make matters

worse, this narrow electrochemical window will limit the output voltage of Zn-S batteries and excludes many high capacity redox pairs which lie below the hydrogen evolution reaction (HER) or above the oxygen evolution reaction (OER). There are many positive strategies to widen the narrow electrochemical window, including constructing a solid-electrolyte interphase, regulating the pH value, using electrolyte additives, employing competitive redox pairs, and designing a better electrode structure.<sup>[18]</sup>

(2) Irreversible reactions of H<sub>2</sub>S. The irreversible discharge production of H<sub>2</sub>S will escape in the neutral and acid electrolyte, which will lead to the loss of active materials.<sup>[19,20]</sup> Worse still, H<sub>2</sub>S will also corrode the stainless-steel substrate in battery assembly, resulting in safety issues.

(3) Sluggish kinetics. The slow kinetics conversion of the sulfur redox reactions from sulfur to polysulfides and polysulfides to short-chain sulfides prevents high-performance from Zn-S batteries. Efficient methods should be tailored to improve their kinetics.

Despite these challenges, there are opportunities that can be considered for future investigation. In particular, a profound understanding of the atomic structure and molecular level mechanism will help us in the rational design of sulfur cathode, Zn anode, and a suitable electrolyte for aqueous Zn-S batteries:

(a) Electrode Design. An ideal electrode for aqueous Zn-S batteries should possess excellent electronic conductivity and catalytic activity to reduce polysulfides into short-chain sulfides to overcome the huge polarization. For example, a novel cathode consisting of sulfur hosted by a catalyst-decorated carbon matrix is expected to improve the sulfur reactivity and catalytically reduce polysulfides into the short-chain sulfides.<sup>[21,22]</sup> It should be noted that the catalysts in aqueous Zn-S batteries should not boost the HER and OER as well. Therefore, the rational design of the electrode should involve a synergetic combination of a conductive framework, catalytic activity, and the active materials.

(b) Electrolyte Engineering. pH regulation and additive modifications are two efficient strategies to optimize the aqueous electrolytes. In particular, adjusting the pH of an aqueous electrolyte can effectively address the thermodynamic issues caused by the narrow electrochemical window. Moreover, this method also can control the redox direction and avoid the HER or OER side reactions. The aqueous Zn-S batteries have a high activation energy, and a suitable additive can realize redox reactions that would be infeasible under ordinary conditions via reducing the polarization. Therefore, exploring effective additives is another route to achieve electrolyte optimization.

(c) Membrane Engineering. The membrane in aqueous Zn-S batteries is usually used to separate the different electrolyte phases and prevent the 'shuttle effect' of polysulfides. In aqueous Zn-S flow batteries, the membrane also could separate the anolyte and catholyte, and allow the redox reactions to take place separately in the anode and cathode. Moreover, some functional membranes, for example a membrane with sulfonic acid functional, can repulse polysulfides and decrease their chemical crossover.

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## Conflict of interest

The authors declare no conflict of interest.

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