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Materials and Structure Design for Solid-State Zinc-Ion Batteries: A Mini-Review

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Solid-state zinc-ion batteries (SSZIBs) are receiving much attention as low-cost and safe energy storage technology for emerging applications in flexible and wearable devices, and grid storage. However, the development of SSZIBs faces many challenges from key battery materials development to structure design. Herein, we review the most recent progress in the development of polymer electrolytes, cell chemistry and configuration, and demonstration of SSZIBs. In conclusion, perspectives for future research in materials, interface, and assessment of SSZIBs are discussed.

Keywords: Polymer electrolyte, ionic conductivity, solid-solid interface, Zn dendrite, Zn-ion battery, solid-state battery

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INTRODUCTION

The expanding flexible electronics market has placed significant demands on flexible batteries (Ma Y et al., 2020; Wang et al., 2020). Lithium-ion batteries (LIBs) have dominated the battery market due to their high operating voltage, long lifetime, and high energy density (Mossali et al., 2020). Unfortunately, LIBs have unsolvable challenges, such as safety issues associated with flammable organic electrolytes, the rarity of their elements (e.g., Li and Co), and the cost of lithium (~\$19.2 US kg^{-1}) (Borah et al., 2020; Mossali et al., 2020), all of which necessitate the need for alternative batteries to suit these flexible designs. Of the next-generation batteries, zinc-ion batteries (ZIBs) show several advantages related to Zn, including high abundance, low cost (~\$2.4 US kg^{-1}), high theoretical capacity (820 mAh g^{-1}), environmental friendliness, ease of manufacture, and high safety (Tang et al., 2020; Zhang N et al., 2020).

Recently, aqueous ZIBs have drawn attention due to their high safety, low cost, and high energy density (Tang et al., 2019). However, the commercialization of aqueous ZIBs has been hindered by challenges associated with aqueous electrolytes, including Zn dendrite formation and parasitic side reactions (Zhang N et al., 2020; Zhang Y et al., 2020). In particular, dendrite formation results from uneven Zn deposition on the anode, altering morphology and inducing 'dead' Zn deposition. This leads to low Coulombic efficiency, and with extended cycling, these dendrites may pierce the separator and internally short-circuit the battery. Moreover, Zn corrosion and H_2 evolution occur at the anode, resulting in the accumulation of Zn^{2+} insulating byproducts on the anode surface and battery gassing that degrade the cycling and rate capability of these ZIBs (Ma L et al., 2020; Zhang N et al., 2020; Zhang Y et al., 2020). On the cathode, transition metal dissolution (e.g., Mn from MnO_2) has hindered stability and cycle life. Despite many strategies to address these problems, the performance of aqueous ZIBs remains unsatisfactory for practical applications (Dueramae et al., 2020; Zhang N et al., 2020; Zhang Y et al., 2020).

Solid-state Zn-ion batteries (SSZIBs) employ solid-state electrolytes (SSEs) and have drawn increased research attention. Due to the lower quantity or absence of active liquid in solid

electrolytes than in aqueous electrolytes, they may fundamentally address Zn corrosion, Zn passivation, dendrite formation, and cathode dissolution common in aqueous ZIBs (Tang et al., 2019; Zhao Q et al., 2020). Additionally, the higher modulus and microporous structure of solid electrolytes may add to dendrite suppression (Zhang N et al., 2020; Zhao Q et al., 2020). Of added convenience, SSEs can act as both the separator and electrolyte, easing manufacture and improving operational stability (Zhao Q et al., 2020; Zhang Y et al., 2020). Moreover, solid electrolytes provide flexibility, making them an ideal candidate for SSZIBs in flexible devices (Yu et al., 2019; Wang et al., 2020). Although solid electrolytes have been broadly investigated in solid-state LIBs (Zhao Q et al., 2020), they have yet to be fully explored in ZIBs.

The development of SSZIBs is in its infancy and requires further research. This mini-review is intended to provide a concise summary of the state-of-the-art progress in the materials and architecture design for SSZIBs and critical analysis on the performance and limitations in current SSZIBs. Challenges in SSZIBs development is discussed, followed by suggested directions of future research. This work is the first focused review on SSZIBs and provides an overview of SSZIBs in hopes to stimulate future research on multivalent solid-state battery chemistry.

SOLID ELECTROLYTES

During cycling, SSZIB solid electrolytes facilitate Zn^{2+} transport between the electrodes while remaining electrically insulating. This requires solid electrolytes with high ionic conductivity (0.1 mS cm^{-1} at room temperature (RT)), low electronic conductivity, wide electrochemical stability window, and high thermal and chemical stability (Bekaert et al., 2017; Zhao Q et al., 2020). In addition, SSEs should have high mechanical strength to suppress Zn dendrite formation (Young's modulus E = 108 GPa) (Wang M et al., 2019).

To date, ZIB solid electrolyte research has focused on polymer electrolytes due to their high chemical stability, mechanical toughness, flexibility, low cost, ease of synthesis, and scalability (Zhao Q et al., 2020). Polymer electrolytes for SSZIBs contain gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs) (shown in **Supplementary Figure S1**). GPEs—often referred to as quasi-solid-state—consist of a polymer matrix interspersed with a salt(s) and solvent (plasticizer). In contrast, SPEs contain only a salt dispersed throughout the flexible polymer matrix, relying on segmental polymer motion for ionic transport (Bekaert et al., 2017; Zhang Y et al., 2020). **Supplementary Table S1** summarizes GPEs and SPEs for SSZIBs, along with their main components (polymer, salt, and plasticizer), ionic conductivity, and other prominent characteristics. It is seen that GPEs provide much higher ionic conductivities (1–40 mS cm^{-1}) than SPEs (10^{-1}–10^{-6} mS cm^{-1}) at RT due to the higher liquid content of GPEs. The following section highlights the main factors governing the performance of polymer electrolytes.

The selection of a polymer matrix with high polarity and an amorphous structure is preferred for polymer electrolytes of SSZIBs. Polymers with a low glass transition temperature (T_g) have higher amorphosity and ease ion (de)solvation. These amorphous polymers hold higher levels of entropy and free volume space, improving local segmental motion and, in turn, increasing ionic conductivity by 2-3 orders of magnitude (Pucic and Turkovic, 2005; Bekaert et al., 2017). However, amorphous structures fail to provide the mechanical strength necessary to maintain interfacial contact with the electrodes needed in flexible applications.

Homopolymer structures have been evaluated for Zn^{2+} transport in ZIBs, and the first homopolymers were PEO (Karan et al., 2016; Karan et al., 2017), PVA (Wang J Q et al., 2018; Wang K et al., 2018; Huang et al., 2019; Zeng et al., 2019), and PAM (Li et al., 2018b; Wang Z F et al., 2018; Liu Z X et al., 2019). However, these homopolymers are single-faceted in providing the needed properties. For example, PEO provides good mechanical properties but low ionic conductivity due to its high molecular weight and crystallinity (Ward and Hubbard, 2012; Bekaert et al., 2017).

To better balance ionic conductivity and mechanical properties, copolymers (e.g., PVdF-HFP) and crosslinked polymers (e.g., PEO-PPO-PEO) have been used to decrease crystallinity without sacrificing strength (Zhao Q et al., 2020; Wang et al., 2020). Using a PVdF-HFP SPE, an ionic conductivity of 0.0244 mS cm^{-1} was achieved while delivering flexibility, thermal and electrochemical stability (~3.45 V), and dendrite suppression (Liu et al., 2020b). Furthermore, several bio-inspired polymers (e.g., kappa-carrageenan) have emerged, seeking balanced characteristics (Hoang et al., 2017; Wang M et al., 2019). For example, a modified metal-organic framework (MOF) electrolyte provided mechanical characteristics similar to a crystalline structure, an ionic conductivity of 0.21 mS cm^{-1} at 30°C, and a high transference number of 0.93 (Wang Z Q et al., 2019). The use of a PANa GPE for Zn^{2+} transport, provided high ionic conductivity (σ = 0.2 S cm^{-1}) in NiCo/Zn batteries, and may prove useful in ZIBs (Liu J et al., 2019).

Beyond the polymer matrix, nanofillers and additives have been investigated (e.g., Al_2O_3, ZrO_2, TiO_2, and pyrazole) to further enhance the electrolyte's properties (Johnsi and Suthanthiraraj, 2015, 2016; Hoang et al., 2017; Nancy and Suthanthiraraj, 2017; Zhao Q et al., 2020). These composite electrolytes provided flexibility, accommodating anode volume change at the anode using fillers, creating a mechanical barrier against dendrite growth (Zhao Q et al., 2020). For example, the combination of fumed silica polymers—a polymer capable of dendrite suppression at the expense of higher Zn corrosion—implements pyrazole as a corrosion inhibitor (Hoang et al., 2017). Suppressing dendrites using solid electrolytes, such as MOFs, poly(ethylene oxide)/aramid, and polyacrylonitrile, has prolonged battery lifespans beyond 300 h (Lee et al., 2018; Wang M et al., 2019; Wang Z Q et al., 2019).

TABLE 1 | Summary of the key components and performance of solid-state zinc-ion batteries.

Cathode/current collector	Anode/current collector	Polymer electrolyte	Energy density	References
α-MnO_2/CNT paper 1.0–2.5 mg cm^{-2} $_{MnO_2}$	[a]Zn/CNT paper 3–5 mg cm^{-2} $_{Zn}$	$ZnSO_4/MnSO_4$ in gelatine-g-PAM/PAN with H_2O	306 mAh g^{-1} $_{MnO_2}$ at 2.8 A g^{-1}; 6.18 mWh cm^{-2} $_{two\ electrodes}$	Li et al. (2018a)
β-MnO_2/carbon cloth 1.5–2.5 mg cm^{-2} $_{MnO_2}$	Zn metal foil	$Zn(CF_3SO_3)_2$ in PEGDGE with PC	177 mAh g^{-1} $_{MnO_2}$ at 0.1 A g^{-1}	Dong et al. (2020)
α-MnO_2/CNT/CC 2–3 mg cm^{-2} $_{MnO_2}$	[a]Zn/Ni-Cu 3–5 mg cm^{-2} $_{Zn}$	$ZnSO_4/MnSO_4$ in NFM/PAM with H_2O	~ 200 mAh g^{-1} $_{MnO_2}$ at 4°C	Wang D H et al. (2018)
γ-MnO_2/graphite 1.3–1.5 mg cm^{-2} $_{MnO_2}$	Zn foil (5 μm)	$Zn(CF_3SO_3)_2$ in PEO with BANFs	~ 146 mAh g^{-1} $_{MnO_2}$ at 15 mA g^{-1}	Wang M et al. (2019)
MnO_2/CNT Fiber	Zn wire	$Zn(CF_3SO_3)_2/MnCl_2$ in PVA with H_2O	290 mAh g^{-1} $_{MnO_2}$ at 0.1 A g^{-1}	Wang K et al. (2018)
MnO_2/carbon paper	[a]Zn/carbon paper	$ZnSO_4/MnSO_4$ in Zn-alginate/PAAM with H_2O	300.4 mAh g^{-1} $_{MnO_2}$ at 0.11 A g^{-1}	Xiao et al. (2020)
α-MnO_2/graphite paper 1–3 mg cm^{-2} $_{MnO_2}$	[a]Zn/graphite paper	$ZnSO_4/MnSO_4$ in PAAM with H_2O	277.5 mAh g^{-1} $_{MnO_2}$ at 1°C	Wang Z F et al. (2018)
MnO_2/CNT yarn 2.5–5 mg cm^{-2} $_{MnO_2}$	[a]Zn/CNT yarn	$ZnSO_4/MnSO_4$ in PAAM with H_2O	302.1 mAh g^{-1} $_{MnO_2}$ at 1°C	Li et al. (2018b)
MnO_2/PEDOT 3.6 mg cm^{-2} $_{MnO_2}$	[a]Zn/CC 6.14 mg cm^{-2} $_{Zn}$	$ZnCl_2/LiCl/MnSO_4$ in PVA with H_2O	310 mAh g^{-1} $_{MnO_2}$ at 1.1 A g^{-1}	Zeng et al. (2017)
MnO_2/N-doped CC 3.2 mg cm^{-2} $_{MnO_2}$	[a]Zn/N-doped CC	$ZnCl_2/LiCl/MnSO_4$ in PVA with H_2O	350 mAh g^{-1} $_{MnO_2}$ at 0.5 A g^{-1}	Qiu et al. (2017)
α-MnO_2/CNT	[a]Zn/CNT 3–5 mg cm^{-2} $_{Zn}$	$ZnSO_4/MnSO_4$ in EG-waPUA/PAAM with H_2O	275 mAh g^{-1} $_{MnO_2}$ at 0.2 A g^{-1}	Mo et al. (2019)
V_2O_5/CNTF	[a]Zn/CNTF	$ZnCl_2$ in PVA with H_2O	457.5 mAh cm^{-3} at 0.3 A cm^{-3}	He et al. (2019b)
V_2O_5/stainless steel 4 mg cm^{-2} $_{V_2O_5}$	Zn/stainless steel	$Zn(CF_3SO_3)_2$ in gelatin with H_2O	450 mAh g^{-2} at 0.1 A cm^{-3}	Zhao et al. (2019)
$V_5O_{12}{\cdot}6H_2O$	Zn foil	$Zn(CF_3SO_3)_2$ in gelatin with H_2O	300 mAh g^{-2} at 0.1 A g^{-1}	Zhang N et al. (2019)
CoHCF/CC 1–3 mg cm^{-2} $_{CoHCF}$	[a]Zn/CC	$Zn(BF_4)_2$ in PVdF-HFP/PEO with EMIM BF_4	149.5 mAh g^{-1} $_{CoHCF}$ at 0.2 A g^{-1}	Ma L et al. (2020)
ZnHCF/CNTF	[a]Zn/CNTF	$ZnSO_4$ in CMC with H_2O	100.2 mAh cm^{-3} $_{ZnHCF}$ 195.39 mWh cm^{-3} $_{two\ electrodes}$	Zhang Q C et al. (2019)
ZnHCF	[a]Zn/CC	$Zn(CF_3SO_3)_2$ in gelatin-g-PAM with H_2O	38 mAh cm^{-3} $_{ZnHCF}$ at 25°C 120 Wh kg^{-1} $_{two\ electrodes}$	Chen Z et al. (2020)
ZOV/graphene foam 4.1 mg cm^{-2} $_{ZOV}$	[a]Zn/graphene 1.5 mg cm^{-2} $_{Zn}$	$ZnSO_4/Na_2SO_4$ in fumed silica with boric acid/H_2O	204 mAh g^{-1} $_{ZOV}$ at 0.1 A g^{-1} 140 Wh kg^{-1} $_{two\ electrodes}$	Chao et al. (2018)
PANI/steel mesh	Zn foil coated with SWCNTs	$Zn(CF_3SO_3)_2$ in PVA with H_2O	123 mAh g^{-1} $_{PANI}$ at 0.1 A g^{-}	Huang et al. (2019)
PANI/CNT	[a]Zn/CC	$ZnSO_4$ in PAAM with H_2O	144 mAh g^{-1} $_{PANI}$ at 0.2 A g^{-1}	Xiao et al. (2020)
PPy/PET	[a]Zn/PET	PVA-based GPE	123 mAh g^{-1} $_{PPy}$ at 1.9 A g^{-1}	Wang J Q et al. (2018)
V-MOF/CNTF	Zn/CNTF	$ZnCl_2$ in PVA with H_2O	30.71 mWh cm^{-3} 1.46 Wcm^{-3}	He et al. (2019a)

BANFs, branched aramid nanofibers; CC, carbon cloth; CMC, carboxymethyl cellulose sodium; CNTs, carbon nanotubes; CNTF, carbon nanotube fiber; CoHCF, cobalt hexacyanoferrate; EG-waPUA, ethylene glycol-based waterborne anionic polyurethane acrylates; PAAM, polyacrylamide; PANI, polyaniline; PEDOT, poly(3,4-ethylenedioxythiophene); PEGDGE, poly(ethylene glycol)diglycidylether; PPy, polypyrrole; PVA, poly(vinyl alcohol); SWCNTs, single-walled carbon nanotubes; V-MOF, vanadium-based MIL-47 metal-organic frameworks; ZnHCF, zinc hexacyanoferrate; ZOV, zinc orthovanadate.[a]Zn anode was prepared by electroplating Zn on 3D substrates.

In addition to the polymer and nanofillers/additives, plasticizers are another key GPE component to enhancing the flexibility and ionic conductivity by increasing the free volume. Traditional plasticizers (solvents) used to enhance the GPE polymer network in SSZIBs include water and organic solvents (e.g., ethylene carbonate (EC), propylene carbonate (PC), and tetrahydrofuran (THF)) (Zhao Q et al., 2020). Although water content improves interfacial contact between the electrode and electrolyte, the evaporation of water may accelerate aging alongside parasitic side reactions. Organic solvents have helped address these challenges, retaining interfacial contact and minimizing evaporation and side reactions, contributing to dendrite suppression and improved Coulombic efficiency (Li et al., 2019). For example, a PEGDGE/$Zn(CF_3SO_3)_2$ SSE using a PC plasticizer addressed evaporation and obtained an ionic conductivity of 0.377 mS cm^{-1} while maintaining constant surface resistance for over 200 h (Dong et al., 2020). The latest research implements ionic liquids in place of traditional plasticizers, increasing the quantity of ions within the electrolyte (Liu et al., 2020a; Ma L et al., 2020). The addition of these ionic liquids increased the ionic conductivity of polymer electrolytes, widened the electrochemical stability window resolving HER reactions, and provided nonflammability, low volatility, and high thermal and chemical stabilities (Liu et al., 2020a; Ma L et al., 2020; Francis et al., 2020). One example uses 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM]BF_4) and zinc tetrafluoroborate [$Zn(BF_4)_2$] salt to form an ILZE electrolyte that reportedly solved both HER side reactions and Zn dendrite issues inherent to ZIBs (Ma L et al., 2020). This

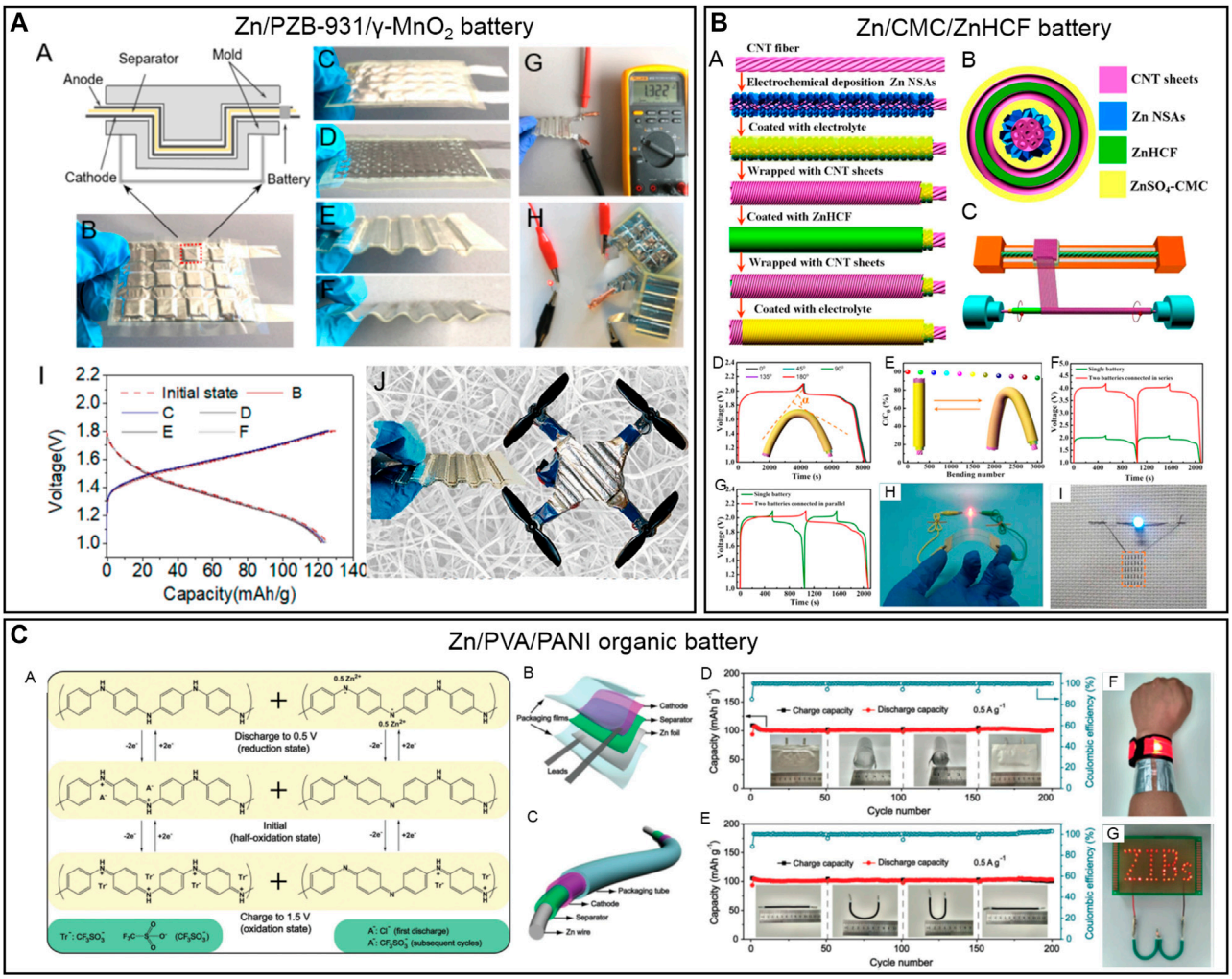

FIGURE 1 | (A) Schematics and pictures of different plastically deformed Zn/PZB-931/γ-MnO_2 SSZIBs, their galvanostatic charge and discharge curves at 0.2°C, and a drone powered by the Zn/PZB-931/γ-MnO_2 planar cells (Wang M et al., 2019). **(B)** Schematic illustrations showing the fabrication process of coaxial-fiber Zn/CNC/ZnHCF SSZIBs, their charge and discharge curves under different bending (0–180°C), and LED illuminated by the charged coaxial-fiber Zn/CNC/ZnHCF batteries (Zhang Q C et al., 2019). **(C)** Redox mechanism of PANI cathode, schematic diagrams, cycling performance, and LED demonstration of flexible soft-packaged and cable-type quasi-solid-state Zn/PVA/PANI organic battery (Wan et al., 2018).

electrolyte had an increased electrochemical window (~3.55 V), had a Coulombic efficiency of ~100%, retained 90% capacity over 30,000 cycles, and operated from −20 to 70°C. This electrolyte was also much thinner and stronger (5 orders of magnitude stronger modulus) than other GPEs. Using trifluoromethanesulfonate (EMITf), PvDF-HFP and $Zn(CF_3SO_3)_2$ delivered an ionic conductivity of 0.144 mS cm^{-1}, widened the electrochemical stability window (~4.14 V), and provided excellent thermal stability up to 305°C (Liu et al., 2020a). These ionic liquids have been found to improve both PVdF-HFP and PEO/PVdF copolymer electrolytes (Tafur et al., 2015; Rathika and Suthanthiraraj, 2018; Zhang Y et al., 2020). In summary, the combination of novel plasticizers, additives/fillers, and copolymers and/or crosslinked polymers holds promise in delivering GPEs with desirable properties for SSZIBs.

SOLID-STATE ZN-ION BATTERY DEVICES

With the advancement in polymer electrolytes and cathodes, SSZIBs with different configurations have been demonstrated, including traditional planar (Li et al., 2018a; Wan et al., 2018; Wang D H et al., 2018; Zhang H et al., 2019; Zhang N et al., 2019; Mo et al., 2019; Zeng et al., 2019; Chen Y et al., 2020; Ma L et al., 2020; Zhao Y et al., 2020; Dong et al., 2020; Li et al., 2020; Xiao et al., 2020), deformable planar (Wang M et al., 2019), flexible coaxial (Wan et al., 2018; Zhang Q C et al., 2019; Zhao Y et al., 2020), and twisted-pair (He et al., 2019b) or parallel-pair fiber arrangements (Wang K et al., 2018). The key battery components and performance of these SSZIBs are compared in **Table 1**, and representative examples are illustrated in **Figure 1** and discussed below.

The majority of Zn anodes in SSZIBs were fabricated by electroplating Zn (1–5 mg cm^{-2}) onto 3D substrates, such as carbon nanotube (CNT) paper (Li et al., 2018a; Mo et al., 2019), CNT fibers (He et al., 2019a; He et al., 2019b; Zhang Q C et al., 2019), carbon cloth (CC) (Qiu et al., 2017; Zeng et al., 2017; Ma L et al., 2020; Chen Z et al., 2020; Xiao et al., 2020), and graphene foam (Chao et al., 2018). 3D-substrate–supported Zn anodes not only provide the flexibility required for flexible SSZIBs but also reduce Zn passivation and dendrite formation while improving the depth of discharge and cycling life (Parker et al., 2017). The cathodes for SSZIBs explored to date include traditional inorganic materials (MnO_2 (Li et al., 2018a; Wang D H et al., 2018; Wang K et al., 2018; Wang M et al., 2019; Dong et al., 2020; Xiao et al., 2020), V_2O_5, zinc orthovanadate (ZOV) (Chao et al., 2018), zinc hexacyanoferrate (ZnHCF) (Chen Z et al., 2020; Zhang Q C et al., 2019)), organic materials (polyaniline (Xiao et al., 2020)), and novel metal-organic frameworks (MOF, vanadium-based MIL-47 (He et al., 2019a)). Similar to the anode, these cathode materials were also prepared on various 3D substrates to provide the structural flexibility and high rate capability needed for SSZIBs. These 3D cathodes have an increased specific surface area of active material, shortened ionic diffusion distance, and increased channel size and number of interstitial sites, in turn increasing the number of reactive sites and lessening volumetric change during Zn (de) intercalation (He et al., 2019a; Li et al., 2019; Chen Z et al., 2020). It is worth noting that most SSZIBs reported employ GPEs (**Table 1**), likely due to the higher ionic conductivity and good electrode-electrolyte interface enabled by plasticizers. Strictly speaking, these SSZIBs should be called quasi-solid-state, rather than all-solid-state.

MnO_2 is the most popular cathode in SSZIBs, of which the performance could vary significantly with the phase of MnO_2, GPEs, and cell configuration. A novel PEO/$Zn(CF_3SO_3)_2$/branched aramid nanofiber (PZB) provided a high ionic conductivity (2.5×10^{-5} S cm^{-2} at RT), high tensile strength (58 ± 2.9 MPa), and high Young's modulus (210 ± 11 MPa) (Wang M et al., 2019). Using a corrugated planar design (**Figure 1A**), a Zn/PZB-931/MnO_2 battery was fabricated, and it delivered a stable discharge capacity of 120 mAh g^{-1} (MnO_2) under different elastic and plastic deformations. This cell was integrated into an unmanned aerial vehicle as auxiliary charge storage devices, extending the total flight time. Another arrangement using an α-MnO_2/CNT cathode, electroplated Zn/CNT anode, and gelatin and PAM-based hierarchical polymer electrolyte (HPE) provided an extremely safe and wearable SSZIB. The developed SSZIB exhibited a high areal energy and power density of 6.18 mWh cm^{-2} and 148.2 mW cm^{-2}, respectively (Li et al., 2018a). Moreover, the SSZIBs offered robust structural and property stability under various abuse conditions, such as being cut, bent, hammered, punctured, sewed, and submerged in water or set on fire.

It is essential to develop new cathode materials with high capacity and high voltage to improve the energy density of SSZIBs. Another group developed a new cathode, zinc hexacyanoferrate (ZnHCF), with an open framework structure for the co-insertion/extraction of Zn^{2+}, and applied it to fabricate the first high-voltage coaxial-fiber SSZIB prototype with a $ZnSO_4$-carboxymethyl cellulose sodium (CMC) gel electrolyte and Zn nanosheet arrays on carbon nanotube fiber (CNTF) as the anode (Zhang Q C et al., 2019). The Zn/CMC/ZnHCF coaxial-fiber battery was delicately fabricated by a continuous production process illustrated in **Figure 1B**. The coaxial-fiber battery delivered a large capacity of 100.2 mAh cm^{-3} and an energy density of 195.39 mWh cm^{-3}. Moreover, the coaxial-fiber battery underwent negligible degradation of electrochemical performance at various angles from 0° to 180°, proving exceptional flexibility. Furthermore, the battery's capacity remained at 93.2% after bending at 90° for more than 3,000 cycles. High operating voltages and output currents were achieved by connecting the coaxial-fiber battery in series and parallel for high energy and power applications, as illustrated in the 3.3 V blue LED in a flexible textile.

In addition to inorganic materials, other novel materials (such as organic materials and MOF) have also been explored as cathodes in SSZIBs. For example, polyaniline (PANI) organic electrode with a supercapacitor-like dual-ion mechanism exhibited a high reversible capacity of 200 mAh g^{-1} at 0.05 A g^{-1}, high rate capability, and long cycling stability. A Zn/PVA/PANI organic battery in a planar and cable shape was fabricated using a PVA-based GPE, Zn foil/wire, and PANI/carbon fibers as the cathode (**Figure 1C**). The soft, cable-type quasi-solid-state ZIBs displayed a reversible capacity of 109 and 106 mAh g^{-1} PANI at 0.5 A g^{-1}, respectively. Moreover, both showed stable capacities under severe bending and maintained high capacity retentions of 91.7% and 91.5% after recovering from bending state to flat, after 200 cycles (Wan et al., 2018).

As in **Table 1**, current research has proven the feasibility of fabricating flexible SSZIBs, which require dedicated design of the Zn anode, cathode, and polymer electrolytes. The performance of most SSZIBs was assessed using the specific capacity of the cathode. The energy and power densities of SSZIBs varied significantly in the literature, due to various cell chemistry and evaluation methodology. As a result, comparison among SSZIBs and other battery chemistry (such as LIBs) remains difficult and needs to be addressed in future research.

SUMMARY AND PERSPECTIVES

Herein, we discussed progress in the polymer electrolytes and design of SSZIBs. Quasi-solid-state ZIBs of various configurations have demonstrated excellent structural and electrochemical stability under abuse conditions. Therefore, SSZIBs appear as promising energy storage devices for flexible applications. Nevertheless, challenges remain in SSZIBs, necessitating further research into the materials, interface, structure design, and fundamental understanding of interfacial phenomena in SSZIBs:

1) *Zn/solid electrolyte interface.* The use of solid electrolytes in SSZIBs is motivated by the hypothesis that they may address Zn dendrites and associated side reactions. Despite successful

demonstration of SSZIBs, little information has been presented on the Zn/solid electrolyte interface. Most SSZIBs employed electroplated Zn on 3D substrates, making characterization of the Zn/solid electrolyte interface difficult. Therefore, systematic and in-depth studies are needed to clarify the influence of solid electrolytes on the performance of Zn in SSZIBs, such as critical current density, dendrite growth, and H_2 evolution. Special attention should be given to the plasticizers in GPEs, which is likely to influence Zn interaction at the Zn/solid electrolyte interface.

2) *Polymer electrolytes.* Further research is needed to explore new plasticizers that enhance the overall performance of GPEs. Besides ionic conductivity, other key merits of new GPEs must be comprehensively assessed, including transference number, mechanical strength, and electrochemical and chemical stability. In particular, the content of plasticizers in GPEs dramatically influences SSZIB performance and therefore needs to be controlled, quantified, and documented explicitly.
3) *Cathode.* The use of solid electrolytes makes it possible to couple a high-voltage cathode and Zn anode to further improve the energy and power densities of SSZIBs. Further research needs to be devoted to developing new cathode materials with high voltage, high capacity, and good compatibility with solid electrolytes.
4) *Energy and power density of SSZIBs.* If reported in the literature, the energy and power densities of SSZIBs were estimated based on two electrodes, with no reports on the additional weights of polymer electrolytes, 3D current collectors, packing, *etc.* Therefore, the reported values for energy and power densities of SSZIBs might be over optimistic. Future SSZIB work is encouraged to report the cell chemistry and configuration in greater detail, such as the active material loading, the weight of current collectors and polymer electrolytes, and packing (if applicable). This will facilitate meaningful and comparable analysis amongst SSZIB technologies.

AUTHOR CONTRIBUTIONS

EH organized the data and wrote the manuscript. JL conceived the idea, revised the manuscript, and oversaw the project. All authors discussed the topics and contributed to the organization of this paper.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.