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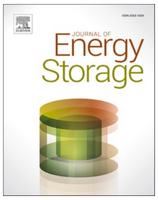

Review article

Advances in zinc-ion structural batteries

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ABSTRACT

Electrical energy storage technologies have become a critical aspect of the whole clean energy system, which is fundamentally based on batteries. In the past decades, innovations in batteries changed the appearance of our lifestyle with portable devices. More recently, electrical vehicles have led the mind toward a promising clean world without fossil fuels. However, minimizing the weight and/or volume of such batteries is the critical design driver, and in the last decade, the idea of moving electric energy accumulation inside structural parts has been proposed and named structural batteries (SBs), in which structural elements should also act as electric energy accumulators. The work on structural batteries to date has mostly involved Li-ion batteries due to their acceptable performance. However, the adoption of Li-ion batteries must face the limited availability of lithium on the earth and safety during their manufacturing and use. These issues encouraged researchers to seek alternative battery systems that do not present their drawbacks. Zn-ion structural batteries are a promising alternative to lithium-ion batteries in the post-lithium era. Zinc is one of the most abundant elements on the planet and can be found at low prices. Zinc-based batteries also have the potential to use lower-cost production procedures because they do not require particular dry room conditions, which means the ability to operate in the air, allowing for large-scale assembly. Although Zn-ion batteries have numerous advantages, the development of Zn-ion structural batteries is still in its early stages (low Technology Readiness Level, TRL), and additional study is required. This review seeks to provide a concise description of current breakthroughs in materials and architecture design, as well as a critical assessment of the performance and limitations of the solutions adopted for zinc-based structural batteries. The difficulties in constructing Zn-ion structural batteries are discussed. This is the first complete examination of these batteries, and it provides an overview of the technology with the aim of promoting future structure battery chemistry research.

1. Introduction

Electrochemical energy storage technologies have a fundamental role in pursuing the goal of sustainable development finding applications in energy production from renewable resources [1], wearable electronics [2], sustainable mobility [3], etc. The mass to capacity ratio of the batteries still represents a major concern in the automotive and aerospace industry. However, novel materials and design solutions are necessary to tackle some of the great challenges related to minimizing environmental impact and maximizing energy efficiency by reducing weight and volume.

To overcome this limitation, in recent years, the concept of structural battery composites (SBCs) has attracted increasing attention. They are multifunctional composites that simultaneously withstand mechanical loads and store electrochemical energy being able to match different materials and architectures [4]. SBCs are often referred to as "mass-less energy storage systems" and have the potential to revolutionize the future design of electric vehicles and devices [5]. The past several years have seen a steady stream of reports on the results of numerous studies on SBCs. The strategies used to construct the SBCs may be at the material level and system level [6–10]. High-strength structural electrode and electrolyte components, as well as packaging film, make up the SBCs at the material level [11–13]. In SBCs the stiffness of structural elements is greatly determined by the mechanical characteristics of the electrolytes that they include [13]. At the system level, high performance structural composites are used to encase the entire batteries or individual battery components during assembly of the SBCs with sandwich structures [4,14].

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A very important performance indicator of a battery is the battery-to-structure weight ratio, i.e. the ratio of the weight of the active battery to the weight of the combined battery and its surroundings. In an ideal case, this ratio should be equal to 1:1 when no additional weight for the support or protection structures is present. However, in many electrical vehicles this ratio is equal to 1:2, i.e. for each battery kilogram, an additional kilogram of protecting or supporting materials is used [15,16]. Therefore, this ratio can be used for evaluating the efficacy of several designs and for looking for new multifunctional materials and designs to enhance the mechanical properties [17] [18] [19].

The first work on structural polymer based composite with battery functionality was realized in 2006 by Snyder et al. [20,21]. Since then, the research has progressed, beginning slowly and more quickly in the last few years as evidenced by Fig. 1 which shows the number of scientific publications presented in the Scopus database with the term “structural battery” in the title, abstract or keywords. A significant increase in related publications has been observed in the last four years. A similar trend is observed in the number of scientific publications related only to zinc-based structural batteries, which appear very recently in the literature but are proving to be an emerging topic. The growing interest in the topic of structural batteries (SBs) and, in particular, zinc-based structural batteries, underlies this review for searching for future research directions in this field.

Most of the research on structural batteries has been performed on Li-ion batteries since they have been the most common electrochemical energy storage devices for the past two decades due to their high energy and power density and their wide application in portable electronic systems and electric vehicles [22]. Despite their many advantages, lithium-ion batteries have several drawbacks, particularly with regard to safety. They have the tendency to overheat and can be damaged at high voltages, and, in some cases, thermal runaway is possible [23]. Moreover, the performance is very sensitive to air and moisture exposure and the batteries must be hermetically sealed and compressed to maintain good contact between the electrodes and separator and suppress mechanical failure [24]. Additionally, the power output of such structural Li-ion batteries is poor when compared to traditional coin-type batteries using the same electrode components. Lithium is an expensive, limited and unequally distributed resource, and, in the long run, it could be not enough to meet the growing market needs for energy storage [1,25] [26,27].

The safety and stability problems of Li-ion batteries and the limited presence of lithium on the earth have driven the research toward alternatives to Li-ion batteries. Several metal ion batteries have recently come to attention, as they offer better life-cycle and less expensive manufacturing than Li-ion batteries while also allowing structural composite batteries to function safely in the air without the need for moisture barrier protection [28].

In recent years, sodium has been used for battery development thanks to its easy availability, low price and properties close to those of lithium. However, there are a few obstacles in this path [29] since sodium presents two drawbacks. First, its weight is three times higher than lithium, sodium-ion batteries are heavier than lithium-ion batteries. Second, the Na^+ ion has a larger ionic radius than the Li^+ ion, leading to a slower diffusion kinetics and less cycling stability [25,30]. For these reasons, very few researchers studied Na-ion structural batteries [31] [32].

Lithium, sodium and potassium can only have one positive electrical charge but other ions with higher charge capacity could be potentially used. Due to their ability to cooperate in more electron-sharing chemical redox processes than the more common Li^+ ion, multivalent metal cations including magnesium Mg^{2+}, aluminum Al^{3+}, and zinc Zn^{2+} have drawn considerable interest in this regard. Magnesium metal possesses good qualities as a battery anode; thus, magnesium rechargeable batteries are emerging as an appealing choice for energy storage. However, slow ion diffusion within the host lattices, resulting in challenging development of magnesium storage cathodes and large activation energy of Mg^{2+} species intercalation, prevents their wide application [33] [34]. In the case of aluminum-ion batteries, the formation of an alumina coating (Al_2O_3) on the aluminum anode could cause harm to the fiber-matrix interlayer, a reduction of mechanical properties, and a decrease in cell conversion efficiency [35].

Another promising candidate to replace lithium-ion batteries is zinc, which is mass-produced at inexpensive prices on every continent and easy to find. Zinc-based batteries have the potential to use less expensive production methods than standard lithium-ion batteries since they can be processed in the air, eliminating the need for inert glove boxes during the construction of structural composite batteries at a large scale [36,37]. Zinc metal can be directly applied as an anode due to its excellent electrochemical stability and reversibility in water [38]. Zinc and zinc oxide can be easily recycled via electrochemical, chemical, or thermal methods. Moreover, zinc-based battery recycling is already well-established and commercialized for primary zinc batteries

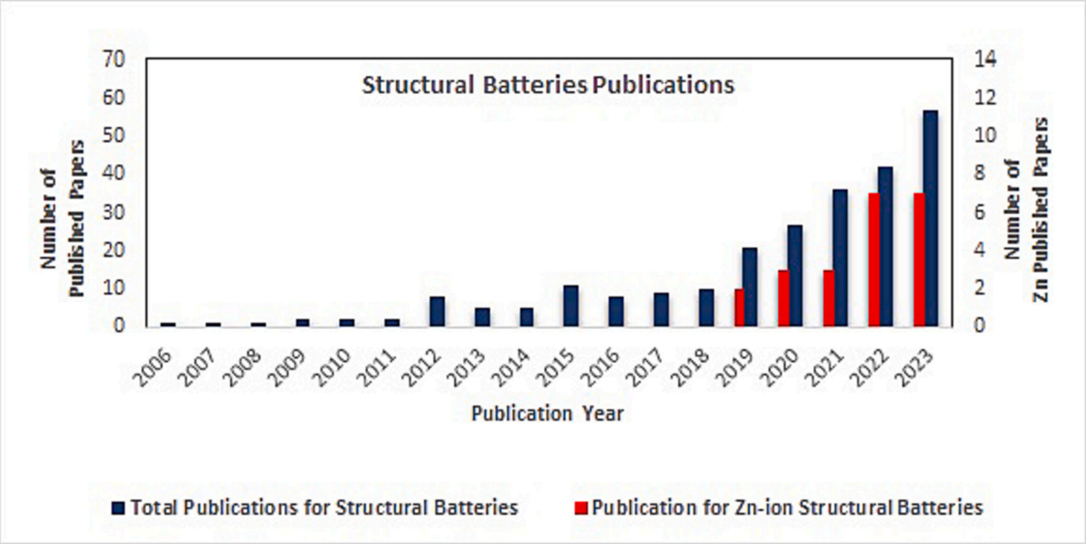


Fig. 1. Number of scientific publications in the last twenty years under the search term “structural battery” in the title, abstract or keyword (from Scopus database accessed in December 2023).

[28,39,40]. Thanks to these inherent advantages, Zinc is also a good candidate for the development of zinc-based structural batteries (ZnSBs).

Zn-ion batteries with aqueous/hydrogel electrolytes are great candidates for ZnSBs due to their moderate interactions and safe applications. In any case, the particular capacity, longevity and electrode thickness of current Zn-ion batteries are limited due to the presence of hydrated zinc particles and their polarization. For the cathode, manganese oxide-based materials can represent a solution due to their appropriate structures, inexhaustible and cost-effective properties and huge working voltage window. However, issues such as constrained intercalated channels, limited intra-material channels for battery charge/discharge forms, and electron conductivity of manganese oxide-based cathodes have to be addressed. In this way, the advance of structures for manganese oxide-based cathodes calls encouraging for investigation.

Although zinc-ion batteries (ZIBs) have numerous advantages, the advancement of zinc-ion structural batteries is still in its early stages at a low Technology Readiness Level (TRL). Further research, development, and testing are required to advance the technology to higher TRL levels. So, due to the influence that this battery can have on the world of power storage, the related studies have to be ascended dramatically.

This review aims to provide a concise description of current breakthroughs in materials and architecture design, as well as a critical assessment of the performance and limitations of zinc-based structural batteries. Thus, after examining the multifunctional level classification of structural batteries and a brief description of zinc-based batteries, the state of the research on zinc-based structural batteries will be presented followed by a section with details on electrodes and electrolytes and the electrochemical and mechanical performances.

2. Multifunctional level classification

Multifunctionality is completely necessary for structural batteries due to the need for simultaneous electrochemical and mechanical properties. All the SB cells under investigation in various research so far used multifunctional systems or materials adopting a different level of integration of materials and systems. An initial classification can be made between multifunctional systems and multifunctional materials (Fig. 2).

A multifunctional system is achieved by assembling a thin film battery within a composite material consisting of, for example, outer face sheets (or plies) and foam core, where, generally, each material has a single decoupled function. When the materials cope with the electrochemical and mechanical tasks at the same time, a structural battery with multifunctional materials (coupled function) is realized (Fig. 2) [32,41,42]. In some studies, single functional materials design is called de-coupled, and multifunctional materials design is called coupled [42].

As sketched in Fig. 2, all the designs for the structural batteries have been categorized into four groups: packing structural batteries, laminated structural batteries, fiber structural batteries and upgraded fiber structural batteries. The last three groups are based on multifunctional materials presenting coupled electrochemical and mechanical performance at the same time. The point is that sometimes there is not an explicit boundary between the groups. Some studies used a combination strategy for their design to improve the properties; the dotted line between the groups shows these interwoven relationships.

When the structural batteries were introduced, researchers looked at how batteries must be designed; the first approach was to pack the commercial ion batteries into a matrix, obtaining the packing structural battery [43], where each part of the battery and supportive materials are responsible only for one function between the electrochemical and mechanical tasks. This simple strategy of single functional materials presents many disadvantages. The bonding between the energy storage component and the composite material is brittle eventually leading to system failure under mechanical loads. Moreover, if the composite, mechanically stressed, deforms, there is a possibility that the electrolyte might leak, or the battery does not work at all [44,45].

Since the full integration of functionalities (i.e., energy storage and load bearing) should result in smaller and lighter devices, the research interest is directed toward multifunctional materials where different types of structural batteries are possible, as schematized in Fig. 2 [45,46]. Such alternative designs include the studies of multilayer

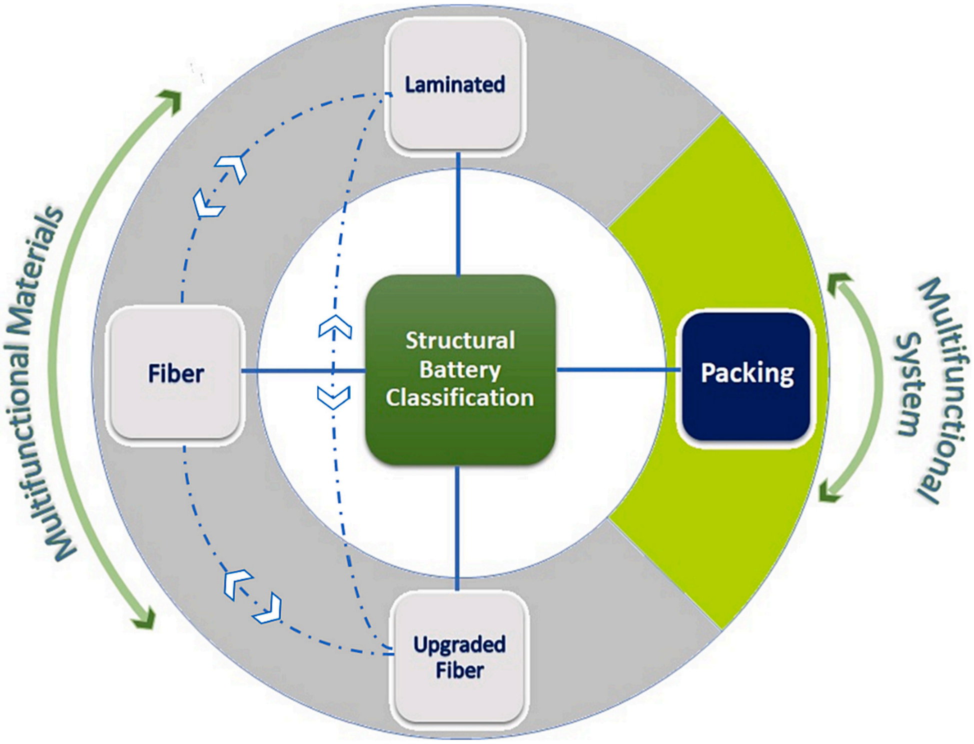


Fig. 2. Multifunctional level classification of the structural batteries.

(laminated) SBs, fiber structural batteries, and upgraded fiber structural batteries [47]. A laminated SB design is highly flexible offering a diverse range of components. Each material with acceptable electrochemical and/or mechanical properties can be used as a component for the SBs considering their compatibility. Regarding fiber structural batteries, the exceptional mechanical properties of fibers provide the reinforcement in the battery design, enhancing the structural integrity and performance of batteries. In addition, the functionalized or coated fibers as upgraded fiber designs are certainly excellent for giving the battery the required properties.

In the following paragraphs, the above designs will be presented in more detail along with suitable related studies.

2.1. *Structural batteries' substructures*

All the approaches discussed in this section are generally applicable to any kind of SBs, including Zn-ion batteries since the design strategies use basic knowledge for setting up the cells.

The substructures for the different designs of SBs are reported in Fig. 3. Packing structural batteries, till now adopted, use sandwich structures (Fig. 3-1), for example made of carbon fiber reinforced polymer matrix with the batteries embedded in the foam core or in the matrix [14,48,49] (Fig. 3-2).

In the case of laminated structural batteries, the design strategies reported in the literature have been concentrated on the innovation on the electrolyte (Fig. 3-3), overcoming the limitations related to liquid or gel electrolytes, which are not able to provide at the same time both ion diffusion and load transfer, and carbon fabric reinforced composites (Fig. 3-4) [11,50–55], showing high mechanical and electrochemical properties.

Regarding the design of fiber structural batteries, fibers can reinforce the electrolyte (Fig. 3-5) and act as a structural electrode (Fig. 3-6). In this latter case, fibers are integrated into the battery structure and actively participate in the electrochemical reactions.

Upgraded carbon fiber is a further strategy to achieve better properties thanks to the enhanced surface area and electrical conductivity provided by the high number of active sites of the carbon fiber electrodes. One possible approach is the growth of carbon nanotube and graphene on the surface of carbon fabric electrode [56] (Fig. 3-7), or the coating of carbon fibers with a polymer electrolyte [57] (Fig. 3-8).

3. Zinc-based batteries

Based on the reaction mechanisms occurring at the positive electrode, zinc-based batteries may be roughly classified into three groups, as shown in Fig. 4. The first category is formed by Zn-ion batteries (ZIB) which are rechargeable devices operating in a similar way to Li-ion batteries. In this type of battery, the reaction at the positive electrode is the intercalation and extraction of Zn ions, and neutral or slightly acidic electrolytes are typically used. The second category includes Ni-Zn and Zn-Ag which use aqueous alkaline electrolytes and have a larger negative electrode potential (−1.26 V vs. SHE) than neutral or acid electrolytes (−0.76 V vs. SHE) [23,27,33,35,36,38,39,42,46,58–63]. The third category is related to Zinc-air batteries in which zinc is negative, an air-cathode is the positive electrode and the common electrolytes are KOH and NaOH [64]. In the following paragraphs, we briefly describe the above three categories of zinc-based batteries. Reproduced from [65] Copyright (2021) with permission from Elsevier. Reproduced from [66]. Reproduced from [67] Copyright (2014), with permission from Elsevier.

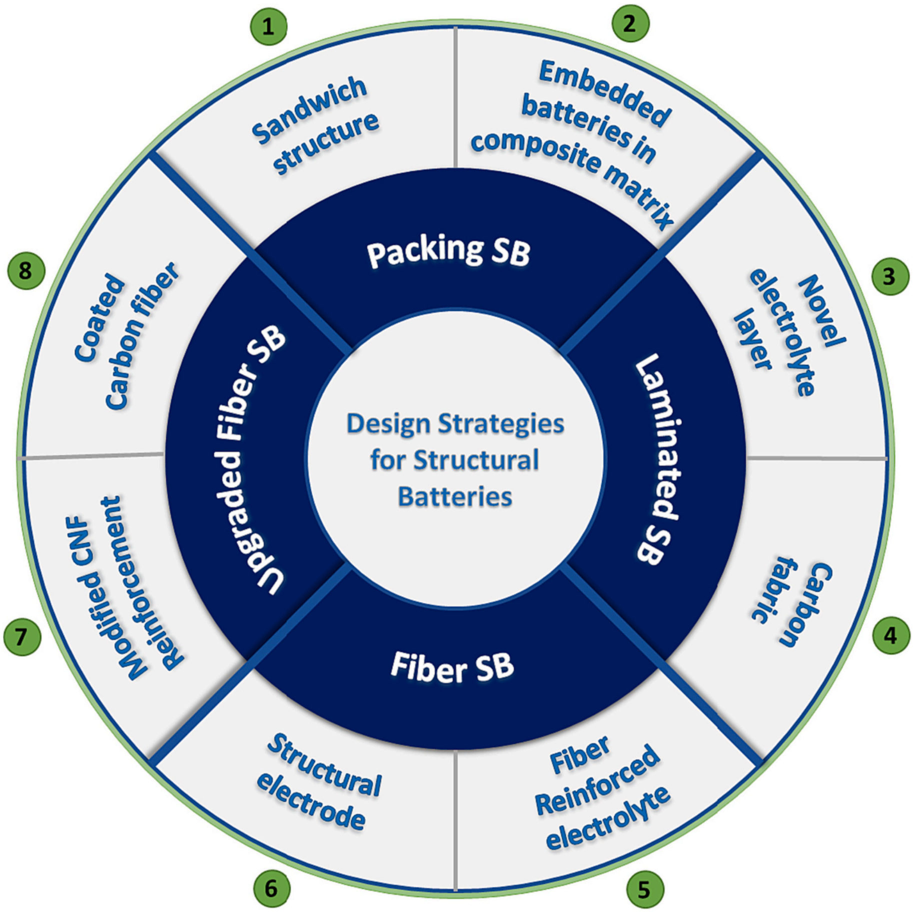


Fig. 3. Design strategies for structural batteries' substructures (CNF=carbon nano fiber, SB = structural battery).

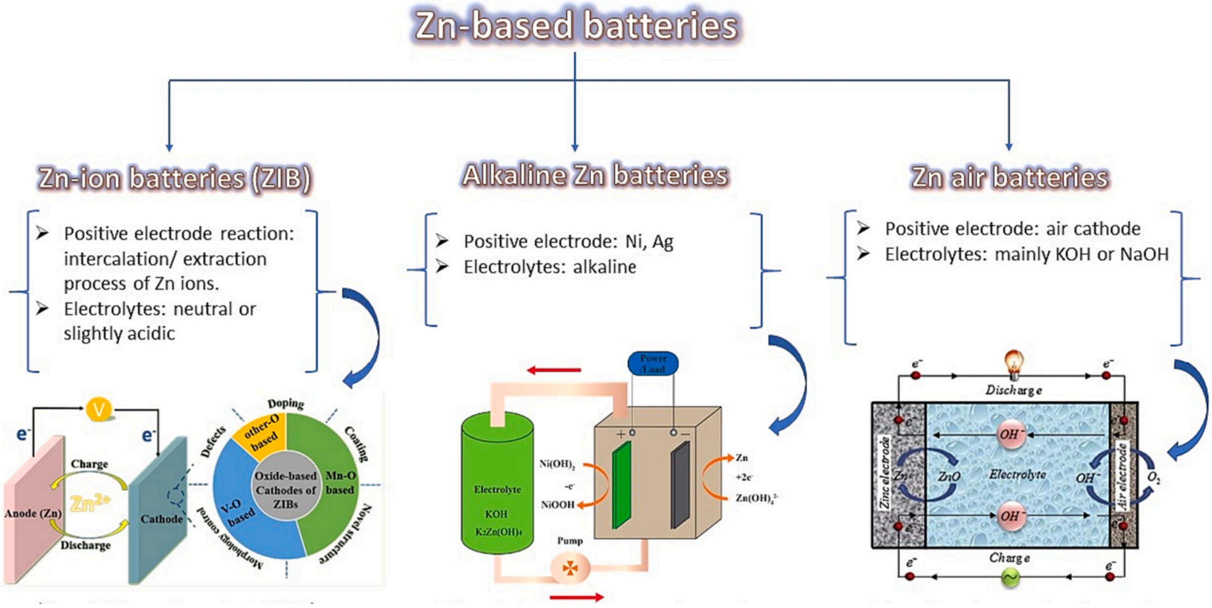


Fig. 4. Zinc-based batteries classified in light of the positive electrode reaction mechanisms.

Zn-ion batteries: ZIBs present several advantages that make them suitable for ZnSBs: high volumetric energy density, exceptional safety and cycle stability, as well as the facile battery installation process which does not require an anhydrous and oxygen-free environment. The energy density of ZIBs is determined mainly by the electrochemical characteristics of cathode electrocatalysts. Among them, Prussian blue analogs, Mo_6S_8, MnO_2, and V_2O_5 have been deeply investigated to attain amazing electrochemical performance. Among these candidates, MnO_2 has been encouragingly studied as an attractive cathode material because of its particular properties in interlayer distance, discharge capacity, etc. and applied in many flexible and aqueous based energy applications [28,50–53,61]. Manganese is a plentiful element in the earth's crust. Therefore, low-cost MnO_2-based materials are particularly competitive for ZIB cathode electrocatalysts in comparison with others [54]. However, ZIBs with MnO_2 as a cathode electrocatalyst have different electrochemical activity depending on the crystalline forms obtained under different reaction conditions. The four most common MnO_2 crystal phases are α-MnO_2, β-MnO_2, γ-MnO_2, δ-MnO_2. Even the thermal stability of different crystallographic structures of MnO_2 is different (Fig. 5) [55].

The creation of Zn-MnO_2 based batteries is a very interesting and exciting breakthrough. Although several past attempts have failed due to the production of irreversible discharged species in alkaline electrolytes, resulting in poor cycling performance, the rechargeability of aqueous Zn-MnO_2 batteries has recently been increased also thanks to the use of a moderately acidic electrolyte [68]. Nevertheless, the mechanism of chemical reactions involving MnO_2 polymorphs is still up for debate [28]. For instance, it has been proven that electrochemical Zn-incorporation in -MnO_2 goes through a phase change from a tunnelled architecture to spinel $ZnMn_2O_4$, layered Zn-buserite, or birnessite. The majority of these structures break down when they are cycled [69].

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.

In Fig. 6, a Ragone plot compares the specific energy and specific power of commercially available zinc-based batteries [62].

Alkaline Zinc batteries: the well-developed ones are especially Ni-Zn and Zn-Ag batteries. Ni-Zn batteries can deliver high power density in aqueous electrolytes with stable cycle performance. This is due to their ability to undergo valence transformations, allowing for multiple redox reactions to occur in aqueous environments [70–73]. For this reason, they are promising candidates for green power sources. However, Ni-Zn batteries still present low energy density and limited cycle life. Additionally, they can be damaged by deep discharging and are not suitable for high current applications.

The other main type of alkaline batteries consists of Zn-Ag batteries, which, besides a very high power density, exhibit a notable energy density, high conductivity, reversible oxidation reactions, and tunability of oxide properties, being promising for various applications, particularly in the field of consumer electronics, diagnostic devices, and biomedical applications [74]. However, their very high cost, their low

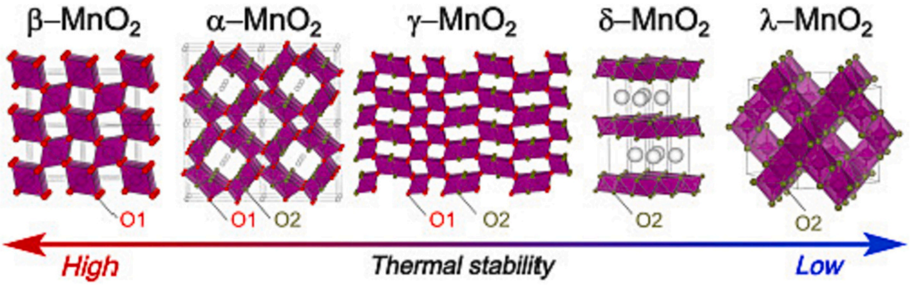


Fig. 5. Crystallographic structure and thermal stability of different MnO_2 crystallographic structures. Reproduced from [55] Copyright (2022) with permission from Elsevier.

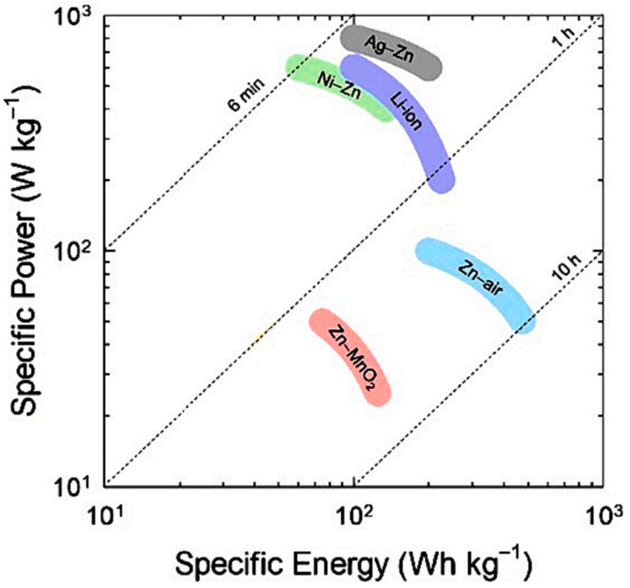


Fig. 6. Ragone diagram of zinc-based batteries and comparison with Li-ion systems. Reproduced from [62] Copyright (2018) with permission from Elsevier.

cycle life, decreased performance at low temperatures, and sensitivity to overcharge still make them suitable for miniature power sources and underwater and aerospace applications [75–78].

Zinc-air batteries: their power from the reaction between zinc and oxygen present in the air. One notable characteristic of these batteries is their extended shelf life and cost-effective manufacturing. They also exhibit a flat discharge voltage and offer a high volumetric energy density, surpassing most primary batteries. However, their performance is reliant on ambient conditions, as exposure to outside air causes them to dry out. Additionally, they have limited output and a relatively short lifespan. Furthermore, the efficiency of zinc-air batteries is influenced by the possibility of air electrode flooding, which can affect their overall potential [79–87]. Although the Zn-air battery has the maximum discharge capability among zinc-based batteries, issues with the half-open system, including CO_2 poisoning and evaporated electrolytes, still cause concern [88]. Moreover, the major disadvantage is their limited power output, which is mainly due to the inadequate performance of air electrodes. Despite extensive study and advances, electrically rechargeable Zinc-air batteries still have a lot of room for improvement. The specific requirements in materials science and engineering for zinc-air batteries are reported in Fig. 7.

Based on the previous analysis of the different types of zinc-based batteries, the studies available in the literature on ZnSBs are focused on Zinc-ion SBs, whose zinc-ion intercalation/deintercalation mechanism is promising for structural composite battery applications [28]. Furthermore, while alkaline and zinc-air batteries have some drawbacks including short service life and cost for the former, and low voltage and weight for the latter, ZIBs have proved to possess the best electrochemical performance in terms of rechargeability and durability among the Zinc based batteries, making them suitable candidates for ZnSBs.

4. Zinc-based structural batteries (ZnSBs)

4.1. Zinc-ion structural batteries design specifications

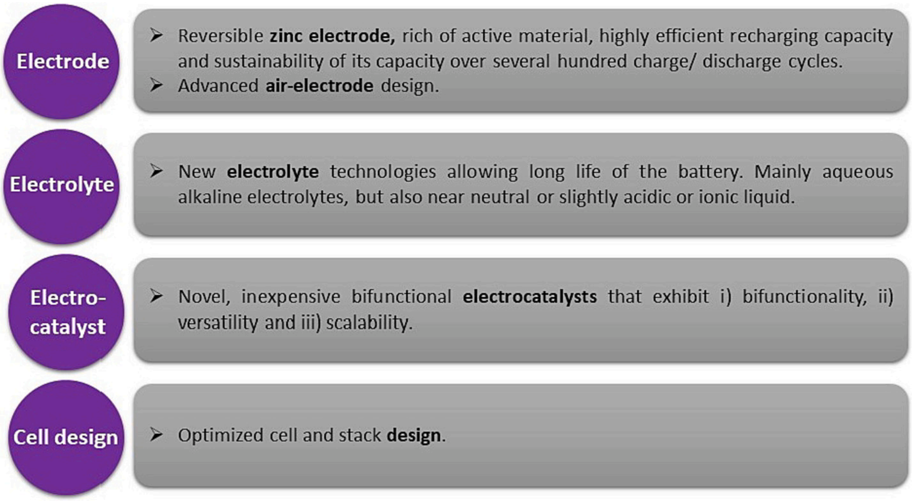
Numerous research teams worldwide are currently focused on enhancing the substructures of multifunctional structural batteries. As a result, zinc-ion structural batteries have gained attention in the research community. ZnSBs are classified according to several factors such as laminae, fiber reinforcement, surface functionalization, etc., to highlight the different approaches and techniques employed, which, in principle can be the same as those used for Li-ion SBs.

In this section the approaches specifically used for Zn-ion structural batteries will be discussed.

The battery-to-structure ratio is obviously one of the important aspects to keep in mind also for ZnSBs and the proposed solutions provide great potential to significantly reduce the weight of future electric transport systems [28]. However, the studies conducted so far on this topic have been on a laboratory scale, aimed at optimizing feasibility, electrochemical and mechanical performance, cycling and durability, and not yet quantitatively evaluating the overall battery-to-structure weight ratio for a commercial device.

The multifunctional level classification for Zn-ion structural batteries is reported in Fig. 8. ZnSBs with lots of potential applications for vehicles, buildings and grid-scale networks, etc., are sketched in Fig. 8(a). Examples of multifunctional systems and material approaches for Zn-ion structural batteries are shown in Fig. 8(b), (c) and (d).

Wang et al. [61] designed a corrugated SB (multifunctional system) by using a novel solid-state Zn^{2+} electrolyte as a composite of branched aramid nanofibers (BANFs) and poly(ethylene oxide) and found that the ionic conductance would be 10 times higher than the original polymer. As the unique packing design of the battery allows for separate functionality of the electrochemical and mechanical aspects, this study represents an example of the packing structural battery design strategy,


Electrode
- Reversible **zinc electrode,** rich of active material, highly efficient recharging capacity and sustainability of its capacity over several hundred charge/ discharge cycles.
- Advanced **air-electrode** design.

Electrolyte
- New **electrolyte** technologies allowing long life of the battery. Mainly aqueous alkaline electrolytes, but also near neutral or slightly acidic or ionic liquid.

Electro-catalyst
- Novel, inexpensive bifunctional **electrocatalysts** that exhibit i) bifunctionality, ii) versatility and iii) scalability.

Cell design
- Optimized cell and stack **design**.

Fig. 7. Specific requirements in material science and engineering for zinc-air batteries.

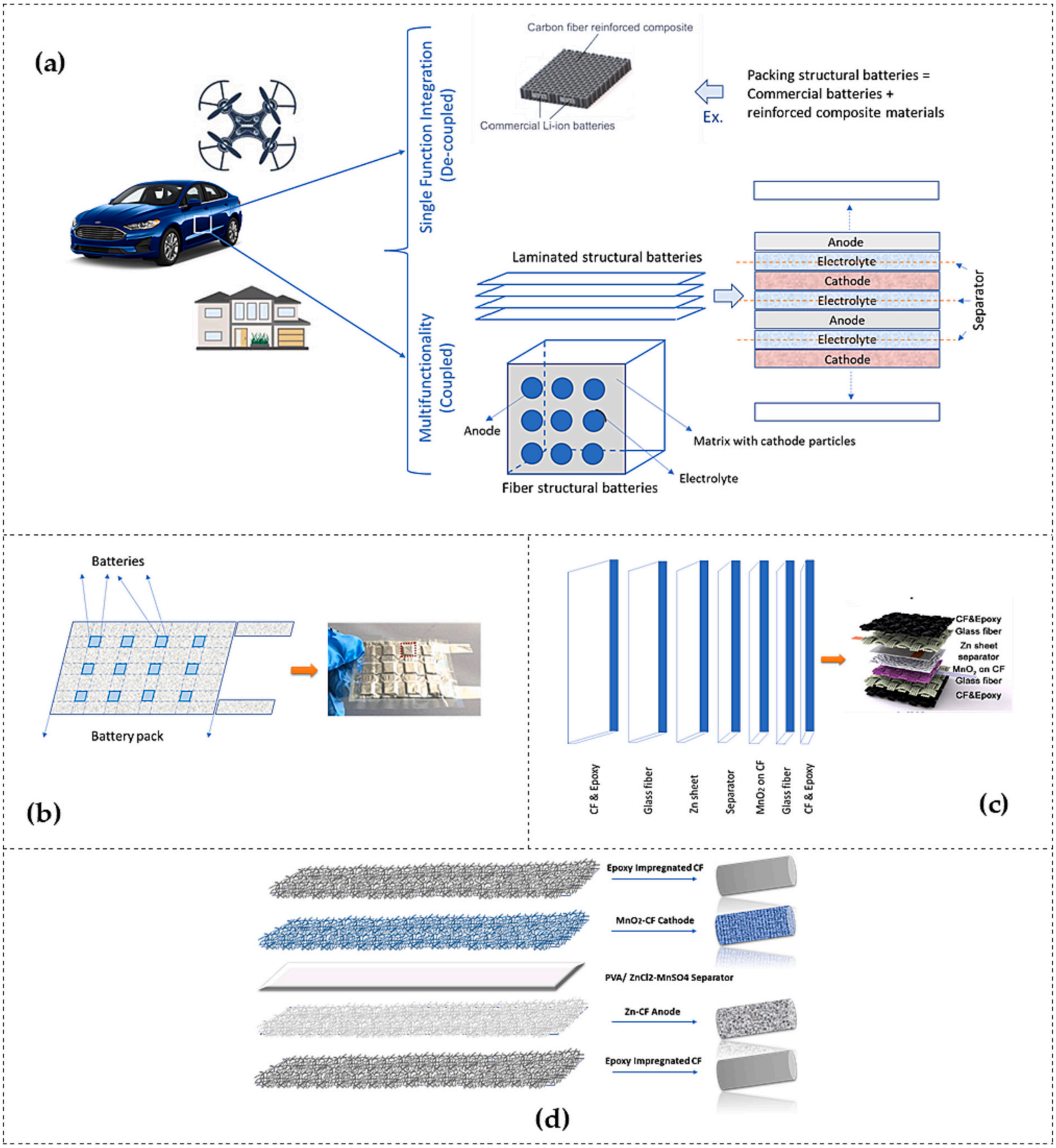


Fig. 8. (a) The multifunctional level classification of Zn-ion structural batteries; adapted from [41] Copyright (2022) with permission from Elsevier; (b) Zn-ion structural battery designed in the form of battery pack connected in series; adapted with permission from [61] Copyright 2019 American Chemical Society; (c) lay-up technique for Zn-ion structural battery; adapted from [89] Copyright (2022) with permission from Elsevier; (d) electrodeposition of Zn flake on the carbon fiber as anode instead of zinc foil; adapted from [28] Copyright (2021) with permission from Elsevier.

as illustrated in Fig. 3-1, wherein the researchers aimed to utilize the battery cells as the sole provider of electrochemical performance within the system (Fig. 8(b)). Their results showed also that the high stiffness of the BANF network combined with the high ionic conductivity of soft poly(ethylene oxide) allow for effective dendrites suppression and rapid Zn^{2+} transport.

The classification reported in Section 2, also when referred to as ZnSBs, is characterized by no explicit boundary among the three design categories of multifunctional materials. This is the consequence of the utilization of layered structural batteries in combination with the exceptional properties of carbon fibers, specifically their electrochemical and mechanical attributes. The layered design of batteries enables easier large-scale manufacturing, making it an appealing option. Additionally, carbon fibers have garnered significant attention in recent years for their potential applications in various types of structural batteries. Regarding these approaches and using the technology of vacuum infusion, Liu et al. [24] were able to create a carbon fabric strengthened ZnSB made of a lay-up of epoxy-impregnated carbon fiber fabric/glass fiber/Zn sheet with a copper tab/glass fiber separator/MnO_2 electrode coated on carbon fiber fabric with a stainless-steel tab/glass fiber/epoxy-impregnated carbon fiber (Fig. 8(c)). In addition, the glass fiber separator was pre-soaked in $ZnSO_4$ and $MnSO_4$ as the electrolyte before being installed in the structural battery. Since the separator is impregnated with a very small amount of liquid, there is no leakage of the electrolyte from the device during the device preparation process. Additionally, intriguing is the fact that the battery was created in the open air, highlighting the potential for massive-scale production of ZnSBs. However, the separator is not capable of transferring shear loads between the semi-structural electrodes, being a liquid impregnated fabric.

In another study of Chen et al. [28], carbon fibers were used to transport current and provide rigidity and mechanical strength; they proposed employing the Zn-MnO_2 layered structural battery, which has a MnO_2 cathode and a zinc ion anode. The manufacturing process was a standard composite lay-up process. Electrodeposition of Zn flakes onto carbon fibers was used for the fabrication of the anode, and mild hydrothermal treatment was used for synthesizing MnO_2 directly on the carbon fibers, for cathode manufacturing. The separator is made of a gel electrolyte of PVA/$ZnCl_2$-$MnSO_4$, while the anode and cathode were then infused with an epoxy resin and cured (Fig. 8(d)). After curing the resin, the two carbon fiber laminates enclosing the separator were structurally and electrically connected to the carbon fiber reinforced electrodes. Also in this case, the gel based separator is not able to transfer shear loads between structural electrodes, dramatically limiting the bending stiffness and strength of this ZnSB.

4.2. Anodes, cathodes and electrolytes for zinc-based structural batteries

4.2.1. Anodes

The Zn-ion anode for structural batteries is generally in the form of zinc foil/sheet. Liu et al. [24] fabricated the Zn-ion structural batteries by using a vacuum infusion process with carbon fabric and glass fiber impregnated with epoxy resin. The anode was a Zn sheet having a thickness of 50 μm, adhered with a cooper foil tab with Epoxy conductive adhesive. Wang et al. [61] used as anode a zinc foil having a thickness of 5 μm of placed in a pouch-like cell assembled with a cathode material layer based on γ-MnO_2 synthesized by a redox reaction obtained mixing using $KMnO_4$ and $MnCl_2$, followed by drying and annealing and a solid Zn^{2+} electrolyte as a composite of branched aramid nanofibers and poly(ethylene oxide).

Another interesting approach consists of the preparation of a structural anode, made of carbon fibers coated by Zn flakes using electrodeposition [28]. The electrodeposition process was performed from a solution containing zinc sulfate heptahydrate and sodium citrate dihydrate at a constant voltage of −1.0 V for 1 h and the resulting mass loading of Zn in the anode was measured to be approximately 6.2 mg cm^{-2}.

4.2.2. Cathodes

Several approaches have been used to prepare cathode for Zn-ion structural batteries. A structural electrode made of carbon fiber fabric coated with MnO_2 slurry was prepared by tape-casting technique, resulting in efficient charge transfer and electrochemical performance, exhibiting a specific capacity of 155 mAh g^{-1} at a current density of 0.1 A g^{-1} [24]. Chen et al. [28] demonstrated the feasibility of producing a MnO_2 hydrothermally grafted carbon fiber cathode by impregnating the carbon fibers with a homogeneous solution of $KMnO_4$, $MnSO_4 \cdot H_2O$ and deionized water. The hydrothermal synthesis offers several advantages that make it suitable for producing cathodes for carbon fiber reinforced Zn-MnO_2 structural composite batteries. First of all, it allows for the uniform coating of the active material (MnO_2) on the carbon fibers. The process ensures that the active material is evenly distributed, resulting in a specific capacity of 145.9 mAh g^{-1} at 0.1 A g^{-1}. In addition, hydrothermal synthesis promotes strong adhesion between the active material and the carbon fibers.

Wang et al. [61] studied a cell with a cathode made of MnO_2 and graphite powders and a solid composite electrolyte made of branched aramid nanofibers and poly(ethylene oxide) which helps prevent the growth of Zn dendrites and enables fast transport of Zn^{2+} ions. They showed that MnO_2 could highlight the transformative effect of the solid electrolyte on the battery functionality and design. The used MnO_2 powder was of the crystallographic type of γ-MnO_2 and it revealed a well- defined reversibility of Zn^{2+} ion in the cell, providing a specific capacity of 146.2 mAh g^{-1} at 0.1 A g^{-1} and a Coulombic efficiency of 96–100 % after 50–100 cycles. Han et al. [90] reported a cell with a MnO_x/N-C nanorod cathode material produced by a hydrothermal synthesis approach starting from a homogeneous solution of $KMnO_4$, hydrochloric acid and deionized water in autoclave. Afterward, the collected precipitate was mixed with two methanol solutions of 2-methylimidazole and PVP, and $Zn(NO_3)_2 \cdot 6H_2O$ and MnO_2, a brown precipitate was formed. The obtained precipitates, were then centrifuged, washed with anhydrous methanol many times, dried and heated to 700 °C in a tube furnace with a flowing Ar atmosphere to obtain MnO_x/N-C nanorods. This cathode guaranteed a specific capacity of 114.8 mAh g^{-1}, still maintained at 61.7 mAh g^{-1} after 500 cycles.

4.2.3. Electrolytes

Mechanically resistant electrolytes possessing suitable ionic conductivity are one of the possible strategies for structural batteries. Therefore, finding an appropriate electrolyte for structural batteries has also been a challenge in recent years. Liu et al. [91] combined the high mechanical properties of glass fiber (GF) fabric with the high ionic conductivity of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVHF) polymer, and fabricated a novel electrolyte for Zn-ion structural batteries. The structural electrolyte provided high ionic conductivity of $4.4 \cdot 10^{-4}$ S cm^{-1} and excellent tensile strength of 110 MPa, along with great properties for the designed Zn-ion structural battery cell in mechanical strength, energy density, capacity retention and Coulombic efficiency. This is very promising and instructive for future works [91].

Zinc ion batteries use electrolytes that can be aqueous, inorganic salt, or organic types. For Zn-based batteries, using the $ZnSO_4$ is very common because it offers great properties such as high solubility, cost-effectiveness and compatibility with aqueous systems [92]. Furthermore, also in Zn-ion structural batteries, the electrode reactions are dependent on their electrolyte, the pH classification of an electrolyte determines the specific reactions that happen for cathodes and anodes in a zinc-based battery (Fig. 9).

4.3. Electrochemical performances of zinc ion structural batteries

Danzi et al. [32] showed that multifunctional structural batteries could approach the electrochemical performance of traditional batteries, providing specific energy values and increased endurance for micro unmanned aerial vehicles. Ekstedt et al. [94] compared traditional lithium-ion batteries and structural batteries in terms of specific energy, revealing the challenges in matching lithium-ion battery performance. Therefore, although structural batteries show potential, they still encounter challenges in reaching the same electrochemical performance as lithium-ion batteries.

For the zinc-ion structural batteries, there is the same trend as the lithium-ion batteries, i.e., there is the need to reach the electrochemical performance of traditional zinc-ion based batteries, as it is still too far from those. In this regard, Hansen and Liu [92] gathered together the capacity for various solid-state zinc-based batteries in a vast range from 123 to 350 mAh g^{-1}.

Han et al. [90] interestingly compared the properties of different lithium-ion structural batteries with zinc-ion structural batteries; as a result, they showed that their new result for zinc-ion structural battery is comparable with previously reported structural energy storage materials based on lithium-ion. The capacity for lithium-ion based structural batteries was between 7.6 and 62 mAh g^{-1} and for the zinc-ion structural battery was 85 mAh g^{-1}, and also energy density for lithium-ion structural batteries was from 36 Wh kg^{-1} to 102 Wh kg^{-1} and for the zinc-ion structural battery was 115 Wh kg^{-1}.

Liu et al. [91] introduced a structural electrolyte GF/PVHF/KL-Z (fabricated with kaolin and Zinc trifluoromethanesulfonate) for use in

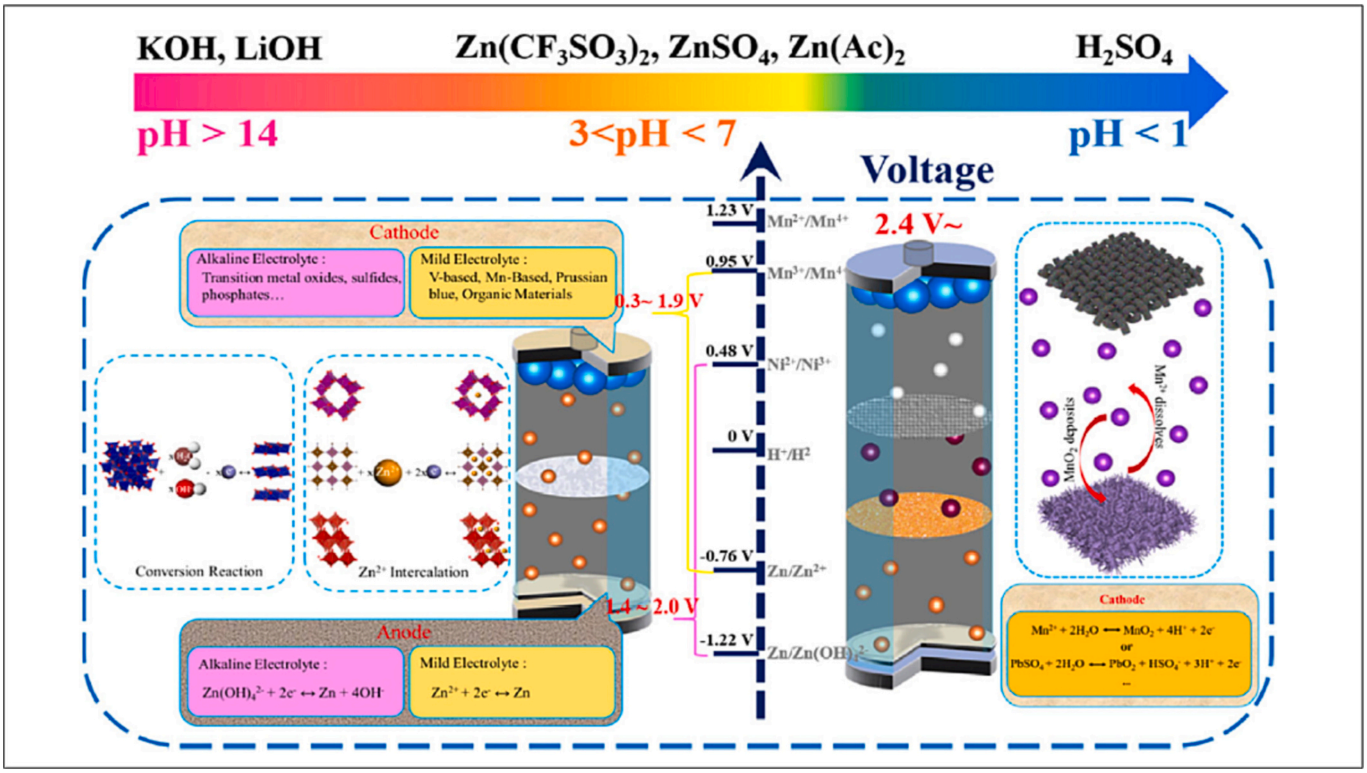


Fig. 9. Reaction mechanism of Zinc based batteries in different electrolytes. Reproduced from [93] Copyright (2021) with permission from Elsevier.

structural Zn-ion batteries, featuring both robust mechanical strength and impressive electrochemical performance. The electrolyte exhibited a high ionic conductivity of 4.4·10^{-4} S cm^{-1}, as reported in Section 4.2.3, enabling fast Zn^{2+} transmission and effective suppression of zinc dendrites. When integrated into carbon fiber-reinforced structural Zn-ion batteries, these devices achieved a high energy density of 159.0 Wh kg^{-1}, maintaining excellent cycling performance with a capacity retention of approximately 94.6 % after 500 cycles and a Coulombic efficiency close to 100 %.

Liu et al. [95] made significant advancements in the field of structural batteries, with a particular focus on electrochemical aspects and power density. In their study, they developed optimized structural Zn-ion batteries that integrate excellent mechanical properties with remarkable electrochemical performance. Their electrochemical achievements are noteworthy, and their optimized structural Zn-ion batteries reached a high specific capacity of 265.0 mA h g^{-1} at 1 A g^{-1}, which surpasses the performance of regular structural batteries. Moreover, they achieved the impressive energy density of 115 Wh kg^{-1}.

Also, Lim et al. [96] conducted a study focusing on the development of multifunctional structural batteries for electric vehicles, with a strong emphasis on the electrochemical aspects. They introduced a versatile approach for incorporating $LiMn_2O_4$ (LMO) active materials into structural batteries, both in a self-standing flexible electrode for multifunctional conformable applications (MFCA) and onto carbon fibers to create electrodes for multifunctional direct applications (MFDA). Their work involved the use of a well-designed aqueous electrolyte comprising lithium-zinc hybrid ions (LiZn), which demonstrated high compatibility and safety. In terms of electrochemical performance, their zinc-based structural battery delivered an impressive specific discharge capacity of 122.9 mAh g^{-1} at a current density of 100 mA g^{-1}, and it maintained a

Table 1
Summary of the key components and energy density of zinc-ion structural batteries.

Description of the structural battery	Anode/current collector	Cathode/current collector	Electrolyte	Energy density (Wh kg^{-1})	References
Carbon fiber reinforced ZnSB	Zn sheet with copper foil tab	Carbon fiber cloth with a stainless-steel foil tab and a MnO_2 electrode coating.	$ZnSO_4$ $MnSO_4$ (Liquid)	205	[24]
Carbon Fiber reinforced Zn-MnO_2 SB	Zn-carbon fiber by electrodeposition	MnO_2-carbon fiber cathode by hydrothermal synthesis	PVA/$ZnCl_2$–$MnSO_4$ gel electrolyte	181.5	[28]
Corrugated Structural Battery with solid-state Zn^{2+} electrolyte	Zinc foil	PEO polymer binder, 10 % graphite, and 80 % -MnO_2 moulded onto aluminum foil	solid-state electrolyte for Zn^{2+} based on branched aramid nanofibers (BANFs)		[61]
Structural energy storage composites made ZIBs, carbon fabric and epoxy resin	Zinc foil	MnO_x/N-C	$ZnSO_4$ $MnSO_4$ (Liquid)	115.2	[90]
Carbon fiber reinforced with PVHF and glass fiber fabric	Zn sheet	CF@$NH_4V_4O_{10}$	GF/PVHF/KL-Z	159	[91]
Carbon fiber reinforced ZnSB composite	CF@Zn	CF@PANI/MXene	$Zn(CF_3SO_3)_2$	115	[95]
Aqueous multifunctional batteries	Zn foil	$LiMn_2O_4$	($LiClO_4$) and (ZnTFS) in water	199	[96]

substantial capacity of approximately 80.3 mAh g^{-1} even after 1000 cycles at a higher current density of 2000 mA g^{-1}.

In order to show an accurate comparison among the zinc-ion structural batteries that most attracted the researchers, a list of various materials used for electrodes and electrolytes along with their energy densities are reported in Table 1.

As it can be seen in Table 1, all of the reported energy densities are in the range of lithium-ion structural batteries characteristics and even acceptable in comparison with the traditional lithium-ion batteries. The highest energy density has been reported by Liu et al. [24] for a zinc-ion structural battery with electrodes made of a composite reinforced with carbon fiber and coated with MnO_2 for cathode aside from the zinc sheet as anode and an aqueous electrolyte containing $ZnSO_4$ and $MnSO_4$.

4.4. Mechanical performance of zinc ion structural batteries

In a structural battery, mechanical performances are critical due to the interaction between the stress/strain behavior and the electrochemical processes and it is highly dependent on the multifunctional design. In packing SBs, poor bonding between the energy storage component and the composite material is generally observed. This may lead to a strain-induced reduction of electrochemical performance, a consistent reduction in the compressive and flexural properties and an eventual leakage of electrolytes under mechanical deformation [32]. The reduction of mechanical properties of packing structural batteries can be due to several factors such as lower mechanical performance of the battery compared to the composite material, geometric stress concentrations caused by the battery and limited load transfer at the battery-composite interface [97,98].

So far, in laminated SBs, fiber SBs and upgraded fiber SBs, generally the achieved mechanical performance is still lower than that of an equivalent unidirectional laminate made of carbon fiber reinforced (CFR) epoxy [99] Therefore, it is essential to provide a good load transfer ensuring that the mechanical stress acting on the battery is evenly distributed across the layers, thus preventing localized failures or weaknesses. For example, the laminated SB designed by Han et al. [90], sketched in Fig. 10(a), where high-strength carbon fiber and glass fiber layers and high-dielectric epoxy resin, with an aqueous electrolyte of zinc and manganese sulphates, were laminated with inner ZIB battery layers, in addition to good electrochemical properties, exhibited also a high mechanical performance without any delamination or cracking. The ultimate tensile strength and modulus reached 154.3 MPa and 10 GPa, respectively, as reported in Table 2. Both tensile and flexural properties were about 90 % of those of the reference carbon fiber composite and are also quite higher than those previously reported for Li-ion structural batteries. Good tensile properties were much more easily achieved than bending ones due to the presence of a liquid electrolyte with a shear strength close to zero [90,100]. But still in similar designs with carbon fiber reinforcement, zinc ion structural batteries had a higher flexural strength than lithium-ion batteries, i.e. 203.2 MPa [90] versus 46.12 MPa [100]. Fig. 10(b) reports also the energy efficiency η_e, which is the ratio of the energy density of the multifunctional material to the conventional energy storage device, and the structural efficiency η_s, which is the ratio of the modulus of the multifunctional material to that of a conventional structure. As observable from Fig. 10 (b), the multifunctional efficiency of the proposed ZnSB was quite higher than the data reported in the literature for Li-ion SBs.

Chen et al. [28] manufactured a laminated carbon fiber reinforced

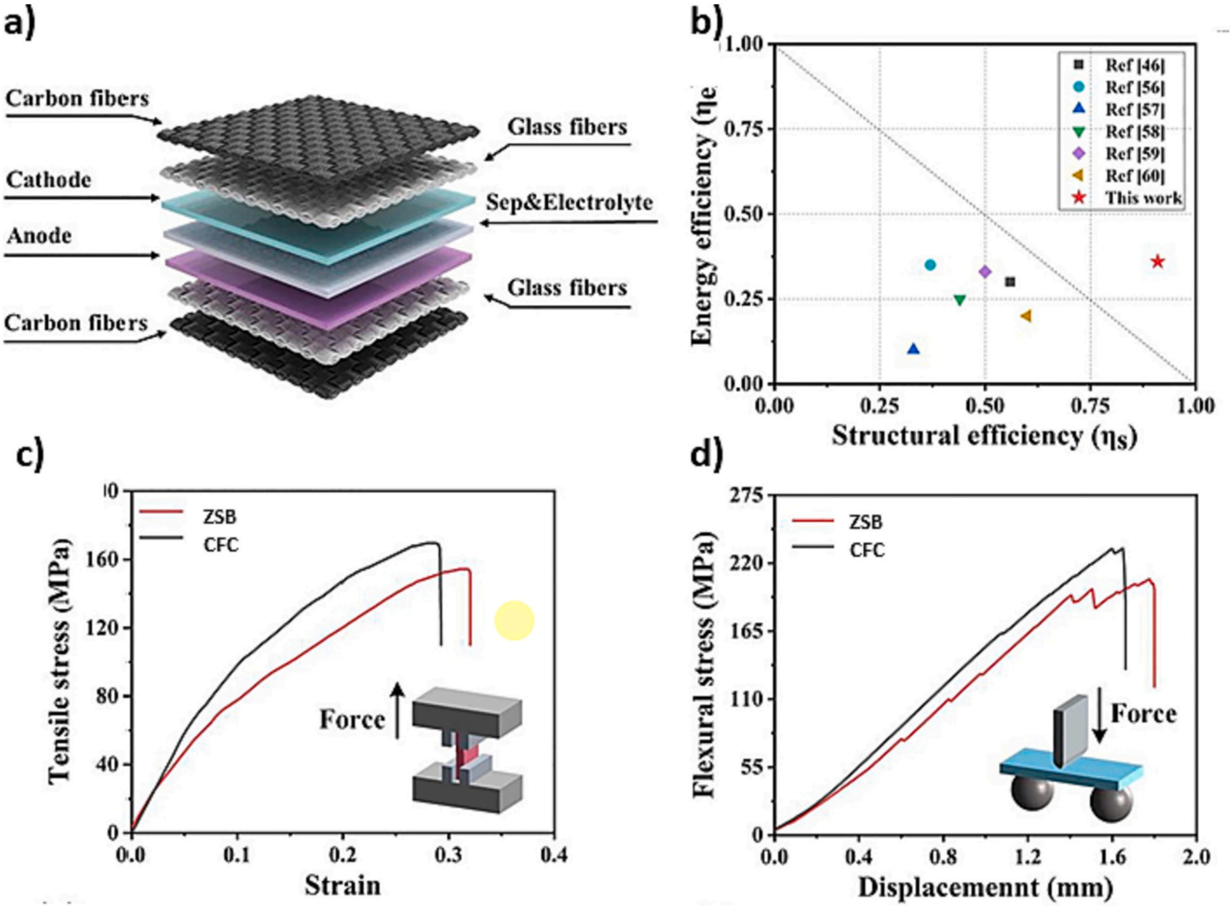


Fig. 10. (a) Lay up of a ZnSB; (b) multifunctional efficiency of ZnSB; (c) tensile test and (d) three-point bending test of ZnSB and a reference carbon fiber composite (CFC). Reproduced from [90] Copyright (2022) with permission from Elsevier.

Table 2

Mechanical properties of some of the zinc-ion structural batteries studies in recent years. TS = tensile strength, E = tensile modulus, CS = compressive strength; E_c = compressive modulus, FS = flexural strength; E_f = flexural modulus.

Anode/cathode/electrolyte	Tensile properties	Compressive properties	Flexural properties	Ref.
Zn-carbon fiber (anode), MnO_2-carbon fiber (cathode), $PVA/ZnCl_2–MnSO_4$ gel (electrolyte)	TS = 293.4 MPa E = 12.8 GPa	CS = 22.2 MPa E_c = 5.0 GPa	FS = 180.8 MPa E_f = 4.4 GPa	[28]
Zn sheet (anode), MnO_2 coated on carbon fiber fabric (cathode), $ZnSO_{4+}$, $MnSO_4$ (electrolyte)	TS = 179.5 MPa E = 3.05 GPa	CS = 179.0 MPa E_c = 5.9 GPa	FS = 229.6 MPa E_f = 12.9 GPa	[24]
zinc foil (anode), MnO_x/N-C (cathode), $ZnSO_4$, MnSO4 (electrolyte)	TS = 154.3 MPa E = 10.0 GPa		FS = 203.2 MPa E_f = 12.1 GPa	[90]
Zn sheet (anode), CF@$NH_4V_4O_{10}$ (cathode), GF/PVHF/KL-Z (electrolyte)	TS = 166.13 MPa E = 5.65 GPa	CS = 171.34 MPa E_c = 3.76 GPa	FS = 584.5 MPa E_f = 52.4 GPa	[91]
CF@Zn (anode) CF@PANI/MXene (cathode), $Zn(CF_3SO_3)_2$ (electrolyte)	TS = 194.6 MPa E = 9.6 GPa	CS = 201.2 MPa E_c = 13.5 GPa	FS = 268 MPa E_f = 8.6 GPa	[95]

structural composite battery by co-curing current collectors, a carbon fiber reinforced MnO_2 cathode and a carbon fiber reinforced Zn anode in a vacuum consolidation method. The obtained ZnSB exhibited a very high tensile strength of 293.4 MPa, higher than the maximum value reported by Meng et al. for lithium-ion structural batteries, equal to 280 MPa [101]. The mechanical properties of the zinc-ion structural batteries reported in the literature are shown in Table 2.

A promising approach to increase the mechanical properties of ZnSB consists in the use of structural electrolytes such as that proposed by Liu et al. [91,98], based on glass fiber fabric and PVHF polymer. The electrolyte had a tensile strength of 110 MPa and was also able to stop the growth of zinc dendrites by enabling a fast movement of Zn^{2+} ions. The obtained ZnSB with this electrolyte showed a tensile strength of 166.1 MPa and a bending strength of 584.5 MPa (see Table 2).

Another strategy to increase the mechanical performance of ZnSB is based on improving the performance of structural electrodes, as proposed by Liu et al. [95]. A structural anode was prepared by electrodepositing Zinc on carbon fibers and a structural cathode was achieved by in-situ growth of metal carbides and nitrides, known as MXenes, on carbon fibers. Besides a poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP)/Zn-MMT separator was saturated with Zn $(CF_3SO_3)_2$ and acted as an electrolyte. The fabricated cell showed exceptional mechanical properties, including a bending strength of 268.0 MPa and a Young's modulus of 4.9 GPa. A recent investigation of Lim et al. [96] devised a novel cell concept based on Li-Zn hybrid ions, where $LiMn_2O_4$ was the cathode material and Zn metal foil the anode. For the cathode, a Young's Modulus of 13.57 GPa was achieved, an order of magnitude higher than conventional slurry coated cathode materials.

Even if the mechanical performance of ZnSBs is promising, ZnSBs have not yet reached maturity for implementation. More research is still needed in order to increase the interface properties between the layers and to reduce the interlaminar stresses caused by the mismatch of material properties between adjacent layers. Suitable strategies would be both the choice of a solid battery electrolyte, where carbon fiber anode, a load-bearing separator, and a cathode material are immersed, and the design of a properly laminated lay-up with fiber orientations that minimize deformations and the risk of delamination.

5. Conclusions

The concept of structural batteries, which can simultaneously withstand mechanical loads and store electrochemical energy, has continuously attracted the researcher's interest toward reducing the weight-to-volume ratio of battery packs in electric vehicles, unmanned aerial vehicles, aerospace, etc. Although most of the research has been performed on Li-ion SBs, the safety, stability and availability issues of LIBs have driven the research toward alternative ion batteries, among which, zinc presents a good potential for the development of zinc-based structural batteries. In this review, the different types of zinc-based traditional batteries have been presented and the new designs of ZnSBs have been categorized and discussed to give future studies a better viewpoint.

The major achievements and perspectives can be summarized below.

1) The design with multifunctional materials, able to integrate enhanced electrochemical functionality and load bearing properties, seems to be the path with the greatest margin of success, based on the existing literature. To optimize the electrochemical and mechanical performance of ZnSBs, upgraded or novel multifunctional materials and new cell configurations are required.
2) New electrode materials and electrolytes are under investigation with plenty of room for improvement. Structural anodes made of carbon fibers coated by electrodeposited Zn flakes which increase the electroactive surface area of zinc anode, reduce local current density, and promote the uniform distribution of zinc ions on the surface of the anode could be a promising approach. Structural cathodes, such as those based on manganese oxides in different crystalline forms are promising for future studies. In addition, mechanically resistant electrolytes, possessing suitable ionic conductivity and stable charge and discharge performance, are another challenge to be faced.
3) The mechanical performance of ZnSBs is interesting and comparable with those of LiSBs, but they are still critical due to the interaction between the stress/strain behavior and the electrochemical processes. The most recent studies have shown that ZnSBs can exhibit favorable mechanical properties, especially a high ultimate tensile strength. The use of laminate sandwich strategies has proven effective in obtaining mechanical performance even in flexural tests. There is still a lot of research to do to increase the interface properties between the layers and reduce the interlaminar stresses caused by the mismatch of material properties between adjacent layers. A suitable strategy would be the design of a properly laminated lay-up with fiber orientations that minimize deformations and the risk of delamination.

CRediT authorship contribution statement

Francesca Lionetto: Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing. **Nasim Arianpouya:** Writing – original draft, Writing – review & editing. **Benedetto Bozzini:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Alfonso Maffezzoli:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Mehrdad Nematollahi:** Writing – original draft, Writing – review & editing. **Claudio Mele:** Conceptualization, Methodology, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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