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Pushing the Limit of Flexible Batteries

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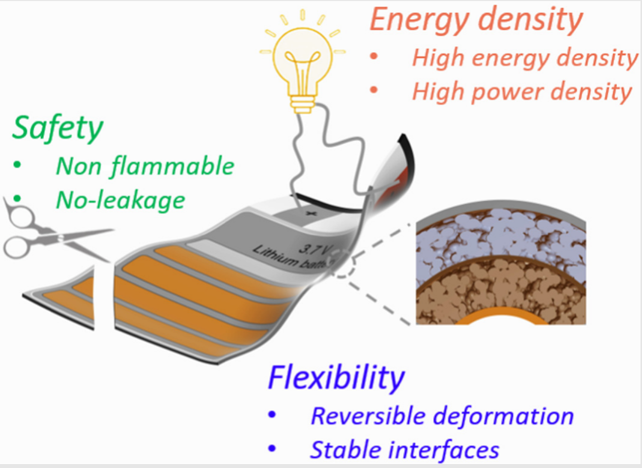
Alongside the rapid development of flexible and wearable electronics, the search for reliable, safe, and high-energy rechargeable flexible batteries (FBs) has become a research hotspot in recent years. Although there are some prototype FBs exhibited by the industry and a rapidly increasing number of publications reported by academia, most demonstrations are shown on a laboratory scale, and it is still difficult to find real implementation of the technology in the market. This perspective aims to discuss and analyze the key metrics, including energy density, flexibility, and safety, that are critical to pushing FBs to a commercially viable level, with a special focus on the lithium batteries and zinc batteries most reported in the literature. We first compare the figure of merit of FBs (*fb_{FOM}*) of existing lithium-based and zinc-based FBs with the requirement for market applications. We then analyze the most desired cell configurations toward high flexibility, followed by systematic discussions on features and materials selection toward high energy density FBs. Third, we discuss strategies to enhance battery safety. An outlook of the future developments needed to address the gaps between the state-of-the-art demonstrations and real applications is provided at the end of this article.



Keywords: **flexible battery, energy density, safety, lithium battery, zinc battery**

Introduction

Over the past two decades, research communities have witnessed the booming development of flexible and wearable electronics.[1–3] Accompanied by the rapid progress of advancing those electronic functions and mechanical compliance, there is also an increasing attention on the need for rechargeable flexible batteries (FBs) that can provide stable energy to power the electronic devices and systems when they are in uniaxial, biaxial, or even omnidirectional deformation. Moreover, FBs offer the opportunity to seamlessly integrate the power supply with flexible devices, from the mechanical point of view, which may eliminate the structural constraint of design form factors of flexible and wearable electronics and lead to the paradigm shift of product developments in the future.

Early works of FBs are mostly developed based on lithium-ion battery (LIB) chemistry.[4] In recent years, there are a rapidly increasing number of reports of FBs using aqueous zinc battery and lithium metal battery (LMB) chemistries.[5] Each of these battery chemistries shows its advantages and disadvantages. For example, LIB chemistry is the most mature, and it is believed that flexible LIBs will be the first to be implemented for practical applications. On the other hand, flexible LMBs may outperform flexible LIBs in energy density but exhibit more safety concerns, while aqueous zinc batteries exhibit higher safety but poor energy density.[6] High-energy lithium/zinc-air systems are not included here owing to their half-open nature and inferior electrochemical kinetics which leads to unsatisfactory long-term stability, complicated configurations, as well as high possibilities of electrolyte leakage and thermal propagation. Other configurations, such as high-power integrated supercapacitors, are not discussed considering the relatively low energy density of every single unit.[7,8] Nonetheless, these energy storage systems of varied characteristics could be integrated to play different roles and functions to further maximize the performances of flexible devices.

Despite the fact that various strategies have been proposed to render the battery flexible, the majority of them significantly sacrifice energy density and cycling stability.[9–11] For example, the energy density of state-of-the-art FBs reported to date is normally lower than 300 Wh L^{-1}, while commercial LIBs can easily exceed 600 Wh L^{-1}. Therefore, the overall performances of FBs have not shown obvious advantages over commercial, rigid types of LIBs. Moreover, the safety issue of FBs has not been verified under the requirement of realistic applications. To date, the development of FBs is still at the proof-of-concept stage. There is a huge tradeoff among energy density, flexibility, and safety.

This paper discusses how to push the limit of the three most important metrics of FBs, including energy density, flexibility, and safety, from the perspective of battery chemistry, materials selection, and structural configuration. In particular, the most frequently reported battery chemistries, lithium and zinc, are taken as a case study for this detailed discussion. We first briefly review the mechanical limits of commercial rigid batteries and compare the performance of state-of-the-art lithium batteries and zinc batteries with the industrial requirements of FBs for practical applications. We then discuss the engineering of battery configurations to realize high flexibility, and how to achieve high energy density based on these configurations, followed by a comparison of the theoretical voltages and capacities of different electrochemical active materials, and the energy density of batteries made of different electrode pairs at a standard cell configuration. In the third part, we investigate the strategies to circumvent the safety issues of FBs. At last, we provide an outlook on the future direction in this field.

Overview of Flexibility and State-of-the-Art FBs

In principle, all materials are flexible when they are thin or soft enough. The flexibility is largely determined by the yield strain of the materials. In commercial LIBs, the yield strains of Cu or Al current collectors are less than 1%. According to the IPC-2292 standard, the minimum bendable radius of curvature (r) of a flexible device should be 10 times the thickness (T) of the device.[9,10] At this point, the applied strain (ε) of the device is calculated to be 5% by the equation $\varepsilon = T/2r$. Considering that the ε is much larger than the yield strains of metal foils, repeated bending of the battery will easily lead to cracking and contact failure of metal foils especially under conditions where the bending radius is rather small but the mass loading/thickness of active materials is relatively low. If the thickness of the electrode is further increased, it is highly challenging to achieve a larger bending radius owing to the breaking/detachment/short circuit/etc. of the active material on top of the current collectors. Also, the allowable bending radius may be large enough to prohibit the breakage of metal foils. In this sense, the breakage of metal foils is highly sensitive to the bending radius while that of active electrodes is more susceptible to the battery thickness. For those high-energy devices under most flexible scenarios, they generally show comparatively large bending radius and hence the failure of active electrodes is more readily observed than that of current collectors.

To improve the flexibility, researchers have developed a number of methods, which can be generally categorized into two strategies, namely “soft structure strategy” and “soft materials strategy.” The soft structure strategy focuses on developing special structures that improve the bendability of conventionally unbendable batteries, while the soft materials strategy aims at developing intrinsically flexible materials to replace rigid ones, such as metal foils. It should be noted that most studies to date describe flexibility by simply giving the smallest r for which the battery can be bent. However, this approach cannot fully reflect flexibility because r is a function of T, and T is closely proportional to the areal mass loading and areal energy density (E_a) of the battery. Therefore, a figure of merit of FB (fb_{FOM}), where $fb_{\mathrm{FOM}} = E_a/r$, is proposed to provide a more balanced evaluation of the energy density and flexibility of FBs.[9] Here, the FOM could be deemed as a theoretical indicator to reflect and evaluate the suitability of the lab-scale FBs for industrial requirements toward real applications. FBs with high FOM but low E_a are highly promising in meeting industrial requirements when adopting thick tandem configurations or other advanced battery fabrication techniques.

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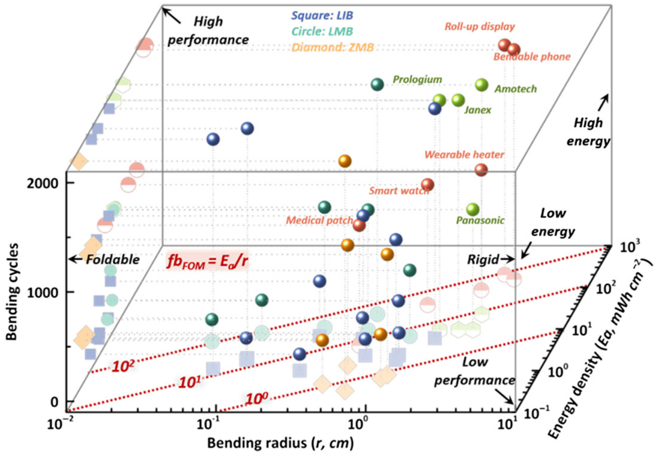

Figure 1 | *FOM of state-of-the-art FBs based on LIB, LMB, and zinc-metal battery (ZMB).*

Here, we plot the fb_{FOM} of representative lithium-based[12–27] and zinc-based[28–32] FBs, and benchmarked with FBs desired by several potential wearable applications in Figure 1. Thereinto, zinc-based FBs show limited energy density and their fb_{FOM} values are far below the requirements for practical applications. In terms of lithium-based FBs, several industrial prototypes using metal foils as current collectors and commercial intercalation-type electrodes show fb_{FOM} values less than 10, which is also not ideal for the listed applications. To overcome these shortages, soft materials with higher yield strain are explored to improve the intrinsic flexibility and novel active materials with high specific capacity are utilized to increase the energy density of the FBs. Directly replacing the brittle Cu and Al foils with electrochemically stable, thin, lightweight, and mechanically tough conductive materials is one simple way to improve the fb_{FOM}. Several potential alternatives such as carbon nanotube film,[12] graphene film,[19] Mxene film,[33,34] metal-coated plastics,[35] and metal-coated textiles[13] have been studied as current collectors and demonstrated largely a reduced bending radius lower than 10 mm. For example, a very low radius of 0.65 mm with a high fb_{FOM} of 16.9 was presented when Ni-coated polyester textiles were used as current collectors.[13] Special attention should also be paid to how to achieve a high mass loading of active materials on these porous flexible current collectors. It is highly desirable to develop innovative binders, optimize the binder content, tailor the slurry viscosity, or intentionally introduce pores during the slurry coating.[36] Additionally, it is also possible to fabricate FBs based on current collector-free electrodes by assembling the active materials with nanomaterials. The building blocks of nanomaterials play important roles as binders and conductive additives to ensure the integrity of the electrodes during repeated flexing. For example, the technique of vacuum filtration,[14] spray coating,[17] electrospinning,[27] and so on are reported to fabricate paper-like flexible electrodes. A flexible battery with low bending radius of 1 mm and a good fb_{FOM} of 18 was reported by sequentially spraying silver nanowires and active materials on fibrous mats.[17]

Apart from making softer electrodes and current collectors, developing high-capacity electrode materials, for example, Si and Li metal anodes and S cathodes can also endow higher energy density, thus a higher fb_{FOM} to the batteries. For instance, through combining a flexible Li metal composite anode with conventional layered oxides-based flexible cathodes, a FB with an E_a of ~9.3 mWh cm^{-2} and a r of 5 mm was reported, resulting in a good fb_{FOM} of 18.6.[21] Further studies suggested that the areal energy density and fb_{FOM} of the FBs can be doubled upon adopting a tandem cell configuration without sacrificing flexibility. By using this method, a very high E_a of 22.7 mWh cm^{-2} and fb_{FOM} of 45.4 were demonstrated, which is very close to the application target of a watch belt.[23] The fb_{FOM} could reach as high as 80 when both the anode and cathode used high-capacity materials, as demonstrated by several flexible Li-S batteries.[24,26] It should be noted that the main disadvantage of these batteries using high-capacity materials is the lack of electrochemical stability and mechanical durability in the long term.

Further increasing the E_a to an applicable level without impeding the flexibility should be the research focus in future studies. The design of battery configurations and the exploration of advanced materials and battery chemistries are two parallel directions toward this goal, which will be discussed next.

Prevailing Cell Configurations Toward High Flexibility

We compare the conventional pouch configuration of a battery cell (Figure 2a) with most reported configurations of FBs, including decoupled-structure FBs (Figure 2b), intrinsically soft FBs (Figure 2c), and fiber-shaped FBs (Figure 2d). As shown in Figure 2b, flexibility can be achieved through the decoupled structure where the functions of energy storage and flexibility are achieved separately by rigid sub-cell units and flexible interconnects. The interconnects bear the strains upon bending while the surrounding rigid sub-cell units maintain the original shape to play the role of energy storage.[37] Spine-like,[38] human joint-like,[39] kirigami-based,[40] and origami-based batteries[41] and other bioinspired structures[42] have been demonstrated to show balanced energy densities and flexibility. The flexibility via this configuration is self-limited because the rigid subcells hamper the conformal bending and the bending direction is unidirectional. Noting that the bending radius of these decoupled batteries should be the curvature when the whole device (both the

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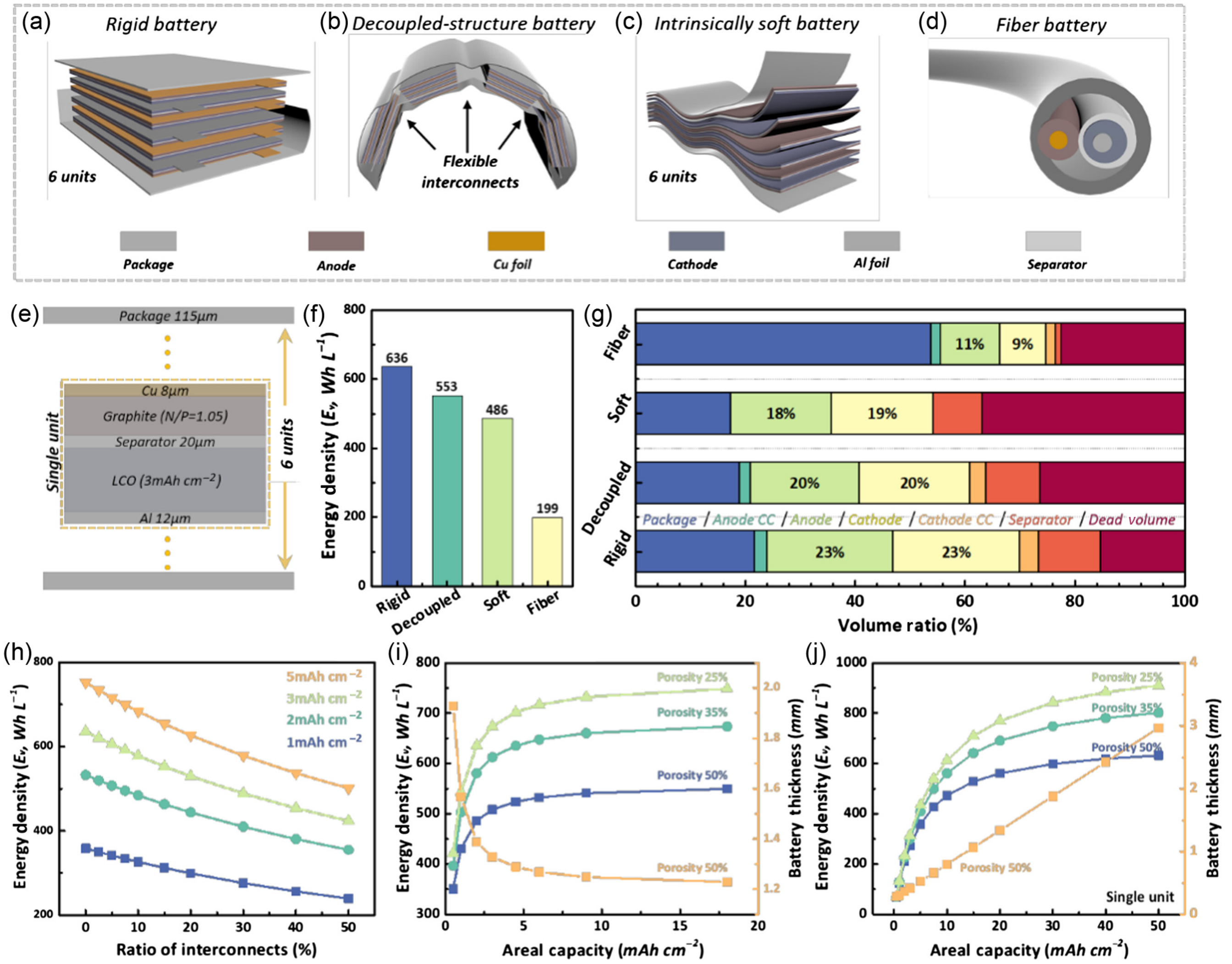

Figure 2 | *Cell configurations toward high flexibility and their merits and demerits. Schematic illustration of the (a) rigid battery; (b) decoupled-structure battery; (c) intrinsically soft battery; and (d) fiber-shaped battery. (e) Simplified graphite/LCO battery of 6 units for calculations with a fixed areal capacity of 3 mAh cm^{-2}. (f) Volumetric energy densities and (g) volume ratio of battery components of the four cell configurations. (h) The impacts of interconnect ratio on the energy density of varied areal capacities in the decoupled-structure battery. The impact of areal capacities and porosities on the energy densities and battery thickness in the intrinsically soft battery using (i) 6 units and (j) one single unit.*

flexible and rigid parts) instead of only the flexible interconnects is conformally applied to a cylindrical rod. From this viewpoint, smaller subcell units could bestow better bending capability. In addition, the electrochemically inert interconnects normally occupy a large ratio of the total volume, leading to lower energy density.

The intrinsically soft batteries that directly rely on soft materials with high tolerance to mechanical flexing can achieve better flexibility than the decoupled-structure batteries (Figure 2c). In addition to flexible current collectors and freestanding electrodes discussed in the previous section, the use of innovative polymeric binders, electrolytes, and flexible skeletons has proven effective in preventing cracks and the detachment of active materials upon flexing.[43,44] Increasing the porosity of the electrodes can also dissipate the strains during deformation and increase flexibility but lower the energy density inevitably.[37] More recently, mechano-graded electrodes with high mass loading were demonstrated to show brilliant intrinsic flexibility without sacrificing the energy density owing to the gradient-distributed maximum allowable strain.[45] In this sense, it's highly crucial to harmonize the mechanics and electrochemistry within the electrodes via tailoring the coating process, slurry recipe, and so on.[36,46]

Fiber-shaped batteries show obvious advantages of omnidirectional flexibility and potential of seamless integration into electronic textiles (Figure 2d). Recent research has demonstrated the mass production of fiber

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batteries in the scale of kilometers, with astonishing durability of over 100,000 bending cycles at a radius of 10 mm. The fiber batteries were woven into textiles and used to power electronic devices such as mobile phones.[47] However, fiber batteries also show distinct disadvantages when compared with other configurations. Their energy density is low and there is still a lack of suitable encapsulation materials.

To better compare the influence of different configurations on the energy density, here we utilize a simplified battery model consisting of a graphite anode and $LiCoO_2$ (LCO) cathode (Figure 2e) to calculate the volumetric energy density (E_V) (Figure 2f), component volume ratio (Figure 2g), and so on of these four cell configurations. The areal capacity of the cathode is fixed at 3 mAh cm^{-2} and the porosities of the electrodes are 25%. For the decoupled-structure battery, an extra volume of 15% is assumed for the inert interconnects.[39] For the intrinsically soft battery, a freestanding electrode with 50% porosity to provide adequate flexibility is taken. For the fiber battery, the data is estimated based on Peng's report.[47] The effective volume ratio of each cell component is then extracted based on these configurations (Figure 2g). The ratio of anode and cathode to the whole cell is 46.0% in the rigid battery, and this value decreases to 40.0%, 36.8%, and 19.3% after being designed into a decoupled-structure, intrinsically soft, or fiber-shaped configuration, respectively. Accordingly, the rigid battery showing an E_V of ~636 Wh L^{-1} could roughly meet the energy demands of all applications. The E_V of the decoupled-structure battery decreases by 13% to 553 Wh L^{-1} due to the dead volume coming from the flexible interconnects. The E_V of the intrinsically soft battery is 496 Wh L^{-1} is due to the high porosity. The fiber-shaped battery exhibits the lowest E_V of 199 Wh L^{-1} (Figure 2f).

Given fixed types of battery materials and battery chemistry, it is necessary to increase the effective volume ratio of the electrodes to increase E_V. For the decoupled-structure battery, it is essential to minimize the volume of the inert interconnects (Figure 2h) even though this may affect the flexibility. A higher mass-loading of electrodes can also effectively improve the E_V of soft batteries since the redundant components, such as the separators and current collectors, can be decreased. The same E_a of 67.5 mWh cm^{-2} can be readily achieved by nine pairs of 2 mAh cm^{-2} electrodes or two pairs of 9 mAh cm^{-2} electrodes (Figure 2i). The resulting E_V, however, will be 486 and 532 Wh L^{-1}, respectively. For an intrinsically soft battery, reducing the volume ratio of pores is critical to improving E_V. The porosity of the currently used electrodes for rigid batteries is normally ~25% for the balance of electrochemical performance and energy density, indicating a huge gap between the state-of-the-art soft batteries (~50%) and the rigid ones (Figure 2i). In the meantime, one can also fabricate high mass loading and intrinsically flexible electrodes to increase E_V. For example, a low E_V of 209 Wh L^{-1} is shown for a single-pair-electrode soft battery when the areal capacity of the electrode is only 2 mAh cm^{-2}. This value covers most reported results in the literature. The E_V can be significantly improved to 473 and 561 Wh L^{-1} when the electrode capacity increases to 10 and 20 mAh cm^{-2}, respectively. The E_V can reach ~600 Wh L^{-1} when a super high loading of 30 mAh cm^{-2} is used (Figure 2j). Several methods have been proposed to achieve the high mass loading and thick electrodes with areal capacity over 30 mAh cm^{-2} including the phase separation method,[48] electrospinning/spray method,[49] and the use of innovative binder.[50,51] However, the impact on the flexibility should be carefully considered and analyzed when making these electrodes.

Material Selection Toward High Energy Densities

As discussed before, commercial electrode materials show difficulty achieving the energy density target for FBs. Thus, the exploration of novel materials and battery chemistries is necessary for future research. Figure 3a shows the theoretical voltages (V) and capacities (C_a) of the available anode and cathode materials in lithium batteries.[52–55] Figure 3b projects the E_V of lithium batteries using different combinations of these anodes and cathodes, based on the cell configuration of the intrinsically soft battery we discussed in Figure 2e.

For the anode side, replacing graphite with SnO_2 (1334 mAh g^{-1}) results in an E_V gain of only 8.1%, mainly due to the relatively high delithiation voltage (~0.65 V) of SnO_2. The use of Si and Mg anode increases the E_V by 22% and 28%, respectively, exceeding 600 Wh L^{-1}. Pairing the LCO cathode with Li metal anode (100% oversize) leads to an E_V of 685 Wh L^{-1}. Ultimately, an anode-free cell could achieve an extremely high E_V of 752 Wh L^{-1}. For the cathode side, developing intercalation-type materials with higher voltages and higher capacities can effectively enhance energy density. The use of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) can increase the E_V to 714 Wh L^{-1} when using Li metal (100%) as the anode. E_V values of 749 Wh L^{-1} and 774 Wh L^{-1} can be obtained when high capacity Li-rich and Mn-rich layered oxides (LMR-NCM) and high voltage $LiCoO_2$ (HV-LCO) are used. Comparatively, conversion-type metal halides, oxides, and chalcogenides are regarded as promising cathode candidates for next-generation high-energy batteries considering their high capacity. For example, the calculated E_V of the Li-CuF_2 battery can reach up to 900 Wh L^{-1}. The high-capacity S cathode does not present a clear energy density advantage due to the low density and low voltage. A high mass loading of S is required to enhance the E_V. It should be noted that the cycling performances of conversion-type materials are poor and should be significantly improved in the future. Moreover, these Li-free cathodes should be

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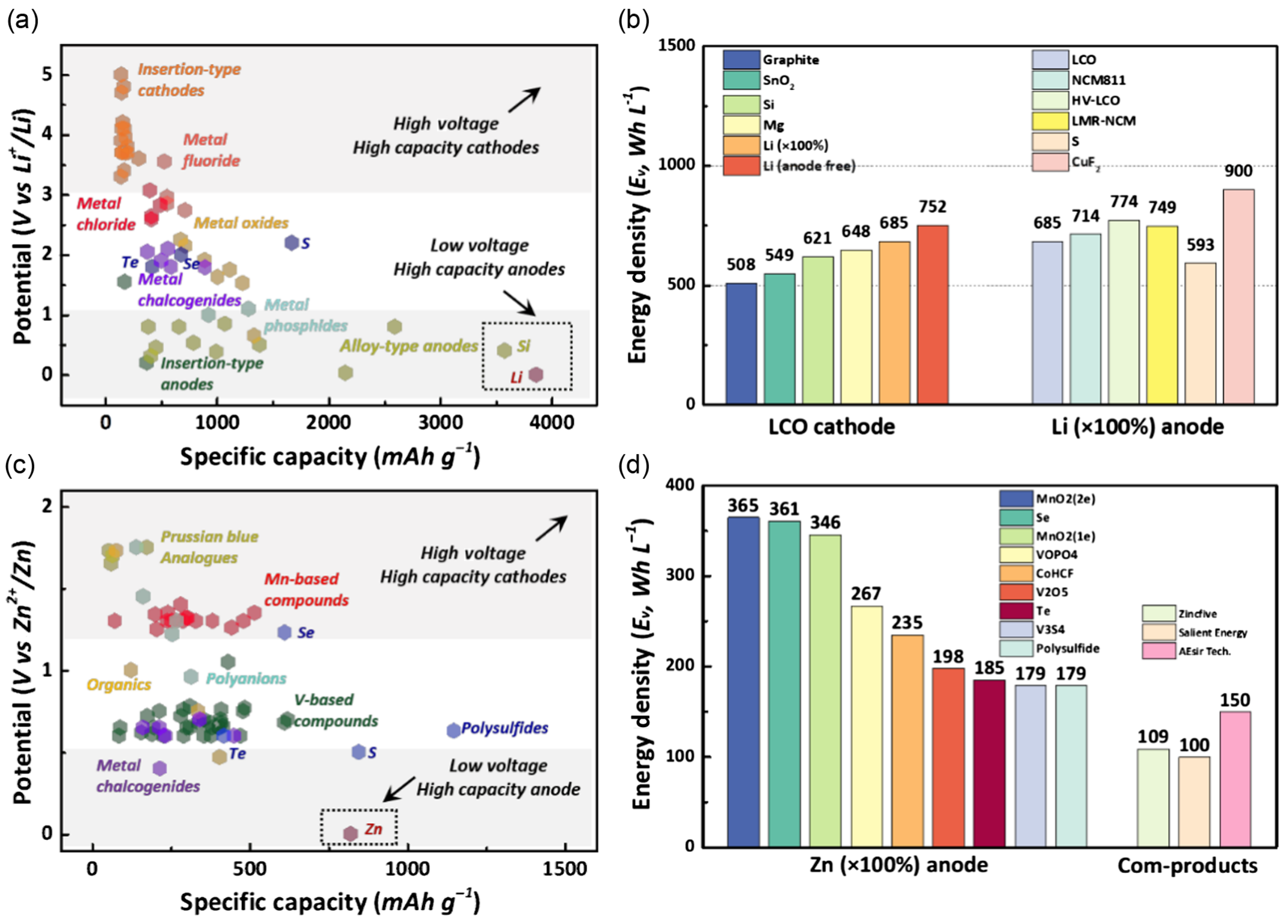

Figure 3 | *Materials selection toward high energy densities. (a) Voltages and capacities of prevailing electrodes in lithium batteries and (b) corresponding energy density of the intrinsically soft lithium batteries using varied electrode pairs. (c) Voltages and capacities of prevailing electrodes in zinc batteries and (d) corresponding energy density of the intrinsically soft zinc batteries using varied electrode pairs.*

prelithiated or paired with Li-containing anode when assembled into batteries.

In terms of aqueous zinc batteries, we discuss the cathodes because zinc is the most ideal and most reported anode. As shown in Figure 3c, cathodes of zinc batteries could be roughly classified into V-based (high-capacity and low-voltage),[56–59] Mn-based (high-capacity and medium-voltage),[60–63] Prussian blue analogues (low-capacity and high-voltage),[64–66] metal sulfide/chalcogenides (high-capacity and low-voltage),[67–70] organics (widely-distributed),[71–73] polyanions (widely-distributed),[74–76] and conversion-type cathodes (high-capacity and low-voltage).[77–79] The same cell configuration is employed to calculate the volumetric energy densities of batteries equipped with these cathodes and the zinc anode. As shown in Figure 3d, the Zn/MnO_2 batteries with a two-electron reaction could deliver the highest E_V (~365 Wh L^{-1}) where both electrodes show deposition/dissolution behaviors. Following are the Zn/Se batteries (~361 Wh L^{-1}) with a representative conversion mechanism. The Se cathode outperforms the other conversion cathode materials including S, Te, polysulfide, and V_3S_4 owing to its high voltage plateau of 1.25 V and decent density of 3.44 g cm^{-3}. The Zn ion and/or proton (co) intercalation/extraction-based cathodes such as MnO_2, $VOPO_4$, and V_2O_5 are also capable of displaying E_V values of 346, 267, and 198 Wh L^{-1}, respectively. As for the Co hexacyanoferrate (CoHCF), an E_V of 235 Wh L^{-1} was delivered owing to the high voltage. Assuming a cathode areal capacity of 3 mAh cm^{-2} could be achieved, most aqueous zinc batteries could merely support their deployment in the medical patch and smartwatch belt. High-tech companies such as Zinc five, Salient Energy, AEsir Tech., and so on recently developed mature rigid types of zinc batteries. However, those batteries only deliver energy densities less than 150 Wh L^{-1}.

Safety Issue of FBs

As discussed before, FBs based on lithium chemistry are the most promising candidates for future high-energy

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applications. However, combustible organic electrolytes pose huge safety hazards, especially upon mechanical, electrochemical, or thermal abuse.[80] The introduction of metallic anodes such as lithium and zinc also brings about dendrite-related challenges which could readily lead to shorts and intensified side reactions.[81–86] More severely, the additional considerations toward flexibility via special configuration design and the daily use under flexible conditions further exacerbate the mechanical abuse.[87] Such battery abuse could readily cause internal shorts and then trigger the chain reaction among heat, fuel (electrolyte vapor or flammable gases generated at the anode), and oxygen (air or oxygen released from the cathodes). It is well acknowledged that the generation of high-energy and hyper-reactive radicals are the keys to extending the chain reaction, finally leading to catastrophic fire and explosion.

To tackle this issue, one representative solution is to introduce fire retardants (FRs) into the battery system. Phosphorus-based FRs are the most widely applied for their nontoxicity and compatibility with existing electrolyte systems. Typical phosphorus-based FRs include trimethyl phosphate,[88] triethyl phosphate,[89] triphenyl phosphate (TPP),[90] ammonium polyphosphate (APP),[91] and so on, which could release free PO radicals to capture the hyper-reactive OH and H radicals, or nonflammable gases to terminate the chain reactions (Figure 4a). Generally, these FRs exhibit decent solubility in organic solvents and thus directly act as electrolyte additives (Figure 4a1). Some polymer-based aqueous FRs, such as APP, can serve as multifunctional binders and be integrated into the electrodes (Figure 4a2). Upon overheating, the APP decomposes to generate ammonia/water gas, followed by self-cross-linking into an insulating polymer layer.[91] However, the addition of FRs into the electrolytes and electrodes inevitably impairs the electrochemical performances by impeding the mass transport and charge transfer kinetics or narrowing down the voltage window. To address this dilemma, FRs can be coupled into the electrochemically inert battery components such as the current collector (Figure 4a3). Specifically, a fire-extinguishing current collector was developed by sandwiching TPP-embedded polyimide between two ultrathin Cu layers.[90]

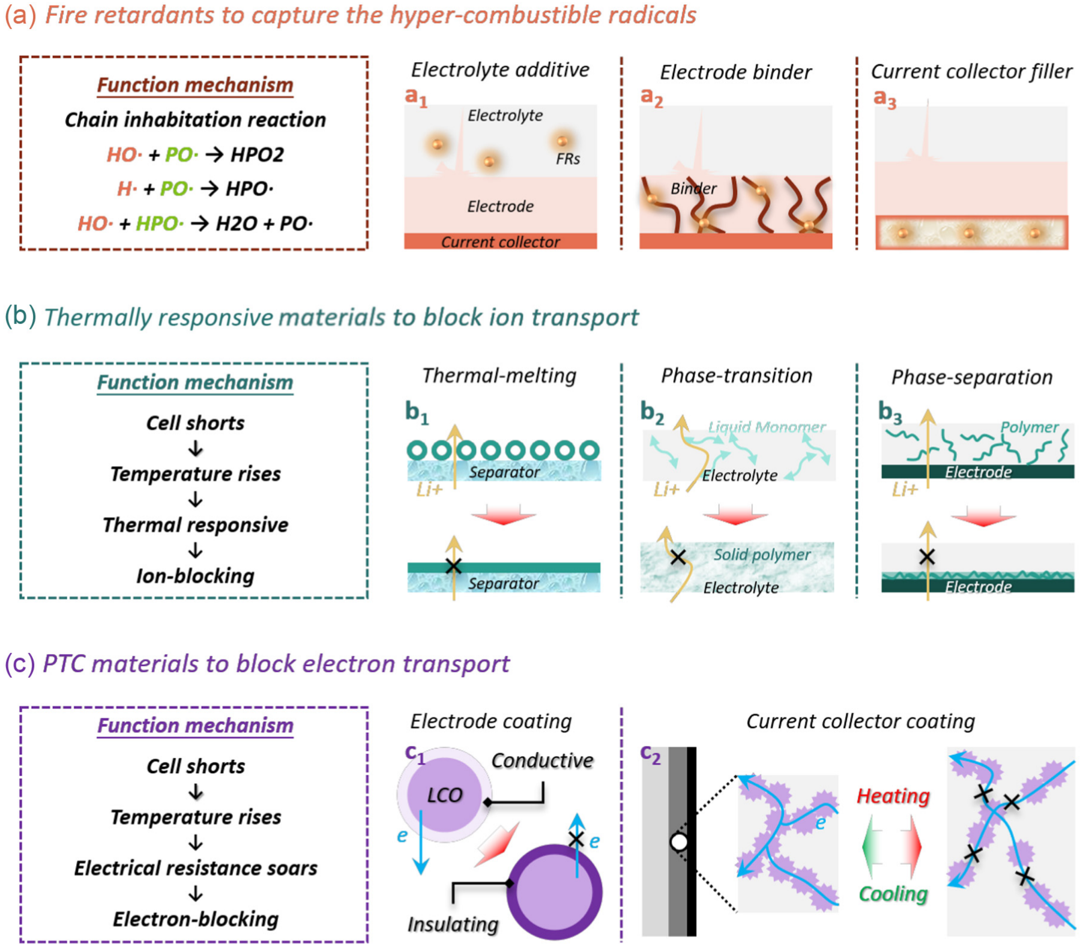

Figure 4 | *Solutions to promote cell safety via (a) fire retardants to capture hyper-reactive radicals. (b) Thermally responsive materials to block ion transport. (c) PTC materials to block electron transport.*

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An alternative tactic to promote cell safety is to employ thermally responsive materials that can generate ion-blocking interphases upon temperature rise to prevent exaggerated overheating (Figure 4b). One route is thermal melting (Figure 4b1). A bilayered separator with polyethylene (PE) microspheres and a porous polypropylene (PP) membrane was developed. Upon heating, the PP could maintain its porous structure without deformation while the PE microspheres could melt into a dense PE layer to block ion transport between electrodes.[92] Another route is thermally induced polymerization (Figure 4b2). A liquid electrolyte of poly(ethylene glycol) methyl ether methacrylate and 2,2,3,3,3-pentafluoropropyl acrylate could thermally polymerize into the solid state at 130 °C to lose its ion-transport capability.[93] The intact formation of polymer layers with extremely low ionic conductivity could also be achieved via phase separation (Figure 4b3). For instance, the electrolyte containing poly(benzyl methacrylate) with a lower-critical solution temperature could undergo phase separation in imidazolium-based ionic liquids.[94]

Positive temperature coefficient (PTC) materials are also adopted to forestall the thermal propagation via sharp resistance increase at the beginning of the overheating (Figure 4c). Here, we discuss polymer-based PTCs given their superb flexibility. For instance, a highly conductive polymer, poly(3-decylthiophene), with a strong PTC effect was spray-coated over LCO particles, which could turn into a highly resistive state at 80 °C to cut down the electron pathway[95] (Figure 4c1). To elevate the electrical conductivity at normal temperature, most polymer-based PTCs are comprised of embedded conductive particles and a polymer matrix with large thermal expansion coefficient. Upon heating, the polymer matrix expands to deprive the electrical contact among embedded conductors (Figure 4c2). Considering the poor reversibility and consequential permanent battery malfunction, a highly reversible, thermally responsive PCT with fast response speed was developed by replacing the conventional conductive filler with graphene-coated nanospiky Ni particles.[96]

In addition, intrinsically incombustible nonaqueous electrolytes were also developed to replace liquid organic electrolytes. Given their application in FBs, systems such as ionic-liquid electrolytes,[97–99] deep eutectic electrolytes,[100–106] and solid polymer electrolytes[97,107–110] are mainly considered. Thereinto, the prohibitive cost of ionic liquid greatly impedes their practical deployment. The low-cost deep eutectic electrolyte exhibits quite similar physiochemical properties to ionic liquids while the highly fixed compositions make them only suitable for specific battery systems. The solid polymer-based electrolyte is highly promising, but it is still challenging to harvest a satisfying ionic conductivity at room temperature, so additional thermal management should be considered. The zinc battery using aqueous or hydrogel electrolyte is long regarded to be extremely safe. However, as mentioned above, the energy density of zinc batteries is difficult to meet the standards of most wearable applications owing to the narrow voltage window of electrolytes and cathode materials.[111] Strategies to broaden the operating voltage of electrolytes via solvation structure engineering such as water in salt, water in gel, or decoupled electrolyte should be adopted. Besides, it is extremely urgent to develop novel cathodes with both a high voltage and high capacity for zinc batteries.

Furthermore, extreme conditions do show a high possibility to trigger such battery failures and thus have significant impacts on safety performance. For instance, long-term use under high temperatures could lead to separator shrinkage, severe electrode aging, and intensified side reactions to release oxygen and other flammable gases. Low-temperate application and consequential impaired reaction kinetics could induce fast dendrite growth at the anode to cause battery shorts. These temperature-related issues need further optimization regarding electrolytes and electrode materials.[112] Another often-considered extreme condition in FBs is high deformation. Such mechanical abuse could result in the detachment of active materials, slippage among cathode/anode/separator, localized strain distribution, inhomogeneous ion concentration, etc. which inevitably increase the accessibility toward thermal runaway. These applications under extreme conditions could potentially hinder the employment of fire retardants and thermally sensitive/responsive parts and thus more refined overall design should be considered.

Conclusions and Outlook

FBs based on lithium and zinc battery chemistries have been extensively studied over the past decade. A high-performance FB should possess a high E_V and a small r at the same time. Nevertheless, these two metrics often show significant trade-offs, and it is difficult to achieve high E_V and small r concurrently. To improve the fb_{FOM}, researchers have made significant efforts to engineer the battery configuration to develop intrinsically soft current collectors and freestanding electrodes, increase the mass loading and reduce the inert materials, and develop novel high-capacity electrodes.

Several prototypes of decoupled-structure FBs and intrinsically soft FBs using high specific capacity materials are approaching the commercial requirements on energy density and flexibilities, among which intrinsically soft FBs are more desired for better flexibility. Minimizing the volume of inert parts such as the interconnects of the decoupled-structure FBs and the functional additives and pores of the intrinsically soft FBs can largely push the E_V to a competing level of the rigid battery.

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For a given configuration, the areal energy density is determined by the areal mass loading, specific capacity, and voltage, of which the loading can be optimized through optimization of the electrode and configuration, and the specific capacity and voltage are decided by electrode materials. The use of ultra high capacity electrodes shows the remarkable potential of achieving high-E_V FBs. Benchmarked with a graphite/LCO electrode pair, replacing the graphite with high-specific capacity Si and Mg can largely promote the E_V by more than 20%. And the Li metal presents the highest enhancement of the E_V by ~35% for the very high specific capacity of 3860 mAh g^{-1} and the lowest voltage. Further pairing the Li metal with next-generation high-voltage and high-specific capacity intercalation type of cathodes extends the E_V to ~750 Wh L^{-1} on a cell basis. Conversion type cathodes with high energy density have rarely been explored despite the high E_V.

The conventional slurry coating process can only achieve a thickness limitation of 200 μm of a double-sided electrode. Several promising methods including the dry battery electrode technique, phase inversion technique, electrospinning/electrospray, and design of composited electrodes are reported to achieve high-loading thick electrodes (with smooth ion diffusion pathways and charge transfer). Besides, for multipairs-electrode configurations, robust elastic binders or electrolytes with high elastic modulus, resilience, and fracture toughness are expected to endow strong interlayer adhesion to preserve the conformal and tight interfacial contact during repeated flexing.[113]

In terms of the safety issue, there are two important aspects. One is to promote safety via applying FRs, thermal-responsive materials, PCT materials, or intrinsically nonflammable electrolytes in the battery, as discussed above. Another is to verify the safety under the requirements of realistic flexible applications. The rigid battery modulus used for power and grid applications is comprised of a series of packs with subcells. Their safety performance is largely determined by the internal battery management systems, thermal management circuit, fire suppressor, coolant circuit, etc. and thus the safety performance of a single cell is not the determining factor. For FBs primarily used for wearable applications, it is unlikely to integrate additional components due to the limited space and flexibility requirement. Therefore, the safety performance of the individual cell unit is of pivotal significance. In addition to standardized tests including overcharge, forced discharge, impact, external short circuit, nail penetration, and so on, additional tests focusing on mechanical abuse should be carried out. Considering that flexible devices are operating with uncertain and multidirectional mechanical inputs, current, voltage, and temperature evolutions should be monitored under dynamic flexible conditions. The standardized testing and reporting of the electrochemical properties, mechanical flexibility, and safety under extreme testing conditions can benefit a better comparison and progress of the field.

In addition to flexibility, energy density, and safety, another pivotal metric to pushing the FBs to commercialization is their connections and collaborations with flexible devices.[114] Design, materials supply, processing, and integration are the four stages in product manufacturing. In this field of flexible devices, most research is currently at a stage of material selection and configuration design. Special attention should also be paid to the processing and integration. In this regard, advanced connection strategies should be developed to ensure the stable transmission of electrical signals or mass transport especially upon stretching, bending, twisting, and other flexing scenarios. Traditional soldering techniques obviously cannot ensure high-resolution flexible interfacing especially under repeated large deformations. Some pioneer works have attempted to achieve high-resolution interfacial collaborations via dynamical chemical bonding,[115] solderless mechanical interlocking,[116] thin magnetic connectors,[117] and so on, which shed new light on the further development of novel smart connections.

Conflict of Interest

There is no conflict of interest to report.

Acknowledgments

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