



Materials and technologies for multifunctional, flexible or integrated supercapacitors and batteries

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Electrochemical energy storage has become a key part of portable medical and electronic devices, as well as ground and aerial vehicles. Unfortunately, conventionally produced supercapacitors and batteries often cannot be easily integrated into many emerging technologies such as smart textiles, smart jewelry, paper magazines or books, and packages with data-collection or other unique capabilities, electrical cables, flexible wearable electronics and displays, flexible solar cells, epidermal sensors, and others in order to enhance their design aesthetics, convenience, system simplicity, and reliability. In addition, conventional energy storage devices that cannot conform to various shapes, are typically limited to a single function, and cannot additionally provide, for example, load bearing functionality or impact/ballistic protection to reduce the system weight or volume. Commercial devices cannot be activated by various stimuli, be able to self-destroy or biodegrade over time, trigger drug release, operate as sensors, antennas, or actuators. However, a growing number of future technologies will demand batteries and hybrid devices with the abilities to seamlessly integrate into systems and adapt to various shapes, forms, and design functions. Here we summarize recent progress and challenges made in the development of mostly nanostructured and nanoengineered materials as well as fabrication routes for energy storage devices that offer (i) multifunctionality, (ii) mechanical resiliency and flexibility and (iii) integration for more elegant, lighter, smaller and smarter designs. The geometries of device structures and materials are considered to critically define their roles in mechanics and functionality. With these understandings, we outline a future roadmap for the development, scaleup, and manufacturing of such materials and devices.

Introduction

Slowly but surely, improvements in energy storage are reshaping our daily life and leading the way to an energy-sustainable future

[1]. Thirty years ago, no one foresaw that the release of lithium (Li)-ion batteries (LIBs) would initiate revolutionary shifts from just a few large cordless devices to unprecedented number of portable electronics and power tools and from combustion of fuels to fully electric transportation and accelerated adoption of renewable energy technologies. Today, most applications that

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demand lightweight and compact energy storage rely on LIBs [2], while some less energy demanding applications require ultra-fast charging, higher power and reliable electrical double-layer capacitors (EDLCs), a sub-class of supercapacitors [3]. Other rechargeable battery and supercapacitor chemistries are also being used or explored for applications that are more cost-sensitive or cannot use flammable or volatile electrolytes [4–7].

While profound understandings of electrochemistry of battery and supercapacitor systems have been critical for technology improvements, the development of scalable, reliable and inexpensive fabrication routes for both active materials and energy storage devices in the form of coin cells, pouch cells, cylindrical and prismatic cells have been equally instrumental for the LIB and EDLC market successes [8,9]. Yet, many emerging cutting-edge technologies require different form factors and mechanical properties of energy storage technologies in order to enhance their design aesthetics and convenience, reduce their overall weight or volume, and further improve system simplicity and reliability. Examples of such technologies include smart clothes, shoes and jewelry [10–12], flexible wearable electronics and displays [13–15], paper magazines or books and packages with data-collecting or other unique capabilities, smart epidermal and other types of sensors for both surveillance and personalized healthcare (diagnosis and therapy) [16–18], which are becoming valuable for athletes and critical for sick and elderly people and for everyone during a pandemic (as currently induced by COVID-19) [19], implantable medical devices [20], flexible solar cells [21–23], asset tracking sensors (such as sensing and reporting temperature, humidity, acceleration and location during shipping of valuable or perishable goods), lightweight drones [24], exoskeletons [25,26], Internet of Things (IoT) accelerated by the 5th generation wireless systems, and many other exciting future applications. The increasing interests in these technologies spur the development of advanced energy storage that can be integrated with other components, adopt to different shapes, or undertake substantial and repeated mechanical deformations at various bending, stretching, or compressing states.

We postulate that the following currently lacking design features of batteries and supercapacitors will be of interest in the future: (i) integration with other devices, (ii) flexibility and conformality, and (iii) multifunctionality (Fig. 1).

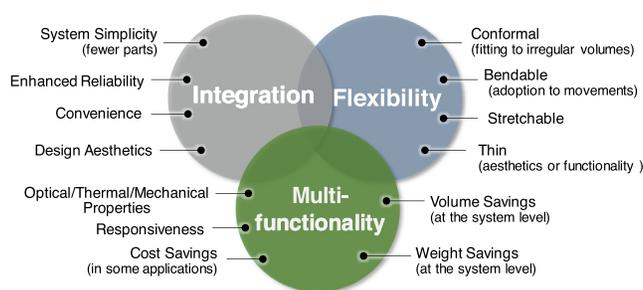


FIGURE 1

Smart energy storage solutions for specialized applications. Key features of advanced energy storage devices with their corresponding benefits that are being covered in the current review: (i) integration, (ii) flexibility, and (iii) multifunctionality.

The development and hugely successful commercialization of integrated circuits demonstrate that combining multiple components in a single device may not only increase device reliability and reduce the costs, but also accelerate the innovation and progress in the field [27–29]. A step further would be to integrate multiple devices (including energy storage) within a product in order to reduce system complexity, reliability and aesthetics.

The emergence of cheap and flexible electronic devices for smarter (e.g., sensing, communicating, and more functional) elastically deformable products and the desire to make them self-sufficient will demand similar mechanical properties in energy storage solutions that powers them. Furthermore, the desire to maximize the use of available volume remaining within a product will independently require energy storage to conform to irregular volumes and shapes. As such, we expect increasing demands for energy storage that could be made thin, bendable, stretchable, or conformable.

Finally, we expect that premium products that value volume and weight savings or particular physiochemical properties (e.g., thermal resistance, transparency, electrochromism, photochromism, mechanical properties, responsiveness to various stimuli, bio-degradability, self-destruction, etc.) would benefit from the development of diverse multifunctional energy storage, even at the extra cost.

To realize certain physical or mechanical properties of the overall energy storage device operating under specific conditions, the properties of its individual components (electrodes, separators, electrolytes, current collectors, packaging, etc.) need to be optimized as well [30–35]. These, in turn, depend on the shape, size, density and other properties of the materials that comprise them [36]. Although the developments of integrated, flexible or multifunctional energy storage systems are still in infancy, we expect that the rapid progress in the frontier of materials science as well as the adoption (from other fields) and further development of scalable materials synthesis and component fabrication and integration techniques will pave new ways for their broad commercial successes. In this Review, we will outline the recent progress and challenges made in the development of energy storage to meet new requirements for those emerging applications. We will describe several strategies for the formation of structural batteries and explain how device designs and materials utilized define device mechanics and functionality. Finally, we will propose a roadmap and a tentative timeline for overcoming major technological gaps in performance and manufacturing costs.

Device architectures

One of the key considerations for energy storage is the device architecture. In commercial batteries and supercapacitors, the assembled device components (anodes comprising anode current collectors and active material layers, cathodes comprising cathode current collectors and active material layers, separators, all filled with electrolyte) are stacked or rolled together and then incorporated into rigid cases. Such rigid design improves safety and reliability but prohibits adapting to mechanical deformations. Several alternative designs have been proposed, which could be classified into three basic types: (i) one-dimensional (1D) cells (e.g., flexible cable- or ribbon-shaped), (ii) 2D cells

(e.g., thin-film or single-layered flexible pouch with regular or stretchable building blocks), and (iii) advanced 3D cells (e.g., multi-layered pouch with sliding relative to each other or stretchable building blocks or cells with inter-penetrating electrodes) (Fig. 2).

One dimensional (1D) cable-shaped devices

1D cable- (e.g., wire or ribbon) shaped energy storage devices fit the design demands for many wearable electronic devices, smart textiles and jewelry, hidden devices, sensors, soft robots and other applications where flexible cables or fibers can be more easily incorporated into device shape and structure without losing overall design uniformity or elegance [44–47]. The fiber geometry allows multiple degrees of freedom in deformation, making it also the preferred option when the highest degree of flexibility is desired. Multiple 1D cable-shaped devices can also be integrated together within a single cable or be embedded into a textile to realize customized functions. For example, aligned CNT fibers and TiO₂ nanowires have been recently successfully used to construct a twisted fiber system capable of photoelectric conversion and energy storage in the same device [48]. Smart integrations of fiber-shaped supercapacitors, and energy conversion systems (like nanogenerators, solar cells, or microbial fuel cells) enabled self-powered textiles with sustainable energy harvesting and storage capability for wearable electronics [49,50].

1D-shaped batteries and supercapacitors are commonly designed to a non-coaxial structure, in which two electrodes are separated by electrolyte (or separator) and twisted in the packing matrix (Fig. 2a). From the manufacturing point of view, the twisted structure could be easily integrated together at scale, as this design has been used for over century for manufacturing of electrical cables. A modification to such a design is to build a coaxial device configuration in which the “core” electrode of strands of active material/current collector starts as a twisted or coiled base for the stack and then the separator and remaining electrode are wrapped around the core to complete the cell [51] (e.g., Li-ion cable battery [37] and supercapacitor yarns in a fabric [38], as examples in Fig. 2a). Finally, thin, and flexible fully coaxial 1D batteries could be produced by stretching larger coaxial fibers [52]. Another alternative 1D device geometry is ribbon-shaped (anode/separator/cathode) sandwich structures with very high aspect ratio (Fig. 2a). While it is typically less flexible compared to twisted or coaxial designs, it can be wrapped around various objects and can offer higher volumetric energy density for applications. It is important to note for many applications of 1D devices, such as knitting and integration into textiles, very high strength, small diameter, and the ability to form loops with a very small radius of curvature is very important.

We would like to emphasize that the physical characteristics and geometry of materials for the device components (current collectors, active materials, separators, etc.) may affect the mechanical properties of 1D-shaped devices rather strongly. In many cases, 1D-shaped materials may be most suited for attaining the best performance characteristics of 1D devices [53–55]. For example, by using a high-strength carbon nanotube (CNT) yarns one can reinforce the winding/sewing, mechanical properties, reliability and overall performance of 1D cells [56–58]. Thanks to the design of helical springs and

serpentines for the current collectors, a bracelet power source can be stretched with tunable degree and directionality while maintaining their capacity [46]. Carbon fibers may similarly be used as mechanically strong and flexible anodes for Li-ion cells [59]. All these 1D configurations can be extended to batteries with new chemistries, for example, Zn-ion batteries [60]. We acknowledge that the fabrication of 1D materials is currently substantially more expensive than that of conventional powders of the same composition. As such, the price-performance ratio for 1D devices should be carefully optimized for a given application.

Two dimensional (2D)/planar devices

2D thin-film energy storage devices are particularly suited for use in thin or layered products, such as smart cards, packaging and labels, magazines, books, skin patches and healthcare devices, jewelry, and a broad range of other products comprising flexible electronic components [61–64]. Thin and flexible supercapacitors and batteries could be produced either by using thin (1–10 μm) film technologies [65–67] or as a single-layer pouch based on a more conventional building block, where particles' based anode (typically 10–100 μm thick), separator layer (5–20 μm) and particles' based cathode (10–100 μm) are sandwiched together, filled with an electrolyte and sealed [68–70] (Fig. 2b).

Similar to the 1D batteries, 1D-shaped materials ((nano)tubes, (nano)wires, and (nano)fibers) or 2D-shaped materials ((nano) flakes) or their combination may be advantageously used in flexible pouch cells due to the superior resilience towards mechanical deformations they typically bring to the device components [71–74]. This consideration not only applies to the active but also to inactive materials. For example, to obtain higher tensile strength, improved flexibility, stretchability and resilience to fatigue, traditional metallic current collectors (e.g. Al, Cu foils) could be replaced by flexible conductive substrates made up of carbon nanotubes, carbon fibers, modified celluloses or polymers [75–77]. It is important to note, however, that high electrical conductivity of flexible substrates is critically needed for their practical applications in relatively high-power and medium-to-large size devices. In addition to planar device applications, 2D supercapacitors and batteries can be folded into 3D architectures, such as kirigami, origami and spine-fold designs that further increase modes of bending [78–80].

Over the past decade, increasing efforts have been devoted to the development of 2D micro-batteries and micro-supercapacitors by integrating device components on rigid or soft substrates. Rigid chips (e.g., based on Si wafers) are the most commonly used in microfabrication for integration with other microsystems [81–83]. However, for applications in flexible electronics, flexible displays, health monitoring and others requiring flexibility or reduced strains under various mechanical deformations, micro-batteries and micro-supercapacitors could be built on soft (e.g., polymer) sheets (Fig. 2b) [65,84,85].

Three dimensional (3D) devices

Here we highlight three classes of advanced architectures for 3D supercapacitors and batteries: (i) devices with interpenetrating electrodes (typically with solid electrolytes and often integrated

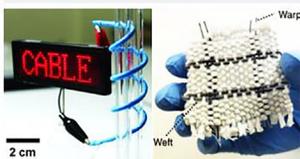
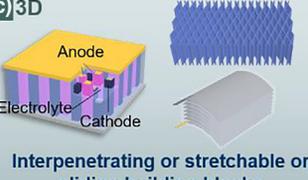
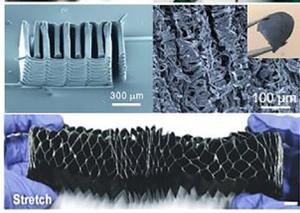
Device Architecture	Features	Applications	Examples
(a) 1D  Cable (wire or ribbon) - shaped	<ul style="list-style-type: none"> • High aspect ratios • Flexible • Stretchable (could be) • Conforming to wires, circles, spirals, antennas, textiles • Multifunctional (could be) 	<ul style="list-style-type: none"> • Smart textiles • Smart jewelry (bracelet, watch, necklace) • Implantable devices • Hidden devices in cables or textiles • Soft robots with fiber structures 	 2 cm
(b) 2D  Thin-film or single-layered pouch	<ul style="list-style-type: none"> • Flexible • Stretchable (could be) • Ultra-thin (could be) • Conforming to various surfaces • Multifunctional (could be) 	<ul style="list-style-type: none"> • Flexible electronics with flexible, on-chip or origami devices • Smart chips/cards integrated with thin-film batteries • Smart printing products (magazines, books) • Smart jewelry 	
(c) 3D  Interpenetrating or stretchable or sliding building blocks	<ul style="list-style-type: none"> • Flexible (could be) • Deformable / bendable (could be) • Stretchable (could be) • High volumetric density (could be) • Multifunctional (could be) 	<ul style="list-style-type: none"> • Smart jewelry, miniature devices with micro 3D power sources • Implantable devices • Microfluidics (redox flow) • 3D devices integrated into bulk objects and structures • Compressive/conformal devices with changing volume/space • Dense energy storage 	 300 μm, 100 μm, Stretch

FIGURE 2

Alternative architectures of energy storage devices, their features, and selected examples: (a) 1D (cable-shaped), (b) 2D (planar) and (c) advanced (deformable) 3D devices. Example panels adapted from: (a) Ref. [37], Wiley and Ref. [38], Springer Nature; (b) Ref. [39], Elsevier and Ref. [40], Springer Nature; (c) Ref. [41–43], Wiley.

with other devices) for achieving higher area-normalized energy density compared to 2D devices [86–88] and higher rate performance compared to traditional cell architectures (all solid state cells typically suffer from smaller power capability); [89–90] (ii) multi-layered devices with highly stretchable electrodes in the direction perpendicular or parallel to that of the electrodes [43,77,91] and (iii) multi-layered pouch cell devices capable of bending and flexing due to ability of their building blocks to slide relative to each other without cracking (like a multi-page magazine or a book with a soft cover, Fig. 2c) [92–94].

Cells with interpenetrated electrodes could be produced by lithography or printing [95–97]. Additive manufacturing (3D printing) and self-assembly, in particular, offer new possibilities for the development of such cells [86,98], as shown in the example micro-battery composed of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and LiFePO_4 cathode produced by printing viscoelastic inks (Fig. 2c) [41]. Highly stretchable cells could be made if electrodes (and separators) are made in the form of (e.g., hierarchical) kirigami or flexible honeycomb or foam-like structures [43,99,100]. For example, extremely stretchable supercapacitor was recently demonstrated by using a honeycomb-lantern electrode architecture fabricated by layer-by-layer (LBL) deposition [43]. In another example, highly flexible supercapacitors and batteries were assembled using cross-linked cellulose nanofibril aerogels with an open-cell foam structure [101]. The magazine-like device architecture could be achieved, for example, either by reducing the friction between device components (e.g., electrodes and separators) or by building such components from low-friction individual sub-layers [102,103]. Note that optimization of mechanical properties and tribology of the layers [104] and the use of solid lubricants [105] may be needed to reduce the friction to a sufficient degree and avoid components' fractures. In many cases, the use of 2D and 3D materials may enhance strength and flexibility of such layers [106–108].

Materials for multifunctional, integrated, or flexible energy storage

Advanced nanostructured materials

Traditional electrodes made of relatively brittle and poorly bonded micron-scale particles deposited on metal foil current collectors commonly fail to sustain repeated mechanical deformations such as bending or stretching [33,36,109]. Development and rational applications of various nanostructured materials that offer enhanced strength, flexibility and resilience to bending fatigue, such as 1D (e.g., nanofibers), 2D (e.g., nanosheets) and 3D (e.g., porous foams) materials, may overcome these limitations (Fig. 3) [110–112]. In addition, such materials may enhance ion transport and rate performance of various cell chemistries [113,114]. Yet, it is important to acknowledge that there is a cost to their applications – higher surface area in contact with electrolyte may lead to a higher rate of undesirable side reactions, lower packing efficiency may lead to a reduced volumetric energy density, and their finely tuned morphology may require meaningful synthesis cost premium. As such, careful consideration should be given for each device market opportunity and their demands and sensitivity to cycle life, calendar life, self-discharge, volumetric energy, and value these new materials bring to specific device functions.

1D nanostructures

1D nanostructures (Fig. 3a) such as nanofibers, nanowires (NWs), and nanotubes feature high aspect ratios which additionally enable enhanced strength, toughness and flexibility [31,118,119]. Carbon nanofibers and carbon nanotubes (CNTs) have been explored for enhancing strength, electrical conductivity and thermal stability of fibers and textiles since the 1990s [120,121]. Individual 1D nanostructures are known to exhibit extraordinary tensile strength. For example, the fracture

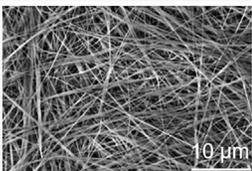
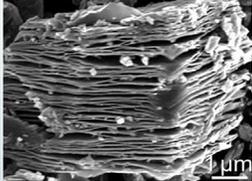
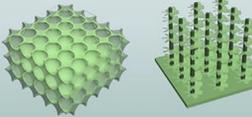
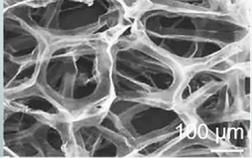
Materials structure	Properties & applications	Examples
(a) 1D Nanostructures 	<ul style="list-style-type: none"> • Flexibility • Rapid ion transport (from electrolyte) • High strength (could be) • High conductivity (could be) • Applications in electrodes, separators, current collectors and electrolytes 	<ul style="list-style-type: none"> • Carbon nanofibers & nanotubes • Insulating (e.g., oxide) nanowires (NWs) • Semiconductor NWs • Metal NWs 
(b) 2D Nanomaterials 	<ul style="list-style-type: none"> • Flexibility • High strength (could be) • Reinforcement • Rapid in-plane ion transport (could be) • High in-plane conductivity (could be) • Applications in current collectors and electrodes 	<ul style="list-style-type: none"> • Graphene • MXenes • Phosphorene • MoS₂ & other layered material nanosheets 
(c) 3D Nanoarchitectures 	<ul style="list-style-type: none"> • High porosity • Deformability (could be) • Increasing areal capacity loading • Accomodation of volume expansion • Applications as 3D current collectors or electrodes 	<ul style="list-style-type: none"> • 3D foams • Aerogel • 3D periodic structures (e.g., inverse opals) • Hierarchical nanoarrays 

FIGURE 3

Structure, properties, applications, and examples of advanced nanomaterials from 1D to 2D to 3D for alternative (flexible, multifunctional, irregularly shaped, etc.) energy storage devices. Example panel contains SEM images of (a) 1D Al₂O₃ nanofibers, (b) 2D MXenes and (c) 3D graphite form, adapted from: (a) Ref. [115], Elsevier; (b) Ref. [116], ACS; (c) Ref. [117], Springer Nature.

strengths of ZnO NWs (with diameters varying from 20–512 nm) ranges from 3.33 to 9.53 GPa [122]. The elastic modulus of the CNT walls can approach ~ 1 TPa and the tensile strength ~ 100 GPa [123]. Individual single-walled CNTs also demonstrated the outstanding thermal conductivity of $3500 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature, which exceeds the thermal conductivity of its allotrope-diamond [124].

Although the extreme strength and thermal conductivity are only achieved by individual 1D nanostructures and could be lost in assemblies (films) where point contacts are typically present, the unique properties of 1D nanostructures enable their effective use in advanced electronic, energy harvesting and energy storage technologies, particularly those that require flexibility and mechanical robustness for use in flexible, multifunctional and integrated devices (Fig. 2) [125–127]. For example, conductive 1D nanostructures enabled formation of the next-generation flexible antennas for wearable sensors [128]. Owing to the large mass density, high surface area and metallic conductivity, 1D nanostructured metal nitrides grown on flexible substrates served as ideal capacitive anodes to assemble flexible asymmetric supercapacitors [129,130]. The network built by aligned silver NWs enabled the electrical or polarized-light-based sensors to modulate signals more efficiently than conventional state of the art devices by boosting electrical and optical anisotropy of ~ 10 and ~ 25 times [131]. The ion-conducting network formed by 1D ionic conductors made it possible to develop the flexible all-solid-state batteries without sacrificing their electrochemical performance and safety [132–134]. For example, ion-conductive garnet-type Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ (LLZO) nanofibers in polyethylene oxide (PEO) polymer matrix delivered high Li⁺ transfer and high ionic conductivity of $2.5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature for all-solid-state LIBs [132]. A binder-free nonwoven ceramic nanofiber membranes overcome the thermal, mechanical and ionic conductivity limitations of polymer separator

membranes for batteries [135,136] and supercapacitors [137]. For example, 100% ceramic Al₂O₃ nanofiber separator (Fig. 3a) demonstrated consistently higher ionic conductivity, superior wettability and dramatically improved thermal stability compared to commercial polypropylene and cellulose fiber separators for LIBs [136], while composite polymer-Al₂O₃ NW separators enhanced rate performance of supercapacitors [138].

2D nanomaterials

2D nanomaterials (Fig. 3b) consist of atomically thin sheets that can offer a great opportunity to achieve high flexibility, packing density, anion/cation-conductivity and rapid charge-transport [139,140]. Their flat surfaces enable their stacking to form free-standing membranes for flexible current collectors, electrodes, interlayers, etc. [141–143]. Graphene, the most widely studied 2D material, has a unique single sp²-hybridized carbon atomic layer with extraordinary physical and chemical properties, such as high surface area ($1654\text{--}2600 \text{ m}^2 \text{ g}^{-1}$) [144,145], high electrical conductivity ($100\text{--}2000 \text{ S cm}^{-1}$) [146,147], high thermal conductivities ($2000\text{--}3000 \text{ W mK}^{-1}$) [148], known chemical routes for controllable functionalization of the defects or edges [149], high tensile strength (1.2 MPa for nanoporous graphene [150], up to 130 GPa for single-crystalline graphene [151]) and outstanding fatigue resistance [152], to name a few. To date, graphene has demonstrated excellent performance characteristics when incorporated in various flexible electronic devices [140]. The great success of graphene inspired the rapid development of other 2D materials such as phosphorene [153], borophene [154], metal carbides and nitrides (known as MXenes, general formula is M_{n+1}X_nT_x ($n = 1, 2, 3$ or 4), where M is an early transition metal, X is carbon and/or nitrogen and T_x represents the surface terminations (such as hydroxyl, oxygen or fluorine) [155], and transition metal dichalcogenide (TMDs) [156]. Some of such materials offered even higher constant/direct current (DC) con-

ductivity than graphene. For example, $Ti_3C_2T_x$ MXenes processed into films demonstrated electrical conductivity of $\sim 1.5 \times 10^4 \text{ S cm}^{-1}$ [157]. Phosphorene (also known as single/few-layer black phosphorous) offer good conductivity, fast ion diffusion property, as well as excellent mechanical flexibility (tensile strain up to 27% and 30% in the zigzag and armchair directions) [158,159]. In addition to 2D inorganic materials, organic 2D materials with framework structures have also emerged with notable electrochemical properties for supercapacitors [160–161] and batteries [162,163]. The breadth of these chemistries and mechanics allows 2D material optimization for multiple applications. Furthermore, various 2D materials can be mixed and stacked together to achieve unique ‘on-demand’ properties [164,165].

The past decade has witnessed a rapid growth of graphene market with the development of multiple scale-up strategies [166], which enables the wide applications of graphene and special focus on multifunctional energy storage. The direct laser reduction of graphite oxide films to graphene was conducted to develop a robust, highly conductive film as high-performance electrodes for flexible thin-film supercapacitors. Electrochemically exfoliated graphene with intrinsically high conductivity exhibits good solution processability and renders the printable techniques for the fabrication of robust flexible film electrodes for supercapacitors and micro-supercapacitors. A surface terminated Ti_3C_2 MXene was coated on commercial natural and synthetic yarns and knitted into fabrics with different structures (e.g., jersey, rib) for 3D knitted energy storage devices with excellent stability (over 10 k cycles) [167]. TMDs have also attracted great attention for energy-related applications. The chemically exfoliated MoS_2 nanosheets with metallic 1 T phase can electrochemically intercalate ions (e.g., H^+ , Li^+ , Na^+ and K^+) with extraordinary efficiency and achieve high volumetric capacitance up to $\sim 700 \text{ F cm}^{-3}$ in aqueous electrolytes. Besides, the development of 2D hybrids composed of different 2D materials is also considered as a smart choice for energy storage applications. Benefiting from the advantages from two components, the 2D hybrids of phosphorene and graphene showed great potentials in high-capacity anodes for sodium-ion batteries [168], as well as flexible electrodes in micro-supercapacitors towards integrated electronics [169].

3D nanoarchitectures

Materials with various 3D nanoarchitectures have started to attract more attention for applications in energy storage due to their safer and easier handling (compared to 1D or 2D nanomaterials), hierarchical porosity with tunable (and very high, if needed) total pore volume, controllable pore sizes [170–172], tunable (and very high, if needed) electrical and thermal conductivities [173,174], high mechanical robustness and good flexibility/deformability attainable [175–177]. Such structures include 3D graphene foams [117,178], hydrogels [179], aerogels [174], inverse opals and other templated porous structures [180], honeycomb [181], MXene foams [182], carbon foams [177,183] and other types of hierarchical, often flexible nanoarchitectures [184–187]. Some of them form by assembling of basic low-dimensional building blocks (e.g., nanoparticles, nanofibers, nanotubes, nanosheets or their various hybrids), while others

form from bulk (e.g., organic or metal–organic) precursors using pore formers, sacrificial templates and related strategies [180,188,189].

3D nanostructured materials have been widely used in thick electrodes, porous current collectors, and structure reinforcement to improve electrochemical performance characteristics, increase areal capacity loadings and enhance mechanical properties [190–193]. Compared to traditional bulk or stacked electrodes, 3D nanostructured electrodes can load more active materials [192,194], their high internal surface area and porosity may enable fast pathways for electron transport and ion diffusion [195–197], while attaining remarkable mechanical properties, such as deformability under tension and compression and shape-recovery for advanced designs of batteries and supercapacitors [195,198,199]. 3D ceramic ion conductive frameworks can be effectively used as solid electrolytes for all-solid-state metal-ion batteries [200,201].

Electrolyte materials and chemistry

Nearly all supercapacitors and batteries utilize liquid electrolytes and those that offer higher energy density typically comprise flammable organic solvents capable of withstanding higher voltages and also offering longer cycle life [202–204]. However, flexible, multifunctional or integrated energy storage devices may be exposed to abusive conditions, such as bending, twisting or even cutting, thus inducing unacceptable safety risks. Replacement of flammable liquid organic electrolytes by nonflammable ionic liquid (IL) [205–206] or aqueous electrolytes may reduce such concerns [207–209]. ILs additionally offer very low vapor pressure at room temperature [210], which may be further advantageous, particularly if cell packaging or seal is imperfect. The next level of abuse tolerance is to move to solid electrolytes, which may further reduce the risks of electrolyte leakage and short circuiting and additionally may enhance mechanical properties of the cells [211,212]. Yet, proper cell design should also consider application requirements, which may define key electrolyte parameters, such as: (i) sufficiently high ion conductivity (for most applications with relatively thick electrodes – within 10^{-2} – $10^{-4} \text{ S cm}^{-1}$ at cell operating conditions), (ii) electrochemical stability or stable passivation on the anode and cathode surfaces, (iii) good wetting in contact with electrode materials, (iv) suitable thermal properties, (v) adequate cost, and (vi) adequate mechanical properties.

Table 1 provides selected examples and summarizes some of the key features of major electrolyte families to compare their advantages and disadvantages.

Liquid electrolytes

Liquid electrolytes could easily adopt to shape or volume changes in the battery or battery materials during cell operation but may also leak if hermetic packaging is damaged (Table 1). The chemical natures of solvents allow liquid electrolytes to be divided into three types: organic liquid electrolytes, IL electrolytes, and aqueous electrolytes (Table 1). Today, virtually all LIBs rely on organic liquid electrolytes due to their high ionic conductivity, ability to form stable passivation on both electrodes (effectively having a very wide potential window) and moderate costs. Most commonly, organic solvents primarily

TABLE 1

Electrolyte families: advantages and limitations. Darker background indicates more favorable properties.

	Chemical Composition (most common)	Ionic Conductivity	Electrochem. Stability	Safety	Cost (incl. incorporation)	Strength	Compliant/ flexible
Organic Electrolytes	Inorganic or organic salts (e.g., LiPF_6 or Li imides for Li-ion; TEABF_4 for supercaps) in organic solvents (carbonates, ethers, sulfones, etc., some of which may be fluorinated)	Moderately High	Moderately High	Flammable (commonly) and may leak	Moderate	No strength	Yes compliant
Ionic Liquid Electrolytes	Salts in ILs (for Li-ion) or pure ILs (for supercaps): organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, etc.) with inorganic or organic anions (e.g., BF_4^- , PF_6^- , TFSI^- , FSI^- , etc.)	Moderate	Moderately High-to-High	Combustible at elevated T and may leak	Moderately high	No strength	Yes compliant
Aqueous Electrolyte	Inorganic salts (e.g., LiCl , NaCl) (for Li-ion & supercaps) or alkali (e.g., KOH) or inorganic acid (e.g., H_2SO_4) in water (for supercaps)	Highest	Smallest	Nonflammable but may leak	Lowest	No strength	Yes compliant
Solid Polymer Electrolytes	Salts (e.g., LiPF_6 or Li imides for Li-ion) dissolved in polymer matrix (e.g., PEO, PAN, PMMA, PVDF, etc.); ILs & organic solvents may be added to enhance conductivity	Lowest (commonly)	Moderate-to-High	Combustible at elevated T	Moderately high, some are expensive to incorporate	Low-to-Moderate	Yes (mostly)
Inorganic Solid Electrolytes	Oxides (garnets, NASICON/LISICON, perovskites, etc.), sulfides, LiPON, anti-perovskites, hydrides, etc.	Low-to-Moderate	Moderate-to-High	Nonflammable, some may be toxic	Moderate-to-high, expensive to incorporate	Low-to-Highest	No (mostly)

comprise a mixture of cyclic carbonates (e.g., ethylene carbonate (EC), propylene carbonate (PC) and others to enable high salt solubility) and linear carbonates (e.g., dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and others to provide higher ion mobility at room or low temperatures) [213]. In addition, other co-solvents (e.g., ethers, esters, sulfones, nitriles, etc.) [214] and/or various fluorinated co-solvents [215] may be added for enhancing stability, reduced flammability or other performance characteristics. Supercapacitors most commonly use PC or acetonitrile solvents [216]. However, in situations when a battery may be exposed to abnormal conditions (mechanical deformations including a physical damage, overcharge, exposure to overly high temperatures, etc.) the use of liquid organic electrolytes may be undesirable due to a thermal runaway danger. The high volatility and flammability of commonly used organic solvents triggered interest to replace them with room temperature ILs, which exhibit dramatically reduced volatility and flammability and feature high chemical and thermal stabilities [217–219]. Unfortunately, they typically suffer from poor performance at low temperatures (unless eutectic mixtures of ILs are used [220]), higher viscosity and lower ionic conductivity (and thus low cell rate capability) [205], as well as relatively high cost [217], and inferior ability to form a stable passivation on low voltage anodes in LIBs (e.g., graphite or silicon). At the same time, they commonly show better oxidation stability and enable higher voltage in supercapacitors [221,222]. The mixture of ILs and organic solvents have been explored to overcome some of the limitations of pure IL electrolytes [223,224]. Finally, lower voltage devices may benefit from using water as the cheapest, nonflammable, environmentally-friendly electrolyte solvent that typically provides the highest mobility and solubility to ions [207,225], and may additionally perform remarkably well at sub-zero temperatures (with high salt concentrations) [226–228]. Some of the commercial supercapacitors utilize aqueous acid solutions as electrolytes [229,230]. Since many devices may eventually end up in the household trash, the use of nontoxic electrolytes (e.g. pH neutral water-based or some IL-based with safe salts) and for that matter nontoxic electrode materials (e.g., Co-free, Ni-free, etc.) may be advantageous, which triggered the renaissance of Fe-, Al-, Mg-, Zn- and organic active materials-based (potentially disposable) battery research [231,232]. The shortcomings

of aqueous electrolytes include gas generation (primarily hydrogen on the anode), high water vapor pressure even at low temperatures and undesirable side reactions with many electrode materials (which may be reduced by using high salt concentrations) [233–235].

Solid polymer electrolytes

Solid polymer electrolytes (SPEs) could be sufficiently elastic to accommodate deformations within multifunctional or flexible cells and may additionally enhance safety and mechanical properties of such energy storage devices (Table 1). If these are made with water-stable polymers and salts, SPE-comprising electrodes and cell fabrication could be conducted via a reasonably low cost, continuous lamination-like processes [236]. Furthermore, some of the polymer electrolytes could be infiltrated into dry electrode stacks in a liquid form and solidify after that [237]. Yet, many of the studied polymer electrolytes for LIBs and other systems are moisture sensitive, which increases electrode fabrication cost. Furthermore, most SPEs must be used in slightly larger quantities (compared to liquid electrolyte) to attain high capacity utilization, which may reduce volumetric energy density in cell designs. The largest challenge, however, is their relatively low conductivity [238]. Furthermore, higher modulus and strength of the SPEs (preferable for enhancing mechanical properties of multifunctional or flexible cells) typically correlate with reduced conductivity [239]. That is why formation of co-polymer electrolytes comprising both softer, higher conductivity segments and harder, higher modulus segments have been explored [240,241].

Most SPEs comprise Li or other metal salt(s) dissolved in dry high-molecular-weight polymers [242]. Organic or IL solvents may be added to the polymer, thus forming semi-solid, gel polymer electrolytes (GPEs) in order to enhance conductivity or make the polymer electrolyte softer and easier to process [243]. Compared to liquid electrolytes, the polymer matrix in GPEs greatly reduce the risk of flammability and evaporation at the expense of reduced ionic conductivity [244,245]. The most widely used polymers for SPEs and GPEs include polyethylene oxide (PEO), polyvinyl alcohol (PVA), poly(methyl methacrylate) (PMMA), and poly(fluoride-co-hexafluoropropylene (PVDF-HFP) [238,246–248]. Single-ion conducting SPEs where the polymer chain comprises chemically bonded anions are also being consid-

ered [249,250], but incorporating such SPEs into electrodes and attaining reasonably good performance in fully function cells has been challenging. Most SPEs offer very moderate ionic conductivity in the range of 10^{-8} – 10^{-4} S cm^{-1} [251–253], which could be insufficient for regular or thick electrodes requiring fast charging, but still adequate for specialized cell designs (with smaller ion diffusion paths) or specialized (low power) applications. An alternative approach to improve the ionic conductivity of SPEs has been the introduction of ceramic (preferably ionically conductive) nanofillers [132,133,254,255]. If such ceramic fillers are in the form of nanofibers/NWs, such reinforced SPEs may additionally gain enhanced mechanical and thermal properties [132,256,257]. In addition to ceramic nanofibers, high-strength polymers such as polyimide [258] and aramid [259], can be used to support SPE subjected to mechanical loadings. Some of the SPEs and GPEs may offer self-healing [260] and high transparency [261].

Inorganic solid electrolytes

Compared with SPEs, inorganic solid electrolytes (ISEs) are much more brittle and thus likely not suitable for applications requiring high flexibility. However, such electrolytes may provide high strength (particularly in compression and especially if in a fully dense, most preferably glassy state). As such, they could be used in either thin film/micro-batteries or some of the multifunctional/integrated applications that do not require mechanical deformations. Some of the ISEs (e.g., S-free, based on oxides) are arguably the safest (Table 1). In addition, ISEs commonly operate very well at high temperatures (provided they form a stable passivation layer on the surface of both electrodes). Most common examples include perovskite-type (e.g., $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$) [262], garnet-type (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) [263], sulfides (e.g., $\text{Li}_7\text{P}_3\text{S}_{11}$) [264], sodium superionic conductor-type and its lithium version (NASICON or LISICON, e.g., $\text{LiTi}_2(\text{PO}_4)_3$) [265], antiperovskites (e.g., Li_2OHCl), [266,267], lithium hydrides [268], lithium metal halides [269], and LiPON [270,271], among others. These materials exhibit a broad range of conductivities (e.g., from 10^{-6} to 10^{-2} S cm^{-1}) [272]. Recently, atomic layer deposition (ALD) has been successfully used to deposit LiPON-type (Li_3PO_4 and $\text{Li}_2\text{PO}_2\text{N}$) ISEs for solid-state 3D Li-ion micro-batteries [273,274], and we expect the use of ALD and chemical vapor deposition (CVD) [275–277] for ISE deposition will be growing. Unfortunately, the integration of the ISEs into electrodes for the formation of fully dense batteries may increase cell fabrication costs (particularly if moisture-free environment, high temperature and high pressure are needed) and additionally reduce volumetric cell energy density.

Manufacturing of multifunctional, integrated, and flexible energy storage

Alternative device designs and the most appropriate materials and electrolytes for such designs discussed in the previous sections are commonly guided by the specific (often unique) needs of the novel applications. In most cases, however, both the synthesis of these materials and the manufacturing of such multifunctional, integrated, or flexible energy storage devices require techniques beyond what is currently used in conventional commercial cells. Fortunately, recent advances in nanotechnologies

for materials synthesis and the adoption of fabrication techniques from other fields offer many opportunities for innovative device concepts and their future commercial successes in various markets. Fig. 4 summarizes some of the most exciting techniques for 1D, 2D and 3D nanostructure synthesis (Fig. 4a), strategies for the fabrication of electrodes and cells with alternative architectures (Fig. 4b), and in some cases integration with other devices or products (Fig. 4c).

Materials synthesis

The most widely used approaches for the synthesis of functional nanostructures include various solution reactions (including hydrothermal and solvothermal processes) – mostly for 0D, 1D and 2D nanostructures, but also for coating formations [278–280], various spinning and electrospinning techniques (including wet, dry and melt spinning) – mostly for 1D nanofibers or nanotubes (e.g., polymers, carbon, oxides, and nanocomposites) [281–284], electrodeposition, electrophoretic and electroless deposition – mostly for the depositing active or conductive coatings on the surface of conductive materials and electrodes [285–287], vapor deposition reactions (ALD, CVD and physical vapor deposition (PVD)) – for both 1D and 2D nanostructure synthesis, the deposition of surface coatings and micro-battery/micro-super capacitor components (current collectors/electrodes/electrolytes/etc.) [288–290], selected dealloying, etching or exfoliation – for 1D and 2D nanostructure synthesis and porous 3D nanostructure formation [119,291–293], and template- or pore former-assisted synthesis and self-assembly (including assembling of complex structures from different building blocks) – mostly for 3D and porous nanostructures [294,295], among others. Once synthesized, the nanostructures may further be subjected to thermal annealing or chemical transformation or coating formation to attain the most desired chemistry, microstructure and nanoarchitecture. Note that these nanomaterials may be produced in the powder form, free-standing form (as a standalone electrode/separator) or be directly grown/deposited on the substrates, which would affect the subsequent steps for the cell production. When comparing different strategies based on their synthesis cost (equipment depreciation, labor, energy, lease, etc.), safety, cost of the materials' precursors (raw materials' costs) and the diversity of available vendors, sensitivity to process parameters and properties of the input materials, precursor utilization yield, handling of exhaust streams, overall control over the product quality, uniformity, reproducibility, and other parameters to satisfy particular applications, it is important to recognize that such factors may change at different scales and may even be dependent on the location of the manufacturing plant. For example, while the use of bulk manufacturing techniques (e.g., the use of volumetric reactors that maximize the use of space in the reactor volume where synthesis takes place) may offer similar costs to the deposition on planar substrates at small scales, the situation typically changes dramatically during scale-up. Indeed, at larger scales the cost of materials' synthesis in volumetric reactors reduces exponentially (on a \$/kg basis or on a kg/hour/reactor volume basis), while the cost reduction for larger planar deposition is very moderate at larger scale (which generated "copy exact" philosophy for the transition from R&D to production for electronic device fabrications that

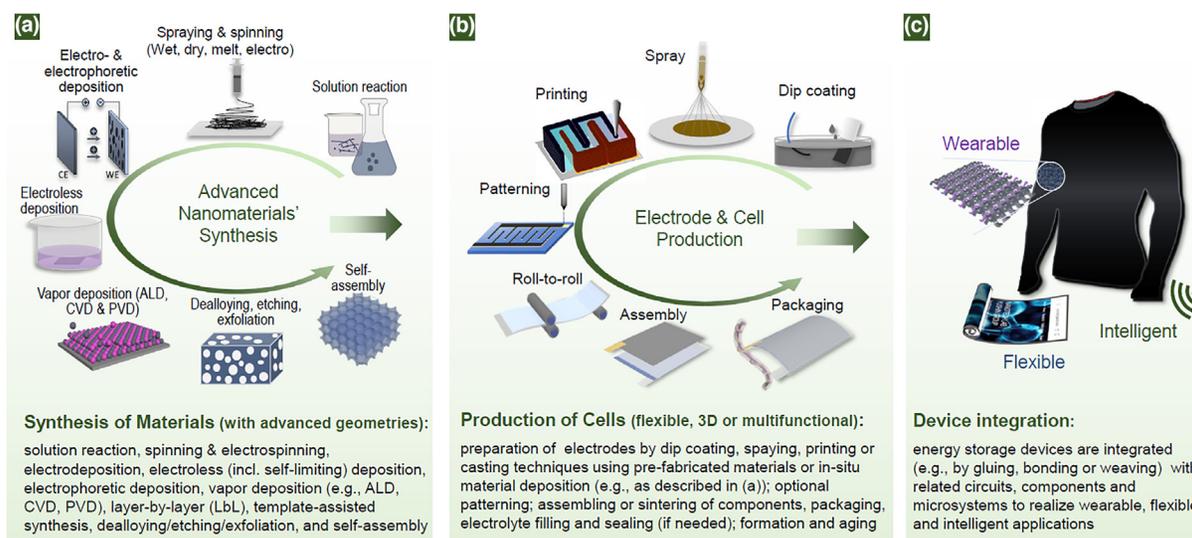


FIGURE 4

An overview of alternative materials synthesis, cell fabrication and integration. (a) Selected synthesis techniques for advanced nanostructured materials. (b) Examples of suitable techniques for alternative electrode and cell production. (c) Examples of integration with other devices in wearable electronics and flexible displays.

commonly use planar substrates in their synthesis steps). Similarly, small differences in the cost of input materials for different processes may either become more dramatic or get reduced further and even get reversed at scale. Furthermore, the planned plant location determines the presence of the existing infrastructure, availability of the precursors (or cost of their delivery or inhouse production), time and cost of securing permits, cost of the electricity, presence of trained workforce (or the attraction of the location for the move), among many other factors.

Electrode and cell production/assembly

Conventional electrodes are produced by casting slurries of active material powders, conductive additives and polymer binder on current collector foils, drying and calendaring (densifying) them prior to stacking anode/separator/cathode building blocks or winding them into the jelly rolls, inserting into (mostly rigid) cell cases, filling with electrolyte and sealing [296–298]. However, very different electrode and cell production may be more appropriate for alternative cell architectures (Fig. 2). For example, formation of porous, free-standing electrode sheets may enable higher flexibility, deformability and strength (in compression or tension) to energy storage devices (Fig. 2) [42,299,300]. Similarly, fiber-formation techniques may similarly be more advantageous for the formation of electrodes for 1D batteries and supercapacitors [301–303]. Even in the case of transferring active materials from a powder form onto current collectors (substrate), slurry casting is not often the best choice for alternative cell architectures because of the limited control over particles' orientation, porosity, bonding between electrode particles, stresses forming during slurry drying, local patterning, shape and size of the final electrodes and other important properties. In the case of transferring electrode materials on 1D fibers, 2D mesh or 3D porous substrates, slurry casting also does not work. In some cases, the use of dip coating [304,305], layer-by-layer deposition [306–308], spraying and spinning [309–311], or the

application of various printing techniques (screen printing, inkjet printing, multiple 3D printing techniques, etc.) [312–316] may provide unique advantages to electrode or cell production (Fig. 4b). Indeed, printing techniques not only enable the direct writing of electrodes on flexible and stretchable substrates [317], but can also fabricate custom patterns for object-tailored energy storage devices [318]. Advanced 3D/4D printing techniques provide opportunities for fabrication of complex 3D electrodes and the formation of stimuli-responsive structures for smart devices [41,319,320]. Fully dense electrode and solid electrolyte layers may be deposited by vapor deposition techniques (most commonly by PVD) for thin film all-solid-state-devices [271,321]. State-of-the-art photolithography and other patterning techniques (e.g., electron/ion beam lithography (EBL/IBL) or nanoimprint lithography (NIL)) may also be utilized for the fabrication of complex patterns and structures on rigid substrates (e.g., a chip) for highly integrated electrodes and compact microelectronics [322–324]. Bulk all-solid-state devices typically require the use of high temperature and high pressure sintering processes to attain low porosity/high strength structures [325–327]. Combining different methods into roll-to-roll assembly will pave the way to accelerate the industrialization of cell production [110].

Integration

In electric-vehicle (EV) or other high-voltage, high-capacity battery systems, LIB cells are typically parallel-assembled in modules (with internal electrical circuits), which are then integrated within a battery management system to provide the needed high total voltage and reliable operation [8]. In the future, we may even expect custom design of LIB cells that are fully integrated within each module. For many multifunctional, wearable, and flexible applications that do not require high voltage (a single or a few cells in series), the integration will likely involve substantially different designs (Fig. 4c). For example, cable-shaped

1D devices (e.g., for smart textiles) may be embedded into textiles. Their aspect ratios and deformability could also make them suitable for integration with energy-harvesting nanowire-based devices (e.g., nanogenerators [328]), NW-based sensors [329], electrical cables [330] or antennas [331]. Thin (2D) planar or thicker/more complex 3D devices may be integrated on a chip or a soft substrate into planar flexible objects or low-power microelectronic devices, flexible solar cells or displays [332–335]. In the longer-run (when sufficiently long calendar life, enhanced mechanical properties and lower costs are attained), energy storage devices may even be integrated into building walls and other parts of the construction or architectural designs, parts of ground, sea and aerial vehicles (including unmanned vehicles and drones), among other applications. Most of such applications, however, would still require extensive research in combination with scientific and engineering developments of: (i) lower-cost, more scalable material synthesis methodologies and tools, (ii) lower-cost, higher conductivity, more reliable, preferably stronger, more flexible and easier to integrate solid electrolytes, (iii) lower-cost fabrication/assembly methodologies for alternative electrode and device architectures and (iv) more standards and references for the complex evaluation of the interlinked mechanical and electrochemical properties, including different aspects for device reliability upon mechanical deformations or other external stimuli [36,336].

Towards multifunctional applications

Structural, load-bearing batteries for mechanical reinforcement

Structural batteries (or supercapacitors) should ideally offer reduced system weight or volume, and offer improved reliability and convenience compared to using assembly of independent structural components and batteries. These are not easy goals to meet since decades of efforts and significant funding have already been spent for optimizing each of such independent components [337–339]. In addition, for most applications it is important for the reliability of the structural batteries to meet or exceed that of the lifetime of the devices. For example, if solar panels, ground and aerial vehicles, and body armor are expected to last several decades, so should integrated batteries do, unless the replacement costs becomes more affordable over time (which is not completely unreasonable because the prices for specialized cells have reduced by nearly 10 times over the last decade [340]). For batteries integrated into smart buildings and construction, the expected calendar life should preferably approach a century (unless of course such construction features are temporary or subjected to slowly changing interior or exterior design fashion trends which stimulate their reconstructions every several decades or so). This contrasts with commercial cells, most of which are not designed to last for more than ~15 years [341]. Other applications (e.g., drones or flying appliances, smart textiles) may demand smaller cycle life (e.g., if used occasionally) and smaller calendar life (e.g., 5–10 years) as technology improvements in these fields are faster and the technology becomes obsolete and needs to be replaced quicker.

Historically, two main approaches for the formation of structural batteries have been explored: (i) further enhancing mechanical properties of inactive materials, such as current col-

lectors, separators and packaging (e.g., by the incorporation of small amounts (few %) of 1D or 2D materials or by selecting or otherwise developing mechanically stronger components) without any significant reduction in the battery energy density or (ii) utilizing strong 1D or 2D-based materials and solid electrolytes as main electrode/separator components to form ultra-strong structural composite batteries (Fig. 5a).

Structural battery components

All battery components can contribute to enhancing mechanical properties of structural batteries – current collectors, electrodes, separators, electrolyte, and packaging.

1D carbon materials, such as high-modulus CNTs and carbon fibers, are invaluable for multifunctional energy storage nanocomposite electrodes and current collectors, owing to their excellent mechanical properties (high strength, flexibility and fracture toughness) in combination with high electrical conductivity and thermal stability. Due to the presence of graphitic phases, carbon fibers exhibit capacity for Li intercalation similar to that of graphite anodes [342] and maintain high strength in a lithiated form [343]. While viable technologies for the formation of long nanofibers of Li or Na intercalation cathode materials have not been developed yet, deposition of thin active material coatings on the surface of CNTs and carbon nanofibers may offer a reasonable intermediate solution [344–347]. For example, FePO₄ deposited onto CNTs enabled formation of high tensile strength cathodes and good stability for 1000 cycles [346]. Deposition of conversion-type cathode materials [35] or alloying type anode materials [73] on the CNT surfaces also enabled high strength electrodes, although these may substantially reduce their properties upon Li insertion. In addition, replacement of common conductive additives (carbon black) with CNTs (including single-walled CNTs, SWCNTs) could meaningfully enhance mechanical performance of “regular” electrodes [348,349]. 2D carbon materials similarly enabled formation of strong electrodes. For example, exfoliated MXene nanosheets together with exfoliated graphene oxide (GO) were vacuum-infiltrated and crosslinked by a conjugated molecule (a π - π bridging agent) to fabricate super-tough supercapacitor electrodes, which exhibited a tensile strength of ~700 MPa, a failure strain of ~12.0%, and a ultrahigh toughness of ~42.7 MJ m⁻³, much better than neat MXene or reduced GO sheets [350]. The combination of 2D nanomaterials (e.g., graphene, MXenes) and high-strength 1D nanofibers (e.g., aramid, cellulose) could guarantee a high mechanical strength without sacrificing the electrochemical performance [351–354]. Dopamine-functionalized GO sheets were infiltrated with branched aramid nanofibers and subsequently treated by Ca [2]⁺ and thermal reduction to fabricate strong electrodes for structural supercapacitors, and the multifunctional electrodes exhibited an ultimate tensile strength of 117 ± 17 MPa, a Young’s modulus of 15 ± 3 GPa as well as high multifunctional efficiency values of 5–13.6 [351].

The use of high-strength aramid fibers and nanofibers (tensile strength of 0.15–4 GPa) enables stronger battery separators [355–357]. Such 1D polymer materials may be further strengthened with low-cost ceramic nanofibers [136,358,359]. Furthermore, the formation of 1D ceramic-polymer nanocomposites may enable low-cost, highly scalable (paper-like) fabrication methods,

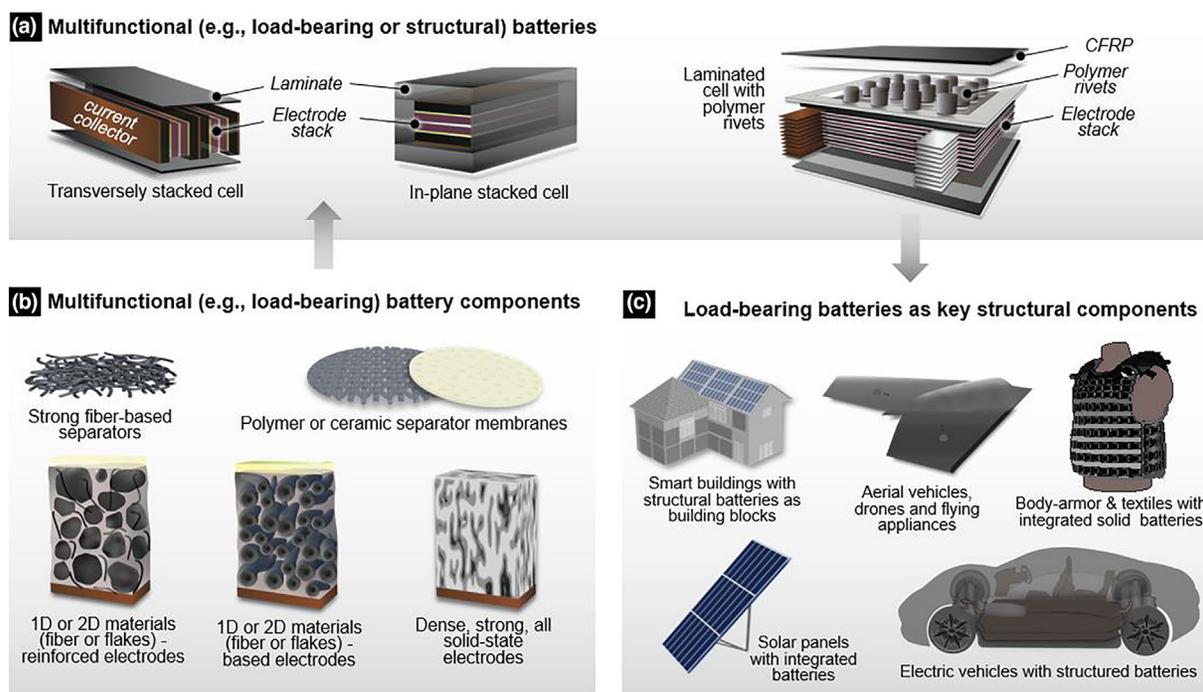


FIGURE 5

Structural load bearing or impact energy absorbing battery formation and integration. (a) Selected examples of multi-layered stacked cells, such as either transversely or in-plane stacked cells, some with polymer rivets accommodating thickness changes. (b) Examples of structural components, including electrodes and separators reinforced or based on strong 1D and 2D nanomaterials as well as fully dense, all-solid-state components. (c) Selected examples of structural battery applications, such as solar panels, aerial and ground vehicles, body-armor, and construction structures. Panel (a) was adapted from Ref. [93], Elsevier.

where increased mechanical resilience and thermal properties could be attained [138]. High tensile strength (>200 MPa) and excellent thermal stability of glass (SiO_2) fibers also enable their use in separators that enhance battery mechanical properties [360]. The large SiO_2 fiber diameter, the resulting large thickness of a fiber mat and resulting large pore sizes are generally undesirable as these reduce energy density or protection against internal short circuiting [361]. However, the use of all-ceramic nanofiber membranes made of Al_2O_3 or MgO nanofibers can overcome these limitations and additionally offer outstanding thermal, electrochemical and mechanical properties at a low manufacturing cost [136,362].

Mechanical deformations in structural batteries may induce significant safety risks when liquid electrolytes are used [363,364]. Besides, liquid electrolytes do not provide any mechanical reinforcement and may induce internal shorts upon separator failure. The addition of silica (or other insulative ceramic) nanoparticles to liquid electrolytes can trigger immediate increase in viscosity to the level of effective composite electrolyte solidification with the application of shear, enhancing impact resistance of batteries [365,366]. However, the content of shear-thickening nanoparticles should be rather high, which reduces battery capacity and rate performance and can trigger undesirable side reactions. In this respect, further development and application of ceramic and polymer electrolytes (Table 1) may offer a more attractive proposition to enhancing strength and improving stability of structural batteries. However, with a few exceptions [237], current techniques for the formation of all-solid-state batteries suffer from high cost and low attainable vol-

umetric capacities. In addition, many ceramic electrolytes are substantially (2–4 times) heavier than conventional liquid electrolytes, which reduces battery specific energy.

Structural battery integration into aerial and ground vehicles

Cell integrations into various devices require significant efforts. In case of structural cells, most of such efforts have been reported for their integration into the load-bearing parts of the aerial (mostly unmanned) vehicles (Fig. 5c), such as parts of a chassis or a wing in order to reduce the vehicle weight and improve its performance [368]. For example, the integration of a battery within the wing may balance the distribution of weight better, improve aerodynamics, and provide more space for the payload [369,370]. For such an effort, cell shape, cell packaging, load distribution and both chemical and mechanical compatibility between battery components and substrate laminate need to be carefully considered for a particular vehicle design [371,372]. Most of the efforts reported embedding batteries into carbon fiber reinforced plastics [370,373]. However, attaining optimal mechanical coupling via strong and reliable bonding and selecting suitable substrates, isolating layers and curing temperature that do not damage LIB cells during composite fabrication and provide reliable operation in spite of constant stresses and strains induced by the mechanical forces on the wing and the volume changes during cell operation remain challenging [373]. Stacking the battery electrode layers transversely relative to the laminate may enhance cell resistance to elastic deformations, improve compression, bending and shear strengths (Fig. 5a) [374], without sacrificing

volumetric energy density or cycle stability [375]. Alternatively, electrode and separator layers within a stacked cell could be bonded with a polymer to avoid slippage during stresses and enhance cell stiffness [93,360]. In order to accommodate some of the strain within the battery during operation, polymer rivets or their mechanical analogs could be utilized (Fig. 5a) [93]. In addition to the applications of structural batteries in aerial vehicles we expect that ground vehicles will eventually move to load-bearing battery packs where individual cells of various shape and size will be embedded within a mechanically reinforced plastic for reduced weight, volume and improved overall rigidity.

In a complementary approach, producing stronger and tougher cell components provide more opportunities for structural batteries and supercapacitors to work as a part or a “building block” that sustains mechanical loads and energy delivery, towards weight and volume savings for various applications. Here we highlight several impressive examples in Fig. 6. Deposition of thin polyaniline (PANI) layers on CNT sheets enabled lightweight supercapacitor electrodes (Fig. 6a) to reach a cycle life over 30,000 cycles as well as ultra-rough mechanical properties [118]. The tensile strength is up to 500 MPa (Fig. 6b), specific ultimate strength ~ 7 times higher than 1030 carbon steel) and the modulus of toughness is much higher than a variety of structural materials (e.g., ~ 5 times higher than titanium alloys) (Fig. 6c). Such a multifunctional composite film is strong, flexible and can be further integrated into lightweight products that would operate under extreme strength. Direct integration of pouch-free LIBs into a carbon fiber containing composite matrix via a traditional composite layup process can produce structural battery panels (Fig. 6d) [376], which can be used to fabricate a 1U CubeSat frame (4 panels in series) to create free volume. High-strength carbon fiber composites along with interlocking polymer rivets can stabilize electrode layer stack mechanically, and

inhibited any discernible capacity degradation even after 1000 cycles under 700 N (200 lb) bending loads [93], demonstrating promising applications in an electric skateboard with 10 cell-integrated deck (Fig. 6e) and drones or mini aircrafts with extended total flight time. A small drone was integrated with the corrugated Zn–MnO₂ batteries [24], which used a solid electrolyte with a composite of branched aramid nanofibers and PEO to enhance the stability and abuse tolerance (Fig. 6f). These illustrations indicate that structural energy storage firstly holds promise for applications in low-weight, high-mobility, or small-size products, including electric scooters, electric bike and drones all around the world.

Other applications for multifunctional power sources

In addition to the discussed above structural, mechanically strong batteries for load bearing applications (Fig. 5), we want to highlight some of the other multifunctional or otherwise unique cells with unusual properties or characteristics, often enabled by alternative cell architectures (Fig. 2). These are: implantable (e.g., 3D) battery cells, drug delivery-triggering cells, transient, biodegradable or self-destructing cells, biofluid activated cells, electrochemical actuator cells and water desalinating cells (Fig. 7).

Energy storage devices for implantable devices

Due to high voltage, high power, and high energy density, primary Li-metal batteries and rechargeable LIBs dominate the field of implantable medical devices, such as pacemakers, cochlear implants, among others [377]. A range of cell chemistries with versatile voltage and power characteristics have been used to meet the requirements for such applications [378]. Development of transcutaneous battery chargers allows one to avoid frequent surgeries to replace primary cells [379]. Further developments of implantable batteries (Fig. 7a) will focus on increasing their

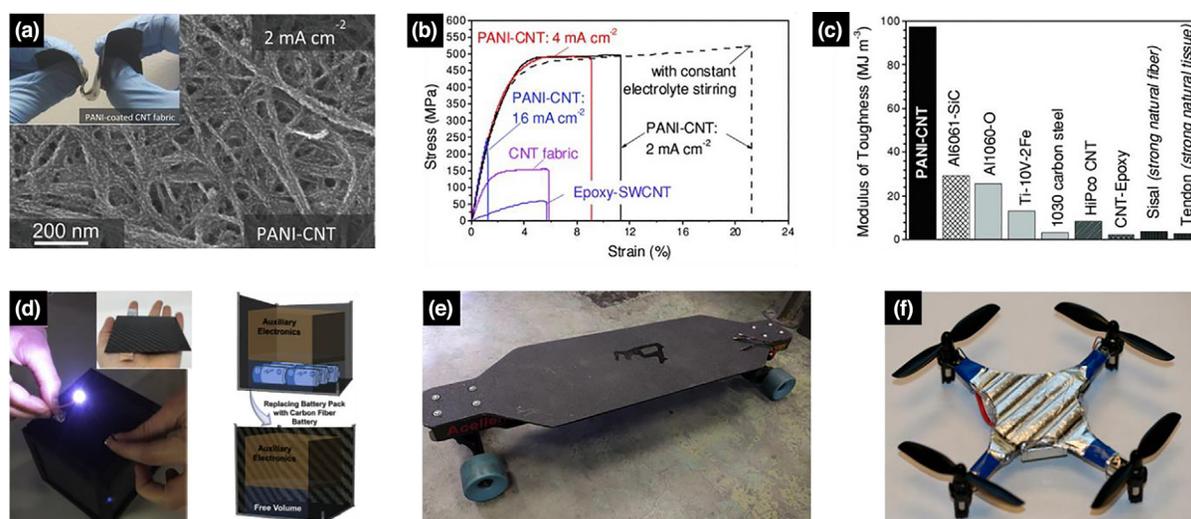


FIGURE 6

Selected examples of structural energy storage. (a) PANI-coated CNT fabric electrodes and (b) their tensile tests and (c) modules of toughness in comparison with other materials. (d) Carbon fiber reinforced structural LIB panels in a CubeSat frame can create free volume. (e) An electric skateboard integrated with structural LIBs. (f) A small drone integrated with corrugated Zn/MnO₂ structural batteries. Figure panels adapted from: (a-c) Ref. [118], Wiley-VCH; (d) Ref. [376], Elsevier; (e) Ref. [93], Elsevier; (f) Ref. [24], ACS.

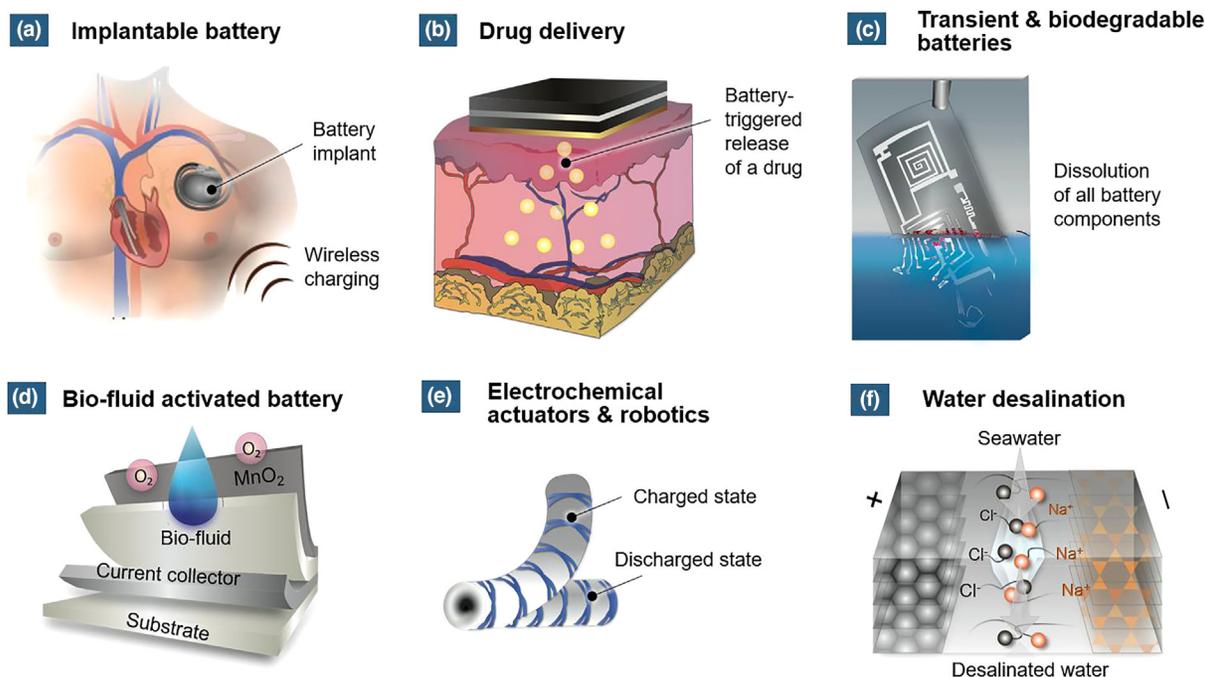


FIGURE 7

Selected other applications for multifunctional or otherwise unique power sources including (a) 3D implantable medical batteries to power artificial organs, (b) 2D cells for localized drug delivery, (c) transient, biodegradable batteries, (d) bio-fluid activated batteries, (e) 1D electrochemical actuator cells (robotics) and (f) water desalination cells.

calendar life, further miniaturization, improving biocompatibility and environmental friendliness, and most-importantly increasing power/energy characteristics [380–382]. Previously discussed 3D batteries may significantly outperform miniature conventional batteries in terms of energy and power performance due to the reduced fraction of inactives and shorter average ion transport length [383–385]. The very high quality, and low electrical resistance of thin solid electrolyte layer is needed for preventing a self-discharge of such cells, while high room temperature ionic conductivity is important for attaining better rate performance [386]. The advances in solid-state electrolytes (beyond lithium phosphorous oxynitride and perovskites [387,388]) and methods of their deposition may improve cell performance characteristics and additionally allow higher capacity anodes and cathode to be used. Newer chemistries for miniature batteries should enable further increase in their energy density [389]. For example, the use of Si anodes can increase cell capacity [390], while advanced micro- and nano-fabrication techniques can allow for accommodating volumetric expansion of Si during charge [391]. Efficient strategies demonstrated for high capacity conversion cathode chemistries, such as FeF_3 , FeF_2 , can be further translated to 2D and 3D batteries, especially when used with Si or Li metal anodes [392,393]. To alleviate possible issues associated with prolonged presence of batteries in biological systems, biocompatibility of fully hermetic enclosures needs to be improved [394,395]. The importance of cell improvements for implantable device applications could easily justify 10 and even 100 times higher cell price needed for initially small-scale fabrication. Once the technology becomes more mature, gradual price reduction may open this technology for other more

cost-sensitive applications. In addition to batteries, in-plane micro-supercapacitors can serve as implantable power sources either working complementally with miniaturized batteries, particularly when high power is needed [71,396]. The unique in-plane configuration enables micro-supercapacitors with high space utilization capability, which is beneficial for the integration of on-chip electronics. To sustain the external pressure and adapt to the body environment, all-solid-state, flexible, stretchable features are generally considered for fabricating implantable micro-supercapacitors. In this sense, micro-supercapacitors comprised of stacked 2D electrode materials (e.g., graphene, MXenes, TMDs), solid polymer electrolyte (e.g., PVA/LiCl, PVA/ H_2SO_4 , PVA/ H_3PO_4), and flexible/stretchable substrates (e.g., polyethylene terephthalate, polyimide, and polydimethylsiloxane) represent the current research trend [61,314,397].

Batteries for drug delivery

Active drug delivery devices allow precise control over the rate of a drug release. The role of a battery (Fig. 7b) in the active device is to power its circuitry and on-board electronics to release the drug either via electrothermal (where passage of a current ruptures a thin film) [398] or electrochemical (where passage of a current oxidizes and dissolves a thin film) [399] routes. In an alternative (passive) design with a much lower fraction of circuit components, a galvanic cell could be used to passively induce formation of gases (e.g., H_2 bubbles during spontaneous Zn oxidation and hydrogen reduction), which activate a drug release *in vivo* [400]. In many cases 2D battery architecture may be particularly suited for this application. Prior work on the use of polymer micelles and other nanocap-

sules for drug-delivery may inspire future innovative battery designs [401].

Transient, biodegradable and self-destructing batteries

Autonomous transient devices (including transient batteries (Fig. 7c)), which aim to function and then disappear over the time, are gaining a momentum in the biomedical engineering, data security and nature sensing [402–404]. The construction of transient devices is quite challenging as it requires the use of many smart materials that are affected by the transiency stimulus, such as fluid, heat, mechanical force or light [404,405]. For example, a battery designed only from organic materials, such as *p*-benzoquinone/hydroquinonesulfonic acid potassium salt redox couple, carbon current collector and beeswax encasing, undergoes degradation into environmentally benign chemicals, such as CO₂, CH₄, H₂O, and N₂, under the influence of microorganisms in the water or soil [406]. Batteries made of materials essential for human body, such as those providing dietary functions, represent another promising direction [394]. Biologically derived bioresorbable redox active melanin and polydopamine molecules may be used in rechargeable transient Li/Na-ion batteries [407,408]. Unlike bio-inspired batteries, transiency of more traditional and higher energy density LIBs is much more challenging to achieve as common LIB materials are toxic, not biocompatible and not easily degradable. However, some approaches have been explored to deactivate LIB cells upon changing the environment. For example, the use of some of highly water-soluble polymer binders may trigger rapid degradation of electrodes into a colloidal particles upon contact with aqueous solutions [121,409]. High and controllable transiency can be achieved by using bilayer PVA/PC packaging, which is stable in water, but fully degradable in basic solutions [410].

Magnesium (Mg) with its low redox potential (only ~0.67 V above that for Li/Li⁺) and high volumetric capacity (87% higher than that of Li) is an example of bioresorbable and biocompatible, high capacity battery anode, and, when used with other biodegradable Zn, Fe, Mo, W, Au cathode foils, can enable transient metal-air batteries [411–413]. A fully transient Mg-air battery was demonstrated on the biodegradable silk fibroin substrate with 100 nm layer of Au catalyst for oxygen reduction reaction to enable relatively high voltage of 2.3 V [414]. Biocompatible polypyrrole cathodes can be also utilized in Mg-air battery for achieving high cell voltage [415]. The Mg–MoO₃ battery encased in polylactic-co-glycolic acid (PLGA) polymers is able to deliver an output voltage up to 1.6 V for 13 days and completely degrade subcutaneously in mice within 4 weeks [416]. Thermo-sensitive batteries can be realized through the encapsulation of a corrosive material, such as methanesulfonic acid into low-melting point wax [417]. Thermal triggering releases the acid onto the Mg electrodes and depolymerize polyanhydride substrate [417,418]. Apart from solution-based transience, electrochemically triggered transience of Si-based electronics by lithiation of Si (to form highly reactive Li_xSi) may enable on-demand failure of Si electronics, due to the generation of microcracks from the accelerated Li penetration [419]. Further integration of this transience mechanism with LIBs and remote control circuits could be used to purposely destroy devices if needed for security or privacy reasons.

Biofluid-activated batteries

Biofluid-activated batteries (Fig. 7d) turn on upon the electrolyte addition. Therefore, they do not need casing and electrolyte, which may benefit point-of-care biomedical devices, such as glucose monitors for diabetes management, gastric and intestine sensors, and other bioassays. Low manufacturing cost, variety of available chemistries and accessible on-chip designs leverage the utilization of such batteries. However, the difference in physical and chemical properties of biofluids, large sheet resistance of electrodes, and high internal resistance of separator layer and metal-anode corrosion pose challenges [94,394,420].

Biofluid-activated Al-air and Zn-air batteries are gain momentum owing to their high energy density and miniature size [381]. Their preparation is also relatively simple and requires the enclosure of Al foil, particles, or wires, in the paper substrate with deposited oxygen reduction catalyst such as MnO₂, Ag or Pd [421–424]. A range of other suitable chemistries comprise of Mg/CuCl [425], Mg/AgNO₃ [426], Al/CuSO₄ [427], Al/Ag₂O [420], C/MnO₂ [428], Zn/Pt [402], and other electrode couples. When manufactured in stacks, these can deliver high voltages and high powers. For example, a micro-battery composed of Zn and Pt electrodes when using a gastric fluid as an electrolyte can stably generate 0.6 V for 39 min powering 500 Ohms load resistor [402]. To overcome air-associated metal-corrosion and thus limited anode capacity, cell voltage, and current density [381], phosphorous rich and neutral pH biofluids could be used to form a protective surface layer, which prevents permeation of O₂ to the anode surface [413,429].

Battery actuators

Actuators are controllable work-producing devices that can change shape or dimensions using the energy of a power supply, and they generally draw their energy from different sources (e.g. chemical, electrical, and mechanical) [430]. Because conversion of chemical energy into electricity occurs through the substantial volumetric strain of the electrode active materials, a battery combines electromechanical and power characteristics needed for the actuation (Fig. 7e). For example, silicon, germanium and tin exhibit gigantic volume changes (up to 400%) upon lithiation and delithiation [431]. Harnessing electrode designs, by adding stiff fibers or sheets [432], can enable control over the complex shapes and induce large amount of actuation strain (up to 300%) and load-bearing capabilities (up to 1 GPa) [433,434]. For example, a Si nanowire actuator exhibits greater control over the actuation strain as compared to the Si thin-film or macroscale actuator, which is critical for some applications like nanopositioning [433,435]. Among other advantages of batteries over piezoelectric, shape memory alloy-based and electrostrictive actuators is their non-volatile actuation mode, as the lithium alloy composition does not change even after voltage switch-off [436,437]. Additionally, the actuator's displacements can be controlled by the state-of-charge of a battery, and more importantly, battery actuators exhibit cycling performance attributes [432,435].

Water desalination

Currently, the scarcity of fresh water threatens over 2.5 billion people [438]. Electrochemical water desalination could be an

alternative solution, in addition to traditional seawater reverse osmosis (SWRO, often limited by investment, geography, environment, energy supply, etc.) [439,440]. Electrochemical desalination generally functions via different electrochemical processes (e.g., capacitive-deionization (CDI), surface redox, ion insertion or conversion reactions) to exhibit good cyclic efficiency and reversibility. Generally, CDI cells consists of two porous carbon electrodes sandwiched by a separator as the feed flow channel. Alternatively, the desalination electrodes can be other battery (intercalation or conversion) materials such as graphite [441], TiO_2 [442], sodium manganese oxide (NMO) [443], bismuth (Bi) [444], or redox electrolyte (e.g., iodide or bromide based) [445,446]. Due to the similarities of desalination electrodes with energy storage devices (aqueous batteries and supercapacitors), the incorporation of desalination and energy storage in an integrated system or device could hold the promise for portable energy storage and water purification in some emergent situations [447–450]. On operation of a desalination battery (Fig. 7f), the discharge process leads to the removal of NaCl from the saline electrolyte and the capture of Cl and Na ions by two electrodes. Before the subsequent charge process, the desalinated water is replaced with seawater and then to release ions to produce concentrated brine during charging. As a result, the cell can generate two streams along with reversely energy storage.

Inspiring examples

In addition to previously discussed battery integration into transportation devices (Fig. 6), we want to highlight a few inspiring examples of the integration of small or compliant batteries or

capacitors into medical devices, electronic devices, smart textiles, jewelry, toys, and soft robots (Figs. 8 and 9).

Recently, a flexible, non-cytotoxic LIB with millimeter size and ultra-light weight (just 236 μg) was developed and integrated into an intra-oral implantable device for orthodontic treatment (Fig. 8a) [63], demonstrating great potential for personalized health-care applications. Transient electronics for implantable devices require all components of the device to be biodegradable, digestible or absorbable by cell systems [451,452]. A bioabsorbable capacitor was recently produced to power transient implantable medical devices (Fig. 8b) [453], since it can be fully degraded in vivo and reabsorbed by a Sprague-Dawley (SD) rat. In another example, a microfluidic–microelectronic, skin-interfaced device was mounted on the chest to simultaneously monitor heart rate, sweat chloride (Cl^-) and sweat pH (Fig. 8c) [454]. Such a device can be powered by a sweat-activated biocompatible battery (e.g., a flexible Mg anode, a printed Ag/AgCl-based cathode and a cellulose membrane impregnated with NaCl as a separator that uses sweat as both an activating cue and a natural, biocompatible electrolyte). A concept of flow dual-ions electrochemical deionization was recently proposed to develop a desalination generator device that consists of two electrodes (BiOCl and NMO) with anion and cation exchange membranes (AEM and CEM), with an aqueous flow feed of NaCl electrolyte (Fig. 8d) [455]. Under positive electric current operations, the two ions are released for NaCl water electrolyte to flow, while switching to negative the Cl and Na ions are electrochemically captured into the two electrode and thus prevented from flowing into the salt solution. Such a system works as a desalination generator as energy can be released during discharge process.

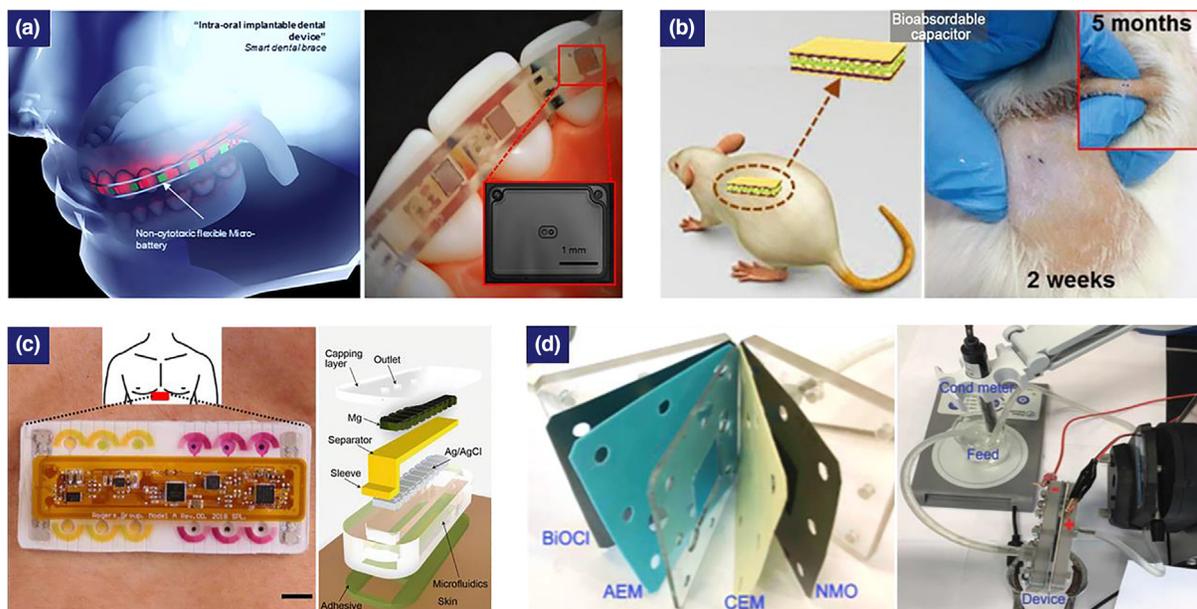


FIGURE 8

Selected examples of small or compliant energy storage for biomedical and other applications. (a) Flexible, non-cytotoxic, millimeter-sized LIBs that can be integrated into an intra-oral implantable device, (b) a bioabsorbable capacitor implanted in the dorsal subcutaneous region of a Sprague-Dawley (SD) rat and the implanted site containing the device before and after degradation at different time, (c) a sweat-activated battery-powered, skin-interfaced hybrid microfluidic–microelectronic system and the scheme of the sweat-activated cell (left), (d) the internal structure of dual-ions electrochemical deionization device and the experimental setup. Figure panels adapted from: (a) Ref. [456], Springer Nature; (b) Ref. [453], Wiley; (c) Ref. [454], Springer Nature; (d) Ref. [455], RSC.

Fig. 9a illustrates 1D flexible triboelectric nanogenerator (TENG) and asymmetric supercapacitors (ASCs) yarned into a smart textile that harvests mechanical energy of human motion and converts it into electricity storing in ASCs [457]. Fig. 9b shows a jewelry-integrated power source design with a compliant battery and a photovoltaic module [46]. Flexible active-matrix organic light-emitting diode (AMOLED) displays (Fig. 9c) [458] to power flexible cell phones and tablets would benefit from using integrated, flexible batteries. The incorporation of electrochromism (reversible color change triggered by electrochemical reactions) and energy storage can visualize energy storage level in real time and additionally reduce the energy consumption of electrochromic devices [397,459,460]. Fabry-Perot (F-P) cavity-type electrochemical supercapacitors allowed the device to exhibit exceptionally aesthetic versatility (Fig. 9d) [461], which may provide an elegant solution for smart displays and smart windows integrated with energy storage. Smart implantable or epidermal devices have been developed to better realize the monitoring and therapy of human body. Among them, smart contact lenses can be used to monitor the vital signs in the eyes or in tears [462], and such devices have been recently

integrated with a wirelessly rechargeable, arc-shaped solid-state supercapacitor to enable continuous operations (Fig. 9e) [463]. The use of energy storage in hydraulic fluids enables electrolytic vascular systems for energy-dense robots such as a lionfish-inspired robot (Fig. 9f), which can be powered by integrated zinc iodide redox flow battery for up to 36 hour-long operation [464]. Besides, power sources with self-protection capability over extreme situations (like high temperature, overcharge) were reported by introducing stimuli-responsive polymer electrolyte devices. For example, micro-supercapacitors equipped with thermoresponsive polymer electrolytes can be reversibly switched on/off along with the temperature decrease/increase [465]. Such temperature-dependent behavior can not only work as a temperature indicator/sensor, but also protect the device from destruction induced by high temperature. Moreover, the use of pH-responsive polymer electrolyte in zinc-iodine aqueous batteries empowers the device with overcharge self-protection capability [5]. Once the battery is overcharged, the slightly changed electrolyte pH rapidly triggers the sol-to-gel transformation of the battery electrolyte, thus protecting the battery from continuous damage by blocking the ion transportation in the electrolyte.

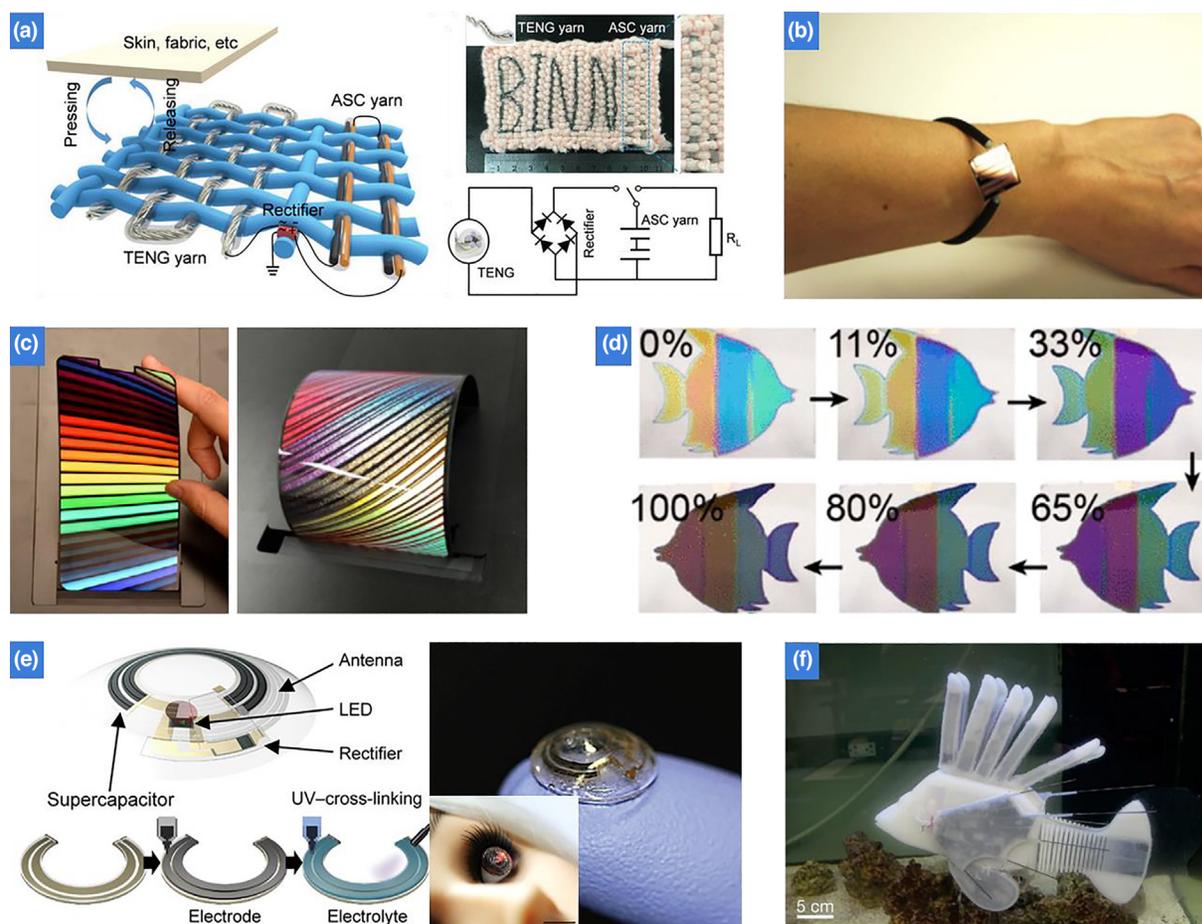


FIGURE 9

Selected examples of integrated systems with batteries and supercapacitors. (a) Self-charging power textile by integrating triboelectric nanogenerator (TENG) and asymmetric supercapacitor (ASC) yarns in a common fabric, (b) photovoltaic module and 1D wire battery integrated into a wearable bracelet, (c) flexible AMOLED displays of flat and arch types that can be integrated with flexible batteries, (d) Fabry-Perot (F-P) cavity-type electrochromic supercapacitors with a “colorful fish” pattern, (e) soft, smart contact lens integrated with arc-shaped supercapacitors, antenna, LED and rectifier, (f) lionfish-inspired robot powered by a multifunctional zinc iodide redox flow battery is swimming underwater via tail fin actuation. Images adapted from: (a) Ref. [457], Wiley; (b) Ref. [46], AAAS; (c) Ref. [458], Wiley; (d) Ref. [461], ACS; (e) Ref. [463], AAAS; (f) Ref. [464], Springer Nature.

Challenges and market opportunities

Despite the great promises for the discussed emerging technologies and unfulfilled market needs, several challenges need to be overcome through additional research and development to unveil full potential of flexible, integrated, and multifunctional batteries and supercapacitors. We want to summarize (often reiterate) these challenges below.

Power/energy density. Attaining high volumetric energy and power densities are important for most (although not all) applications. Maximizing volumetric capacity of electrodes typically require dense packing of the active materials. Yet, 0D, 1D, 2D and even 3D nanomaterials typically suffer from reduced packing densities, particularly in cases when high degree of flexibility or deformability is required. Development of both guiding principles and manufacturing techniques for the formation flexible and yet dense electrodes will be highly beneficial. At least an occasional high-power requirement is another challenge. For example, the average power consumption of Bluetooth Low Energy (BTLE) application can be low, but sometimes much higher power is needed for short time periods. The power of most energy storage devices is limited by the slow ion transport rather than electron transport. Many solid electrolytes, in particular, suffer from insufficiently high ionic conductivities (Table 1) or high charge transfer resistance in contact with active materials and their performance should be sufficiently improved.

Self-charging of integrated energy storage. While we have become accustomed to charging electronic devices by plugging in or more recently wirelessly, there is an unfilled desire to use similarly integrated energy harvesting technology to charge them. The most common way to charge batteries or supercapacitors is by a constant current – constant voltage (cc-cv) protocols. Yet, most energy harvesting technologies provide irregular inputs. For example, mechanical energy harvested using TENG and similar technologies may come in the form of electrical pulses, whose amplitude and frequency varying depending on the external environment and conditions. Optimizing electronics and charging protocols for such irregular inputs will likely remain important in the future [466]. Interestingly, pulsed power inputs may improve cycle life and overall performance of batteries in many cases [467,468], and deeper fundamental understanding of such phenomena may benefit novel self-charging technologies [469].

Leakage current. Leakage current is one of the key challenges in many supercapacitors, particularly those that comprise redox materials or functional groups [470,471]. Multiple factors have been proposed to contribute to leakage currents, from localized electrolyte decomposition [472] to redistribution of the charges on the surface [473] to the formation or presence of redox mediators (that may effectively move electrons through otherwise electrically insulative and ionically conductive electrolytes) [474] to thermal fluctuations and photo excitation which may induce electron emissions [475,476]. In batteries, self-discharge is typically linked to side reactions between electrolyte and electrodes, such as electrolyte decomposition or active material dissolution [477]. In case of solid electrolytes, some of them may exhibit meaningful electronic conductivity and the formation of certain defects during deformation or ion

dissolution and migration may undesirably increase this conductivity [478,479]. Overall, deeper understanding of the leakage current-inducing phenomena for different electrolyte and electrode chemistries may particularly benefit novel design architectures that often feature thinner separator layers.

Safety. In most case we should discuss not insufficient safety, but rather insufficient “abuse tolerance”, i.e. how the battery behaves under abnormal conditions (physical damages, exposing to bending, twisting or tensile stresses, overcharge, exposure to high temperature and others). We expect that in medical patches, smart clothes, smart printing products, shipping labels and various other applications of flexible, wearable or integrated batteries, physical damages may become inevitable and may potentially result in electrolyte leakages, short circuits, flammable fumes and catastrophic failures (fires, explosions, environmental or human poisoning). Therefore, there is a strong desire to use more environmentally friendly chemistries and nonflammable or fire-resistant materials [231,232]. Some of such safer cells are now becoming available commercially through Molex[®], Imprint Energy[®] and other companies producing thin and flexible batteries. Yet, safer cells commonly suffer from reduced energy and power characteristics.

Cost. Many applications are cost-sensitive and the immaturity of some of the discussed materials, electrodes and cell fabrication technologies makes them too expensive for broader market acceptance. For example, electronic devices developed for the internet of things (IoT) applications, medical patches, small and often disposable medical or consumer devices may cost \$1-\$10 and the battery price should preferably not exceed 1–10% of the device cost. For large batteries integrated into transportation (cars, drones, electric planes) or construction, the low energy storage price is also critical. Therefore, further development of the discussed manufacturing technologies (initially for less cost-sensitive applications), increasing their throughput, reducing labor and amortization costs will become critical for the commercialization success.

Disposability. Many of the inexpensive devices with integrated batteries eventually end up in the household trash, so the use of environment-friendly materials and chemicals as well as nonflammable electrolytes to fabricate disposable batteries become particularly important.

Despite the current challenges, successful development of multifunction, flexible and integrated energy storage technologies hold great promises for many emerging applications. The market of flexible batteries is growing rapidly. From the current market of around \$100 M this year, it is expected to expand to \$500 M by 2030 and exceed \$1B by 2040 with advances in cost-effective scale-up techniques (Fig. 10a, data collected from market reports [480] and our further predictions). The market of integrated energy storage is expected to grow rapidly within a decade. By 2030, the average price of integrated LIBs may approach ~\$100/kWh [481]. Based on the total predicted market size and assuming a very conservative (1%) penetration the market should grow to over \$2B, triggered by the increasing demands of lightweight transportation and consumer electronics. The market of integrated and multifunctional energy storage is expected to be eventually at least 20 times larger than flexible batteries. Under

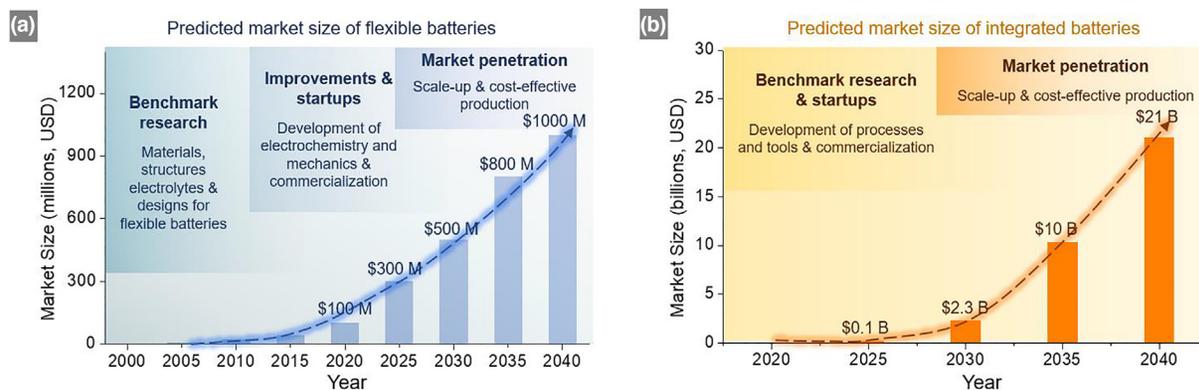


FIGURE 10

Forecasts of flexible & integrated battery markets. (a) Predictions of the flexible battery market (data adopted from market reports and our further predictions), (b) speculative predictions of the integrated battery market by the authors.

a hypothesis that a very modest market penetration with 5% of all the energy storage devices in these applications will become integrated by 2040 and that the average price of integrated storage may be lowered to \sim \$70/kWh [482], we may expect over \$21B market by 2040 (Fig. 10b). This exciting market opportunity should encourage further investments into materials research and novel material processing techniques.

Conclusions and outlook

In this Review, we have discussed 1D, 2D and 3D batteries and supercapacitors with alternative design or device architecture that may be more suitable for accommodating mechanical deformations, conforming to various shapes, integration with other devices and load-bearing functionality. We demonstrated in our review that in contrast to traditional electrodes made of relatively brittle and poorly bonded to each other micron-scale particles casted on metal foil current collectors, the use of 1D, 2D and porous 3D nanostructured materials in both active and inactive device components may not only overcome these limitations, but also strongly enhance such devices' mechanical properties, ion transport and rate performance for a broad range of cell chemistries. We reviewed advantages and limitations of ionic liquid, polymer, inorganic solid electrolytes, and their hybrids compared to traditional organic and aqueous electrolytes for use in multifunctional and integrated cells and concluded that further enhancements in ionic conductivity and processability of alternative electrolytes are still required for most applications. Alternative device architectures and the formation of novel nanostructured materials often demand the use of alternative device fabrication and synthesis methods. We reviewed the use of dip coating, layer-by-layer deposition, electrodeposition, electrophoretic and electroless deposition, spaying and spinning, various printing techniques, lithography, vapor deposition techniques (ALD, CVD, PVD, etc.), dealloying, etching, exfoliation, self-assembly and others technologies. We further reviewed the examples of structural batteries and other multifunctional and unique cells with unusual properties or characteristics, such as implantable cells, drug delivery-triggering cells, transient, biodegradable or self-destructing cells, biofluid activated cells, electrochemical actuator cells and water desalinating cells.

Despite the significant progress and creative ideas demonstrated to date, the fabrications and applications of multifunction, flexible and integrated batteries and supercapacitors are still in their infancy. Alternative device architecture currently remains very expensive to implement. The production volumes of suitable nanostructured materials are tiny. Many modern material synthesis and deposition techniques needed for their fabrication already offer very good reliability and precise control but suffer from relatively small scale or expensive production. may lead to faster self-discharge, shorter cycle and calendar life and reduced volumetric energy density. Technical principles and standards need to be developed for testing and comparing performance of multifunctional cells. Furthermore, such standards may need to be tuned for particular applications.

On a positive side, with the rapidly increasing progress in materials science, electrochemistry, micro-/nanofabrication, process engineering, simulations, calculations, and machine learning, we expect that many of the present materials and synthesis limitations will be gradually overcome over the next 1–2 decades. The rapidly developing markets in flexible electronics, sensors, the Internet of Things, alternative energy, autonomous vehicles, electric aviation, and drones, smart packaging, smart clothing, and smart paper products will fuel the demand for such developments. As such, we expect that the future investments into the joint efforts of both academic and industrial communities will lead to the rapid progress in commercialization of such energy storage technologies.

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.

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