

Perspective

Self-rechargeable energizers for sustainability

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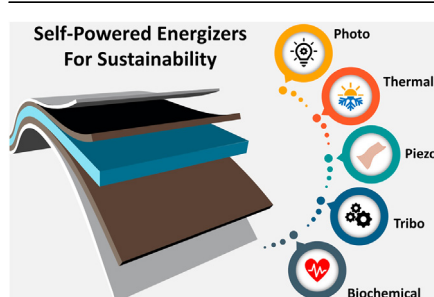
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HIGHLIGHTS

- Self-powered energizers for wearable/implantable/microelectronics are proposed.
- Ambient energies as sources for energy generation and storage are reviewed.
- Self-rechargeability mechanisms and the required modifications are discussed.
- Energizer designs for yarn/thread/textile applications are reviewed.
- Challenges for each self-powered energizer are pinpointed.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrical energy generation and storage have always been complementary to each other but are often disconnected in practical electrical appliances. Recently, efforts to combine both energy generation and storage into self-powered energizers have demonstrated promising power sources for wearable and implantable electronics. In line with these efforts, achieving self-rechargeability in energy storage from ambient energy is envisioned as a tertiary energy storage (3rd-ES) phenomenon. This review examines a few of the possible 3rd-ES capable of harvesting ambient energy (photo-, thermo-, piezo-, tribo-, and bio-electrochemical energizers), focusing also on the devices' sustainability. The self-rechargeability mechanisms of these devices, which function through modifications of the energizers' constituents, are analyzed, and designs for wearable electronics are also reviewed. The challenges for self-rechargeable energizers and avenues for further electrochemical performance enhancement are discussed. This article serves as a one-stop source of information on self-rechargeable energizers, which are anticipated to drive the revolution in 3rd-ES technologies.

1. Introduction

In the Fourth Industrial Revolution (IR4.0), both information and energy are pivotal elements for the advancement of modern society.

Increasing demands for uninterrupted health monitoring and communication have fueled tremendous research activities to develop suitable textiles and implantable microelectronics [1,2]. However, powering these through physical wire connections is not an option, so equivalent

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portable and flexible energy storage devices are required. Among the rechargeable energy storage technologies, the electrochemical capacitor (EC, also known as the supercapacitor) is regarded as a sensible choice of power source over batteries, owing to its higher power density as well as superior cycling stability [3]. However, its low energy density means the EC requires constant charging to continuously drive electronics components, triggering research into self-powered units for wearable/microelectronics.

Modern society is mobilized by two main networks: information (the Internet) and energy (Fig. 1). The Internet has advanced phenomenally ever since its establishment in the 1980s, making communication possible and information accessible globally through either cable connection or wireless transmission. In comparison, access to the current energy network is limited to physical wire connections, aside from a few implanted devices powered through induction charging. Recent research on energy storage has mainly focused on high-power applications, owing to (i) efforts to decarbonize the production and transport sectors, (ii) rapid growth in the market share and value of this sector, and (iii) the need to overcome the intermittency of renewable energy power plants. However, a potential burst of development in wearable/microelectronics, together with the Internet of Things (IoT) in the coming decades cannot be ruled out, and methods for powering these appliances are the subject of intense research. These electronics could be installed in remote places or embedded within confined space that are not easily accessible, such as the human body, making physical connection with the energy grid infeasible. Mimicking the information network, efforts have been made to develop wireless power transfer technology that allows electricity to be sent to electronics wirelessly [4–6]. However, wireless power transmission efficiency is extremely low (< 20%), and it plummets with increasing distance between the emitter and transponder (dropping to ~2.6% at a distance of 10 km) [7]. In addition, the higher microwave intensity required to increase the power transmission efficiency raises fears about the effect of long-term exposure to these microwaves on physical and psychological health [8–10], with research on electromagnetic wave shielding materials gaining tremendous attention [11,12]. Another technique would be to integrate storage and harvesting devices, allowing ambient energies to be directly utilized via the storage constituents [13,14].

Numerous self-powered energizers, based on two main configurations (either in tandem or incorporated), have been reported. In tandem configurations, both the nanogenerator and energy storage are connected through an external connection or a common electrode [15,16]. For example, in a photocapacitor developed from low-cost solution-processable perovskite solar cells and an electrochemical capacitor, both compartments were connected with a common multiwalled carbon

nanotube electrode [17,18]. Such tandem design allows energy to be generated in one compartment, then channeled to the second compartment for storage, demonstrating the possibility of alleviating the intermittency of renewable energy [19,20]. Tandem configuration have been widely adopted for developing self-powered energizers, as they are easy to manufacture without disturbing the physics, chemistry, and principal working mechanisms of both generator and storage device [21–23]. However, the tandem configuration consists of repetitive components (i.e., current collectors, substrates, separator, etc.), which bring additional weight and cost and affect the device's mechanical integrity when it is subjected to distortion (i.e., bending, twisting, folding, etc.) [24,25]. A configuration capable of self-powering while retaining fewer components is preferable. Incorporated configurations, on the other hand, give the energy storage device the capability to harvest energy on its own by tuning the properties of its components (i.e., electrode, electrolyte, or separator) [26–28]. While numerous reviews on self-powered energizers with incorporated configurations have been published [29–31], most have focused on piezoelectric-based tertiary energy storage technologies, given their simplicity to produce (substituting a piezo-active separator) and the abundance of energy sources, while leaving other counterparts out of the limelight.

Here, we categorize a collection of self-powered energizers and propose tertiary self-rechargeable energy storage (3rd-ES) technologies as the next major development, in line with going beyond lithium-ion batteries, focusing on supplying power for emerging wearable/microelectronics applications. In this article, an energizer is defined as an electronic device capable of storing electrical energy for later use, which includes both batteries and ECs. The proposed 3rd-ES technologies are based on the well-developed physics and chemistries of secondary batteries, with the addition of energy harvesting capability through component modifications. A 3rd-ES should meet at least the following criteria: (i) it is multifunctional, especially with the capability to generate and store electricity, (ii) it utilizes ambient/waste energy as the electricity generation source, and (iii) it is miniaturized to allow easy integration into microelectronics or to be deployed in implants. Herein, we focus on addressing (1) the future major market for energy storage technologies, (2) the revolution in energy storage to meet the requirements of future electronics, and (3) the achievability of self-rechargeability and subsequent required modifications to battery constituents. Discussions are focused on a collection of self-powered energizers based on a wide range of ambient energy as their source, to offer a more holistic view on the concept of 3rd-ES technology. Self-rechargeable batteries with both harvester and storage connected through an external circuit or a common electrode are not included within the

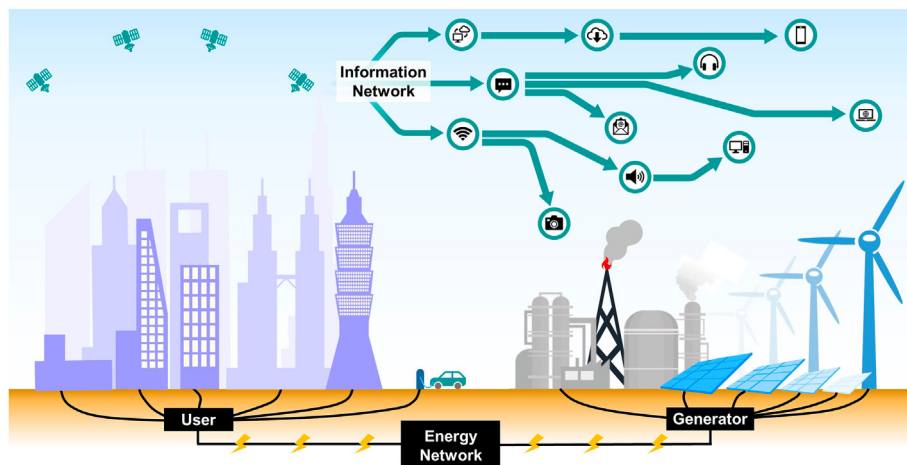


Fig. 1. Illustration of future modern society. Modern reliance on uninterrupted information flow, communication, and the electronics to support these abilities has led to the development of information and energy networks, which are believed to be the backbone for advancing future modern society.

concept of 3rd-ES technology because no changes are being made to the storage component.

2. Energy storage market analysis and prediction

Lithium-ion batteries were introduced to the market more than three decades ago, leading to widespread applications ranging from consumable electronics to electric vehicles (EVs). Recently, the demands for secondary rechargeable energy storage devices have increased drastically due to initiatives and movements to curb global warming in line with the 2016 Paris Agreement. Several developed countries have initiated the petrol-to-gas transition in the energy and transportation sectors. For example, in 2020, the UK government set the target of totally eliminating petrol-based vehicles by 2035, paving the way for developing the renewable energy sector. The United States of America followed in 2021, giving impetus to initiate facilities construction for the electrification of the transportation sector. With rising demands for communication electronics, the Internet of Things (IoT), and EVs, the market for lithium-ion batteries is forecast to be worth ~\$94.4 billion in 2025 and \$129.3 billion in 2027, nearly treble its value of \$44.2 billion in 2020 [32,33]. Fig. 2a summarizes the market shares in term of lithium-ion battery applications for 2013 and 2020, showing significant growth in demand in both the transportation and smart-grid sectors. Such increases are

understandable given that a single EV unit or power storage station require tens to hundreds of thousands of batteries. Even though the market share of consumable lithium-ion batteries has dropped, a CAGR of 8.87% in 2020 signaled that the market for portable electronics is still growing (Fig. 2b), with telecommunication and small electronics contributing 52% of the total sales [34]. Together with IR4.0, wherein cyber-physical system integration plays a major role, both artificial intelligence and IoT applications will become mainstream in daily communication. Future development in portable electronics is dynamic, with self-powering ability being one of the main features. Inevitably, the next major development in energy storage is most likely to revolve around providing energy to power wearable/microelectronics without any intervention from the energy grid [35]. These appliances will only achieve self-powering ability when power-harvesting modules are included; given the limited space within microelectronics, combining both energy harvesting and storage modules into a single entity would be a smart choice.

3. Evolution from primary to secondary energy storage

Fig. 2c summarizes the evolution of energy storage technologies during the past four centuries. In brief, the idea of storing electrical charges was first visualized independently by German cleric Ewald Georg

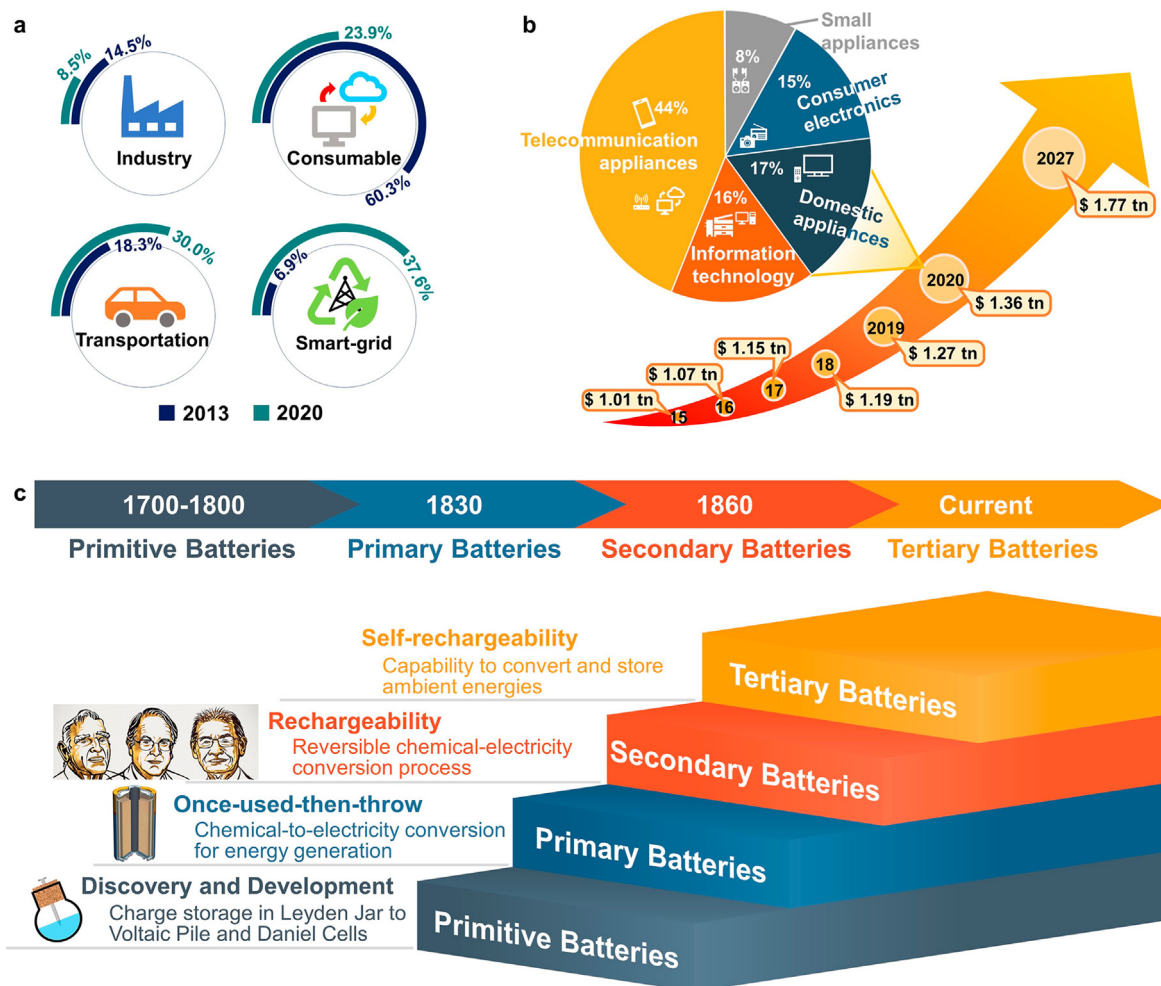


Fig. 2. Market statistics and future progress of energy storage technologies. (a) Drastic increases in the market shares of the transportation and smart-grid sectors can be related to the huge number of batteries involved in single electric vehicle units or power stations. (b) Explosive market value for information electronics, with increasing demand for communication devices. The next endeavors in energy storage technologies will most likely focus on meeting the requirements of future communication appliances. (c) Evolution of energy storage technologies from the 1700s to the 2020s. Based on this evolutionary history, the concept of self-rechargeability has been proposed for tertiary batteries.

von Kleist and Dutch physicist Pieter van Musschenbroek back in 1745, leading to the invention of the Leyden jar [36]. Its discovery started with the intention to capture the electrostatic force generated from rubbing materials against each other (known these days as the triboelectric effect). Back in the 16th–17th centuries, electricity was theorized as an unobservable fluid, which Von Kleist hypothesized could be captured (or stored) within a corked glass jar filled with alcohol, wherein the alcohol was connected to the energy source through a nail [37]. While holding the glass jar, Von Kleist accidentally touched the nail, receiving a significant electric shock.

Energy storage evolution then took another big leap with an observation by Luigi Galvani, who noticed the jerking of a frog's leg when it was subjected to a current between two metals. Inspired by this discovery, he successfully demonstrated electric current generation by separating two metals with a brine-soaked cloth. Through piling more metal–cloth–metal layers on top of one another, a voltaic pile (named after its inventor Alessandro Volta) with the ability to offer higher electric current was discovered in 1799 [38]. A subsequent development occurred about 40 years later when John Frederic Daniel created a new cell, called the Daniel cell, to overcome the hydrogen bubble issue in the voltaic pile. In brief, the Daniel cell consisted of a copper pot filled with copper sulphate, immersed in a container with sulfuric acid as the electrolyte and zinc metal as the counter electrode. Better known as the galvanic or alkaline battery, the Daniel cell was used extensively in household applications due to its ability to provide a continuous supply of electricity while also being portable. However, the “use once then throw away” nature of galvanic batteries aroused great concern about their environmental impact, given that sulfuric acid was deployed as the electrolyte.

The next major evolution in energy storage was unlocking rechargeability, which led to widespread electrification efforts in transportation sectors, along with smart grid storage stations. Distinguished by their ability to be recharged, these energy storage technologies were designated secondary (rechargeable) energy storage (2nd-ES). The first among the 2nd-ES to be introduced was the lead–acid battery, in 1859. The lead–acid battery is still widely used in 21st-century petrol-based automobiles because it can supply the high surge current required during acceleration [39]. In 1899, the nickel–cadmium battery attracted attention but became less impressive over time due to the high toxicity and expense of cadmium [40].

With the discovery of the lithium-ion battery by Nobel Laureate John B. Goodenough in 1980 [41], research in battery technologies entered new heights. A brief description of the discovery and development of the lithium-ion battery can be found elsewhere [42]. Surprisingly, adopting LiCoO_2 as the cathode and graphite as the anode offered a theoretical voltage window of 4.2 V, with an actual operational voltage of 3.6 V [43]. Such high operating voltage in a lithium-ion battery offered remarkably higher energy density compared to its predecessors. Unfortunately, the Li_xCoO_2 cathode can only be delithiated to $x = 0.5$, as further removal of lithium ions will lead to irreversible collapse of the crystal lattice, causing severe capacity deterioration and poor cycling stability [44–46]. To further improve the capacity of the cathode, cobalt was partially substituted with nickel (higher specific capacity) and manganese (better cycling stability), leading to the extensively studied layer-structured lithium nickel cobalt manganese oxide (NCM) materials [47–49].

To date, cathode materials with different crystal structures (namely layered, spinel, and olivine, as shown in Fig. 3a) and different working potential or gravimetric capacity (Fig. 3b) have been studied thoroughly,

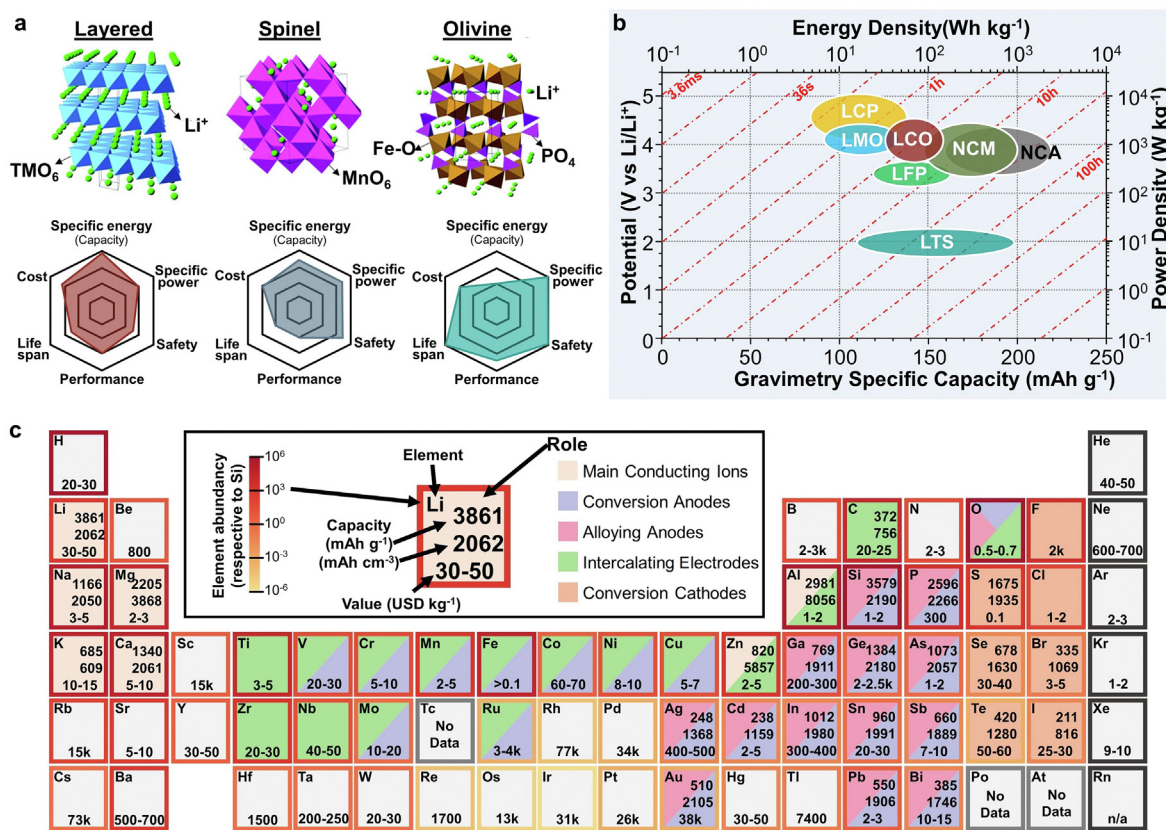


Fig. 3. Electrode materials in lithium-ion batteries. (a) Cathode materials with different crystal structures (layered, spinel, and olivine), along with comparison of their general performance. (b) The electrochemical potential, gravimetric specific capacity, energy density, and power density of layer-type (NCM, NCA, LCO, LTS), spinel-type (LMO), and olivine-type (LFP, LCP) cathode materials. (c) Periodic table tabulating the role of each element in the lithium-ion battery. The market value (last row) is determined from the cost of elements between 2020 and 2021; these values are subject to change from time to time.

with insightful reviews published elsewhere [50–54]. The quest to further enhance the energy density of the lithium-ion battery also drove the replacement of intercalating graphite (gravimetric capacity of ~ 300 mAh g⁻¹) with conversion or alloying type anode materials [55–57]. Alloying type anode materials have attracted tremendous research attention due to their superior gravimetric capacity (> 1000 mAh g⁻¹ compared to ~ 300 mAh g⁻¹ for an intercalated graphite anode), which is crucial for increasing the energy density of the lithium-ion battery [58–61]. Among the alloying anodes, silicon has emerged favorably with a theoretical gravimetric capacity of > 3000 mAh g⁻¹, a significant ten-fold enhancement over intercalated graphite. However, the tremendous volume expansion that occurs in the alloying anode (> 400 vol% for a silicon anode) during lithiation is associated with rapid capacity fading. Extreme volume changes during lithiation/delithiation also destabilize the SEI layer, increasing its thickness and shunt resistance [62–64]. To overcome these drawbacks, small amounts of silicon were added to graphite to enhance the capacity without severely damaging the cycling stability [65,66]. A conversion-type anode, on the other hand, offers a gravimetric capacity of 700–1000 mAh g⁻¹ with mild volume expansion (~ 100 vol%), allowing better energy density than a graphite anode without silicon-like capacity loss during cycling [67–72]. However, the large initial capacity losses in a conversion-type metal oxide anode due to irreversible crystal structure/phase transformation and high material resistivity do not guarantee favorable deployment of these anodes in lithium-ion batteries. Fig. 3c summarizes materials used for cathode or anode electrodes as well as their cost and capacity.

Aside from lithium-ion batteries, the supercapacitor (also known as an ultracapacitor, which means the same thing) has started attracting tremendous attention because it can supply a high power surge (high power density) as well as superior cycling stability across tens of thousands of (dis)charging cycles. The working mechanism of a typical supercapacitor is identical to that of the Leyden jar, but instead of water or alcohol, activated carbon with a large surface area is the electrode material [73,74]. Unlike lithium-ion batteries, in which charge storage is a bulk phenomenon, a supercapacitor stores charges through non-faradaic surface adsorption, making surface area the main criteria in determining the electrochemical performance of electrode materials [75, 76]. That said, ~ 200 F/g is the limit for capacitance achieved through surface engineering of porous activated carbon [77,78], so incorporating a metal oxide to induce pseudocapacitive storage and thereby further enhance the capacitance has been widely adopted by the research community [79,80]. Unfortunately, metal oxide-based electrodes are inferior in term of cycling stability, with merely 75% of the initial capacitance retained after 500 cycles of (dis)charging, compared to $> 99\%$ for activated carbon [81,82]. To circumvent this drawback, a range of metal oxide/porous carbon composites have been devised [83,84]. With its ability to instantly store electrical energy, the supercapacitor has a high power density, deemed crucial for storing intermittent energy sources, such as the ambient energy utilized by 3rd-ES technologies.

Undeniably, the push toward secondary rechargeable energy storage technologies with higher energy and power density has pressured both electrodes and electrolytes to operate at their fundamental limits, sometimes even exceeding their thermodynamic stability windows. To achieve a wider potential window, the anodes (graphite, silicon, or metal oxide negative electrodes) and cathodes (LiCoO₂, LiFePO₄, Li₂Ni_xCo_yMn_{1-x-y}O₂, etc.) are lithiated to extremely low (0.01 V vs. Li/Li⁺) and high (4.5 V vs. Li/Li⁺) potential, respectively, where either oxidation or reduction of the organic electrolyte occurs [85–88]. Even though further electrolyte decomposition could be inhibited through the formation of a passivating layer at both the cathode (cathode–electrolyte interphases) and the anode (solid–electrolyte interphases), severe initial capacity losses (ICL) cannot be avoided [89–92]. At high charging/discharging voltage, cathodes are usually delithiated to the point of irreversible structural transformation and oxygen loss, while anodes are lithiated to

the point that the lattice can no longer accommodate more Li ions and undergoes extreme volume expansion, leading to poor mechanical integrity that severely impacts cycling stability [93,94].

In light of these limitations, the lithium-ion battery has had a decade of redesign before the rise of beyond-lithium-ion technologies, although some remain unconvinced and believe that lithium-ion batteries can be further improved [95]. Certainly, technologies beyond the lithium-ion battery have attracted a tremendous amount of attention lately, with a few counterparts (lithium metal, lithium oxygen, etc.) able to deliver a much higher energy density [96,97]. Significant cost reduction is also expected by replacing lithium ions with the more abundant sodium and zinc ions [98,99], which can easily be achieved given the similarities in their charge storage chemistry. Here, we refer readers to the literature to gain a further understanding of the progress and limitations of different secondary batteries [95,100,101].

Redesigning the fundamentals of energy storage chemistry is suggested to be the next major breakthrough in energy storage. In fact, the underlying chemistries and physics of energy storage technologies have remained identical ever since their introduction in the form of two electrodes of opposite polarities separated by a porous separator and an electrolyte with a conductive salt. However, a complete overhaul of the physics, chemistry, and material science of energy storage could take decades of research and development before the technologies are mature enough for commercialization. Following the development of piezo- and tribo-nanogenerators, a self-charging mechanism was proposed as a measure to improve implantable microelectronic devices, one example being an early report on a self-powered cardiac pacemaker [102]. Presently, there are numerous ongoing studies on prolonging the battery lifetime of a pacemaker via self-charging, through harvesting either the body's heat or the pumping motion of the heart using thermoelectric and triboelectric generators, respectively [103–105]. In line with the need for self-powered energizers for wearable/implantable microelectronics, we propose that the next major evolution in energy storage technologies will revolve around achieving self-rechargeability, whereby the 2nd-ES will become capable of harvesting and storing ambient energy.

4. The concepts and mechanism of tertiary self-rechargeable energizers

An external power source that harvests energy from non-renewable or renewable resources is used to drive the charging process of 2nd-ES technologies. However, similar external power sources are not practical for appliances installed in remote places, implanted in the human body, or used in highly portable wearables, where 3rd-ES technologies are envisioned as providing the required energy to drive these electronics. Therefore, 3rd-ES technologies need to be able to generate potential differences from ambient energies (those that are widely ignored or regarded as waste energies) to drive the charging process. Conversion of ambient energy, such as light [19,106], body movements [107], ambient heat [108–110], etc., to electricity has been adequately demonstrated; this is then channeled through an external circuit to the energy storage device. Given that the space within a microelectronic is limited, a combined device structure that simultaneously functions to harvest and store energy is preferable.

In this context, two different configurations have been introduced (Fig. 4a; using photovoltaic cells as the example); (i) a three-electrode tandem device, where generator and storage compartments are connected via a common electrode (Fig. 4a(i)), and (ii) a two-electrode device with the energy harvesting function fully integrated into one of the components of the storage compartment (Fig. 4a(ii)). The three-electrode tandem device will not be discussed further here, as no significant engineering follows the energy storage protocol, given that the electricity generation and charge storage phenomena are disconnected and need to be connected externally (using a common electrode, in this case).

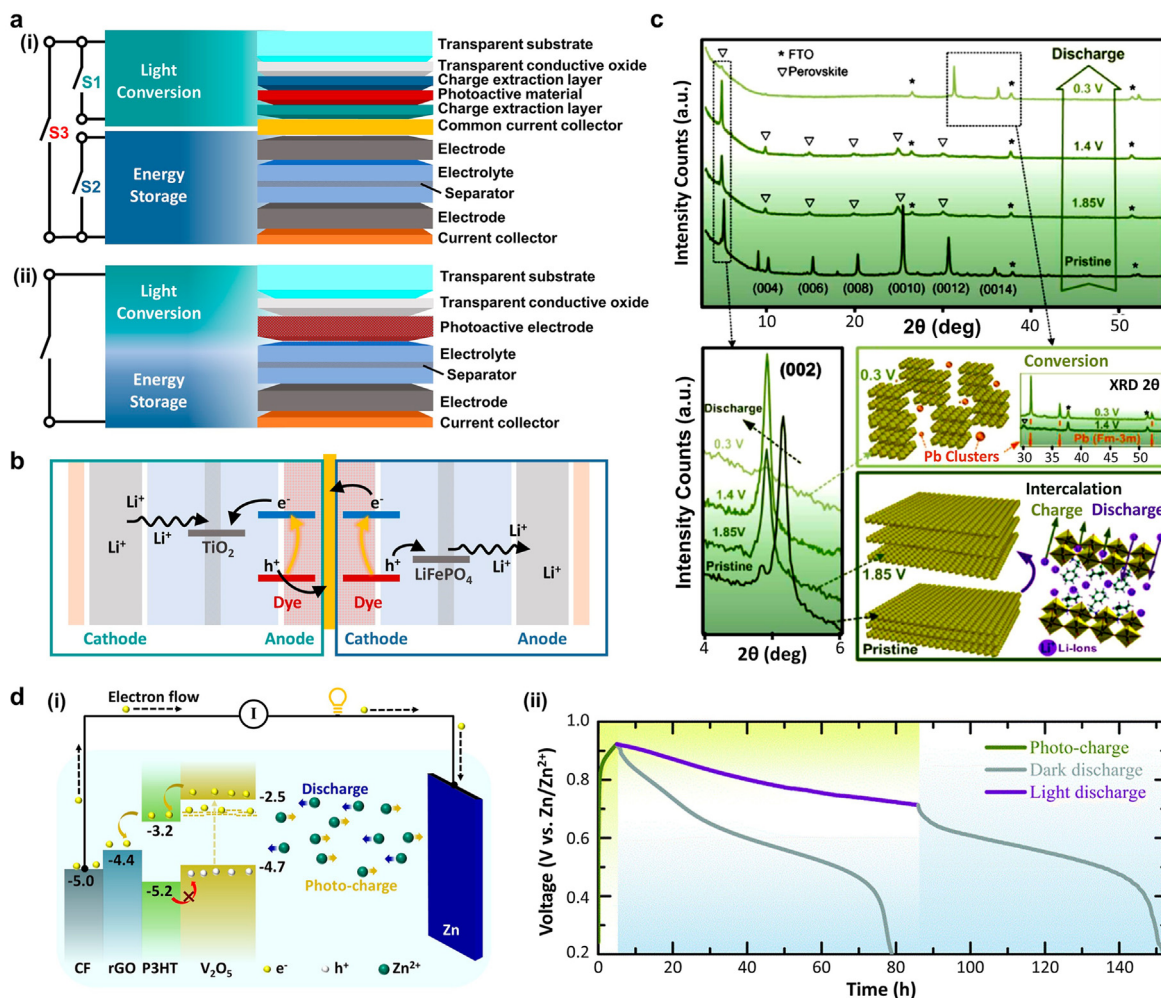


Fig. 4. The concept of photo-rechargeable tertiary energy storage. (a) Two configurations of energy harvest-storage hybrid devices in (top) three-electrode tandem and (bottom) two-electrode hybrid designs. (b) The charge-discharge mechanism of photo-electrochemical cells when (left) anode or (right) cathode is photoactive. (c) The crystal volume expansion of organometallic halide perovskite during lithium-ion insertion. Reproduced from Ref. [113]. Copyright 2018 American Chemical Society. (d) (i) The device configuration of a photo-rechargeable zinc-ion battery; (ii) the typical charge-discharge profile of photo-rechargeable batteries while discharged under or without illumination. Reproduced from Ref. [114]. Copyright 2020 Royal Society of Chemistry.

Further, the three-electrode tandem device results in duplication of components (i.e., current collectors, substrates, separators, etc.), adding weight and cost. Therefore, further elaboration and discussion in this section are focused on the concepts and self-charging mechanism of the two-electrode-based device, wherein the electricity generation and charge storage functions are synergistically integrated into one of the storage components.

4.1. Photo-electrochemical energizers

Photo-electrochemical energizers refer to energy storage devices capable of harvesting light energy and storing it as electrical energy. They can be fabricated by allowing either the cathode or the anode to be photoactive (able to convert light energy), and the working mechanism is summarized in Fig. 4b. Utilizing a bare-TiO₂/LiCoO₂ anode/cathode device, Nagai et al. fabricated photo-rechargeable energizers that can be charged through light illumination [111,112]. The TiO₂ behaved like an insulator when analyzed in the dark but showed n-type semiconductor behavior (energy gap of ~3.2 eV) under illumination, with light-to-electricity conversion capability. However, poor electrochemical performance was observed because TiO₂ can only convert light in the

ultra-violet region. The next logical step is to extend the light absorption range of the photoactive electrode to the visible.

Light region through incorporating dye molecules, as in dye-sensitized solar cells, where under light illumination, the excited negative (positive) charges from the dye-molecule reduce (oxidize) the anode (cathode) and lead to intercalation (deintercalation) of lithium ions. The dye-sensitized TiO₂ anode demonstrated excellent electrochemical performance compared to a bare metal oxide electrode [112,115].

It is crucial to note that the energy level alignment between the dye molecules and the electrode plays a crucial role in ensuring efficient photo-charging. Taking LiFePO₄ as an example, lithium deintercalation results in the formation of FePO₄. That FePO₄ has a lower energy level than the dye molecule hinders hole injection into the cathode material, thereby terminating the photo-charging process. Similarly, with the photoanode of dye-sensitized solar cells, the large surface area of the electrode is vital for ensuring a high photo-response during charging [112,116]. To further improve the weight-to-performance ratio of photo-rechargeable energizers, it is desirable to develop a photoactive material that functions simultaneously as the charge storage electrode and the light absorber. Two-dimensional metal halide perovskite, (C₆H₉C₂H₄NH₃)₂PbI₄, was deployed as a light absorber and anode

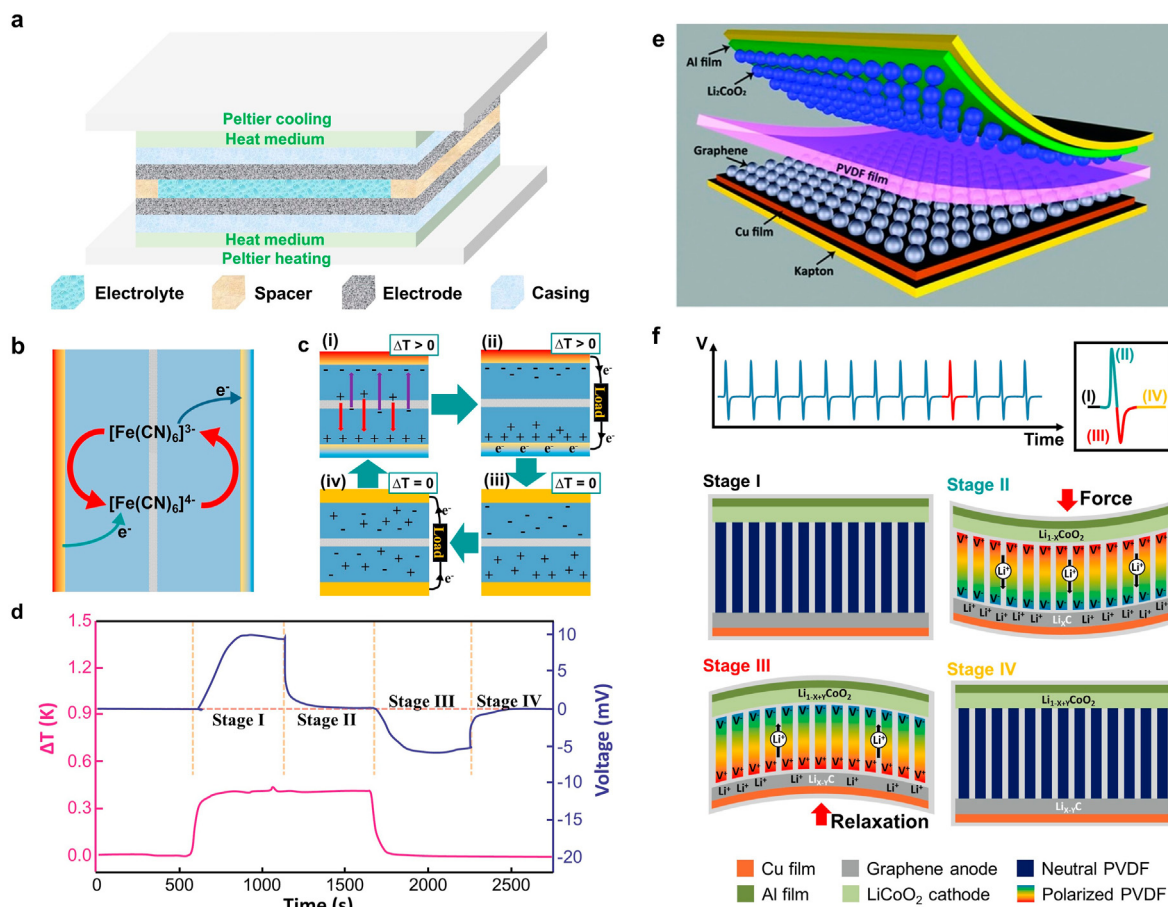


Fig. 5. The concept of thermo- and piezo-electrochemical tertiary energy storage. (a) The simplified device configuration of thermo-electrochemical batteries. (b) The redox reaction of a thermo-galvanic cell with reduction and oxidation of the redox couple at the surface of the hot and cold electrode, respectively. (c) The charging process of thermally charged cells under the influence of the Soret effect. (d) The relation between voltage generated and changes in the temperature gradient applied across the electrodes. Reproduced from Ref. [130]. Copyright 2020 John Wiley and Sons. (e) Piezo-electrochemical cells with PVDF separator as the piezo material. Reproduced from Ref. [131]. Copyright 2013 John Wiley and Sons. (f) Diffusion of charges under the influence of piezopotential: (1) charges are equally distributed before the application of mechanical force, (2) charges diffuse to the respective electrode under the influence of positive piezopotential, (3) some charges back-diffuse under the influence of negative piezopotential, (4) the position of charge in a fully charged state. Reproduced from Ref. [131]. Copyright 2013 John Wiley and Sons.

material for a lithium-ion battery [113]. Subsequent X-ray diffraction analysis verified d-spacing expansion in the crystal structure during illumination (charging), indicating successful lithium-ion insertion into the bulk metal halide perovskite during intercalation. However, when the battery was discharged to an extremely low potential (> 0.4 V vs. Li/Li^+), lithium ions were observed alloying with lead, leading to extreme volume changes followed by fragmentation of the metal halide perovskite film (Fig. 4c). Under such circumstances, a management system would be required to control and limit the discharge voltage to > 1 V in an effort to prevent the alloying reaction.

Other than that, improving the intrinsic stability of halide perovskite against the gaseous by-products originating from the formation of electrode–electrolyte interphases is also vital for ensuring a long and stable operation lifetime. A similar architecture was demonstrated in a zinc-ion battery, where the interface between poly(3-hexylthiophene-2,5-diyl) (P3HT) and vanadium oxide (V_2O_5) was utilized as a light harvester [114], demonstrating the possibility of such device engineering in any secondary rechargeable energy storage device (Fig. 4d(i)). When operating under a constant discharge load, the photo-energizers showed prolonged discharging time under illumination (due to the simultaneous charging process) compared to a counterpart placed in the dark (Fig. 4d(ii)).

4.2. Thermo/pyro-electrochemical energizers

It is crucial to develop thermo-electrochemical energizers for harvesting residual heat energy, which is produced abundantly during the operation of any electronic appliances, as well as by the human body. However, a large portion of this residual heat is below 100°C , making harvesting efforts using a mechanical system (Stirling engine) more challenging [117,118]. Attention has turned to the Seebeck effect as a possible mechanism for achieving high residual heat-to-electric energy conversion efficiency [119–121]. The Seebeck effect can be defined as the development of voltage across the junction of two dissimilar semi-conductors (an n-p junction) when subjected to temperature difference, due to the tendency of charges to instantaneously diffuse from a hot region to a cold one. Materials with thermoelectric properties are currently being studied extensively and have been thoroughly reviewed elsewhere [122–124]. However, these studies mostly have aimed at improving the Seebeck coefficient for a thermoelectric generator with higher heat-to-electric conversion efficiency, whereas work on integrating these materials to form thermo-electrochemical energizers is lacking.

Current developments in thermo-electrochemical energizers mainly pursue two avenues: thermo-galvanic energizers (redox reaction driven by the temperature gradient) and thermally charged energizers

(movement of conductive ions with respect to the temperature gradient). Apart from a thermoelectric generator, which only generates electricity to power electronics, both thermo-galvanic and thermally charged energizers can store heat energy for later use (Fig. 5a). Thermo-galvanic energizers contain two identical electrodes (with platinum and porous carbon electrodes being the most widely used) [125,126] and a redox active electrolyte, whereby the redox couple generates charges through reduction (oxidation) at the hot (cold) electrode (Fig. 5b). The redox reaction in the electrolyte will continuously generate a current that can be stored or transferred across the external circuit to power electronic appliances [127]. The hexacyanoferrate ($\text{Fe}(\text{CN})_6^{3-/4-}$)-based redox couple is widely adopted as the electrolyte, offering a Seebeck coefficient of ca. -1.4 mV K^{-1} ($0.2 \text{ M K}_3[\text{Fe}(\text{CN})_6]$ in water) [128], which can be further enhanced to -4.2 mV K^{-1} with urea and guanidine chloride as additives [129]. However, the existence of a cyanide functional group ($-\text{C}\equiv\text{N}$) would pose a serious threat to human health if such a cell were implanted in the body.

On the other hand, thermally charged energizers have utilized the Soret effect (ion diffusion in response to temperature gradient) for energy generation, where the conductive ion with larger (smaller) ionic size diffuses toward the cold (hot) electrode, as shown in Fig. 5c [132]. Most thermally charged energizers utilize ionic liquid as the electrolyte, which can be dispersed in a polymer to form an ionogel to meet the flexibility requirement of wearable electronics. Ionic interaction between the functional group of the polymer and the negatively/positively charged ions (depending on the nature of the functional group) can disrupt the structure's short-range order, creating channels for ion transport and decreasing the activation energy of the ionogel [133].

Following a similar design, an [Emin][DCA]/WPU ionogel with a Seebeck coefficient of 34.5 mV K^{-1} was demonstrated [130]. Even though both thermo-galvanic and thermally charged energizers offer an operating voltage in the hundreds of millivolts, a short distance between the cathode and anode is required to overcome the low thermal diffusion of the conductive ions. However, reducing the distance between the electrodes makes maintaining the temperature gradient a difficult task; this problem is exacerbated in microelectronics, where the total thickness of the device can be at the micrometer scale [134]. Heat transfer and equilibration through the protection casing also complicate efforts to maintain a high temperature gradient between the electrodes. These things aside, when the temperature gradient is removed, an opposite flow of charge will take place, generating a negative voltage on the appliances (Fig. 5d).

4.3. Piezo-electrochemical energizers

Piezo-electrochemical energizers can be achieved by replacing the typical polyethylene (PE) separator with a piezoelectric film (Fig. 5e), mostly with polarized poly(vinylidene fluoride) (PVDF). When mechanical compression is applied, a piezo-potential is generated at the piezoelectric separator, driving the migration of lithium ions (in lithium-ion batteries) or conductive ions (in supercapacitors) from the cathode towards the anode [135,136]. The achievable working voltage of a reported piezo-electrochemical lithium-ion battery is directly proportional to both the applied compression force (355 mV for 23 N to 379 mV for 45 N) and its frequency (350 mV for 0.7 Hz and 380 mV for 2.3 Hz) [135].

The ionic conductivity of the PVDF separator can be further enhanced through surface porosity engineering, which showed tremendous enhancement of both lithium-ion diffusivity and the strength of the generated piezo-potential [137]. Mesoporous PVDF was developed through a hexagonal ZnO nanowire template, creating diffusion channels for more rapid lithium-ion transportation than with planar PVDF. Such improvement is easily duplicated through adopting an electrospun PVDF matrix, where the inter-fibrous spaces can act as lithium-ion transport channels [138,139]. However, the small degree of rigidity in the

enveloping casing can consume a huge part of the applied mechanical stress, greatly reducing the efficiency of the piezo-materials.

To further improve the energy generation efficiency, the steel casing of a 2016-type coin cell was replaced with a Kapton shell, yielding a voltage of 850 mV in 480 s under a mechanical force of 30 N [131], compared to 160 mV in 250 s with a force of 34 N [137]. Undeniably, the long charging times of secondary alkaline batteries do not suit such an application, given that the input mechanical stress is intermittent, whereas instant charging of an EC is useful [140,141]. A piezo-electrochemical EC can be fully charged to 500 mV in 20 s under a compressive force of 12.2 N [142]. One of the main drawbacks of piezo-electrochemical energizers is their low voltage (in the range of mV), compared to 3.6 V when charged using an external power source (in the case of a $\text{LiCoO}_2/\text{graphite}$ lithium-ion battery). The low voltage could be attributed to the fact that most of the mechanical stress exerted on the device is consumed by the casing, reducing the effectiveness of the piezoelectric material. Techniques to enable maximum performance by the piezoelectric separator have achieved piezo-electrochemical energizers with an open-circuit voltage of 2.5 V under a mechanical stress of 280 mN [143].

Another contributing factor could be the generation of negative piezo-potential during relaxation (processes III and IV in Fig. 5f). Based on this reasoning, rectification was suggested to retain the device's state-of-charge during mechanical relaxation [142]. Such a rectification effect can be achieved by forming an ionic hydrogel via layered stacking of anionic and cationic ionomers [144]. Depletion regions formed at the interfaces of the anionic and cationic ionomers induce diode properties that rectify the charging process of piezo-electrochemical energizers. Aside from this, most studies on piezo-electrochemical energizers have investigated and made comparisons at an operation frequency of $> 10 \text{ Hz}$, which is well beyond the frequency generated by human body motion (4–7.5 Hz). It is also crucial to note that in real-time applications, the force and frequency of mechanical deformation exerted on the device are irregular. The probability of piezo-electrochemical energizers operating at the efficiency reported in literature is highly unlikely, which has not been discussed so far. Despite of all these challenges, biocompatible piezo-electrochemical energizers can be implanted to harvest the peristaltic action of the blood vessel wall to power implantable electronics or drive external applications through inductive wireless charging.

4.4. Tribo-electrochemical energizers

Other than piezoelectricity, mechanical movement can also be harvested through the triboelectric effect, and numerous developments have been reported for triboelectric nanogenerators (TENGs) [145–147]. Triboelectricity is the generation of electrical potential due to the separation of two materials previously brought into contact. While in contact, charge sharing/transfer happens owing to the coulombic attraction between the molecules. However, such sharing/transfer is not instantly reversible, resulting in some charges lingering on the surface after material separation; these can be extracted as a potential difference to power electronics. TENGs have mostly been capable of delivering a surge voltage of $> 150 \text{ V}$ that could be used to charge a high-voltage storage pack, attracting tremendous interest in utilizing triboelectricity as a renewable source of energy [148–150]. However, in terms of wearable/microelectronics, thus far, triboelectric integrated self-charging energizers have been studied in the tandem form, wherein a two-terminal all-in-one self-charging device is significantly lacking [151]. Therefore, this section will discuss efforts to design the architecture of a triboelectric/storage tandem device while exploring possible routes toward achieving all-in-one tribo-electrochemical energizers.

One of the most common techniques adopted to achieve triboelectric self-charged energizers is printing/casting a storage unit on top of a tribo-material, connected through a rectifier to achieve a stable DC power

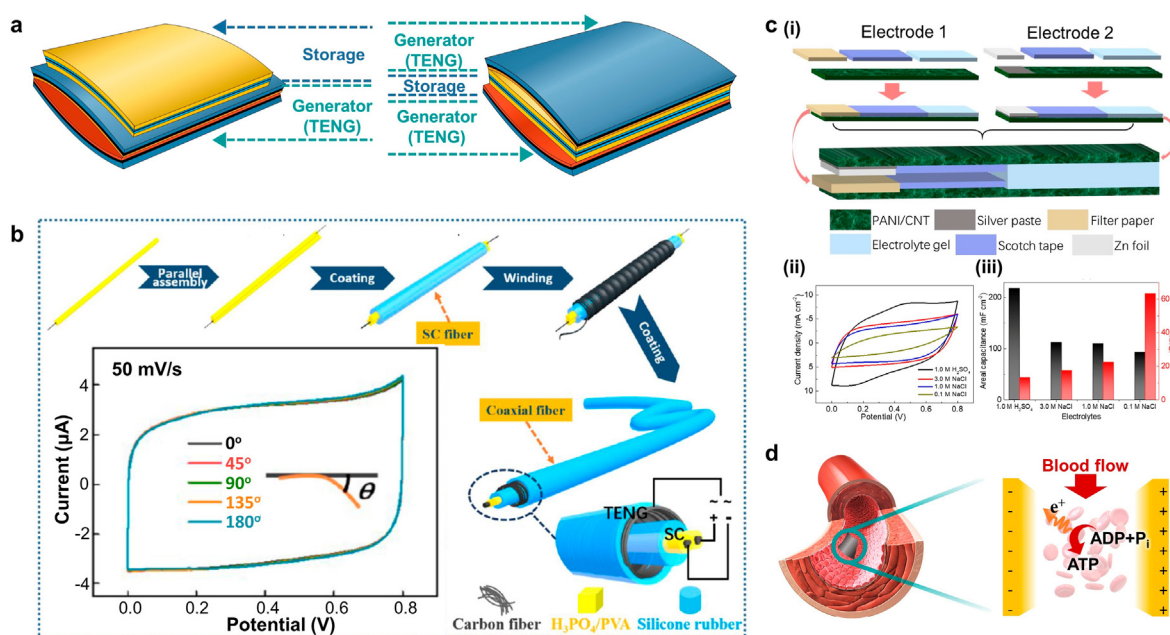


Fig. 6. Concept of tribo- and bio-electrochemical tertiary energy storage. (a) TENG/storage tandem devices that harvest and stored triboelectricity. (Left) Tandem configuration of TENG and storage compartments and (right) Double-layer TENG-sandwiched storage compartments. (b) Coaxial tribo-electrochemical battery, showing stable energy output regardless of the bending angle (inset). Reproduced from Ref. [157]. Copyright 2018 American Chemical Society. (c) (i) A sweat-powered bio-electrochemical battery wherein (ii, iii) increasing salt concentration offered higher energy output. Reproduced from Ref. [158]. Copyright 2021 Elsevier. (d) A bio-electrochemical battery that utilized enzymatic catalysis of glucose in the blood as the source of energy.

source for charging (Fig. 6a-left) [152]. Under ambient mechanical vibration, the EC can be charged to 3 V in under 117 min, simultaneously powering two LEDs and a commercial hygromograph [153]. A similar architecture was also studied in a lithium-ion battery (LIB), where tribo-induced charges were transferred to drive deintercalation (positive charge to the cathode) or intercalation (negative charge to the anode) [154]. The triboelectric/LIB energizer was able to sustain 1.53 V when placed in “sustainable mode” (powering an external load while simultaneously charging), indicating promising self-powering performance for wearable/microelectronics. The architecture was further improved by sandwiching a carbon nanotube solid-state supercapacitor with a wrinkled PDMS-based TENG (Fig. 6a-right), significantly improving the charging speed for 120 mV to under 250 s, compared to only 80 mV for a single TENG counterpart in the same time [155]. The electrochemical performance of the sandwich-structured self-powered unit was further improved by adopting a self-healing $\text{CoFe}_2\text{O}_4/\text{Fe}@r\text{GO}$ supercapacitor, enabling charging to 1.6 V in 31 min under periodic mechanical compression stress [156]. The magnetic attraction between the cathode and anode materials was reported to aid the self-rejoining process after mechanical cutting or ripping, significantly enhancing the device's cycling stability.

To improve device wearability, an all-in-one 2 mm diameter yarn-type triboelectric self-powered energizer was demonstrated, with an EC unit as the core and a TENG as the shell (Fig. 6b) [157]. The coaxial yarn was subsequently knitted and demonstrated stable performance without voltage leakage when kept idle. Generally, a rectifier is required to generate DC power from a TENG to drive the wearable electronics, given that moving the skin away from (nearer to) the self-power unit drives the electrons away from (towards) the core carbon bundle electrode [159]. One of the main bottlenecks of triboelectric self-powered energizers is the low current density (mostly in the range of $\mu\text{C m}^{-2}$) due to the air breakdown phenomenon, which significantly restricts the performance of the TENG and the overall self-powered energizer [160]. However, a high induced voltage of hundreds of volts definitely puts TENG-based self-powered energizers at the forefront compared to other 3rd-ES technologies.

4.5. Bio-electrochemical energizers

The development of wearable or implantable electronics has also led to the redesign of more biocompatible energy storage devices that utilize human biofluids (i.e., sweat, blood, tears, interstitial fluid, etc.) to achieve self-rechargeability, with sweat attracting the most attention, given its noninvasive harvesting route. Previously, self-powered wearable energy storage was demonstrated with a sweat-based biofuel cell and a $\text{MnO}_2@\text{CNT}$ EC screen-printed on the opposite side of a stretchable fabric [161,162]. While the device offered stable performance (charged to 0.4 V after 37 min of exercise) and favorable cyclability, its architecture was different from the design proposed in this article.

Human sweat contains a low concentration of conductive ions (66 mM of Na^+ and 9 mM of K^+) [163], which can be utilized as the electrolyte for self-rechargeable energizers. However, to extract comparable electrochemical properties from an electrolyte solution with low ionic concentration, employing a polymeric electrode with high porosity and conductivity (i.e., PEDOT:PSS, PANI, etc.) is crucial. In general, the energizers remain in an open-circuit condition when the separator between both electrodes is dry, while wetting the separator with biofluids provides the necessary aqueous electrolyte condition to close the circuit and start the self-charging process [164,165]. The volume and concentration of sweat extracted during exercising both play a vital role in determining the electrochemical performance of bio-electrochemical energizers, with the highest capacitance achieved (in the range of μF) during intense exercise (Fig. 6c) [166]. The electrochemical performance can be enhanced through incorporating Zn foil into one of the PANI/CNT electrodes as the nanogenerator (Fig. 6c) [158]. With the intake of sweat, the Zn foil is oxidized to Zn^{2+} , coupled with reduction of O_2 at the counter electrode, mimicking the energy storage mechanism of a zinc–air battery [167]. The device can be charged up to 654 mV after 6 min of rope jumping, successfully powering up a watchband. However, drastic deterioration of electrochemical performance was observed after the first few cycles, most likely due to the poor reversibility of the zinc–oxygen redox reaction, with the device eventually retaining only ~45% of its initial capacitance after 500 (dis)charging cycles.

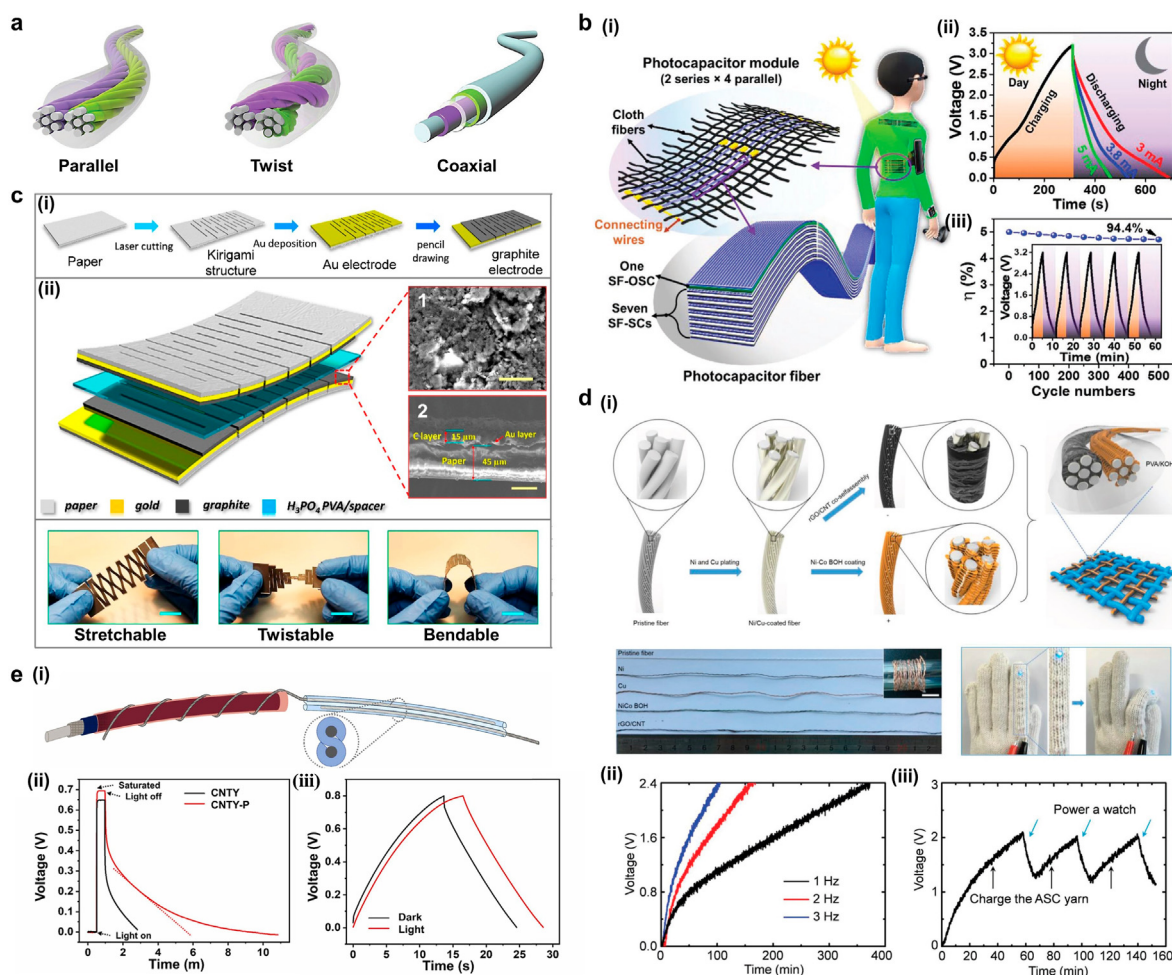


Fig. 7. Device designs for wearable electronics. (a) A schematic of fiber-shaped configurations. Reproduced from Ref. [173]. Copyright 2020 John Wiley and Sons. (b) (i) The stacking of one organic solar cell and seven supercapacitors in tandem design, forming a potential energizer for wearable applications. (ii) Photo-charge/galvanostatic-discharge performance and (iii) cycling stability of the photocapacitor module. Reproduced from Ref. [175]. Copyright 2021 John Wiley and Sons. (c) (i) The preparation of a kirigami structured electrode, where a schematic of a complete device is shown in (ii), demonstrating superior mechanical stretchability, twistability, and bendability. Reproduced from Ref. [176]. Copyright 2016 American Chemical Society. (d) (i) The fabrication of a parallel asymmetrical electrode supercapacitor, which can be knitted with a TENG to form a self-powered energizer. (ii) Charging profile of the energizers under different motion frequencies. (iii) Voltage profile of the energizers at a motion frequency of 4 Hz and discharged by a smartwatch. Reproduced from Ref. [177]. Copyright 2020 John Wiley and Sons. (e) (i) A schematic of photocapacitor yarns fabricated with a combination of three configurations. (ii) Photo-charge galvanostatic-discharge curves of the photocapacitor. (iii) Galvanostatic-discharge profile of the photocapacitor with or without illumination at a current load of 200 μ A. Reproduced from Ref. [178]. Copyright 2022 Elsevier.

Different from sweat-based bio-electrochemical energizers, other biofluids, especially sugar, can undergo enzymatic catalysis during power generation (Fig. 6d), offering a higher working voltage of ~ 1.6 V [168,169]. A comparison of electrochemical performance with 0.9 M NaCl (imitating human sweat), plasma, and blood as the electrolyte showed an additional redox peak in blood, attributed to the enzymatic catalysis of glucose [170]. Even though further enhancement of enzymatic catalysis was demonstrated through embedding the cathode with *Magnaporthe oryzae* fungi in the presence of 8.2 mM glycaemia [169], the body's immunoresponse (especially inflammation) to the presence of fungi within the cathode was not studied. Implanting these devices in the wall of a blood vessel would also result in thrombosis if fouling were to happen on the device's surface, highlighting the criticality of devising anti-biofouling strategies for user safety. Other than that, the overall thickness of the devices needs to be carefully revised, and the location of the implant must be carefully selected to avoid severely restricting the passageway of the blood, otherwise an embolus (possibly from deep vein thrombosis) might become trapped, leading to fatal thrombosis.

5. Flexible/wearable configurations for tertiary self-rechargeable energizers

Following the mounting interest in developing wearable applications, there has been a focus on developing flexible batteries or energizers in either flexible planar or yarn/thread configurations [171,172]. In general, four different configurations are adopted when developing flexible electronics: planar, parallel, twisting, and coaxial, as shown in Fig. 7a [173]. For wearable applications, yarn/thread configurations that can be woven into fabric are more favorable. However, we also include a discussion on planar (also known as strip) device architectures, given these can be attached as patches on clothing and could also play a critical role in microelectronics. Direct coating, deposition, and printing of self-powering energizers on fabric will also be treated as planar, given their flat appearance. Considering the extent of the previous literature and discussions on these device configurations, the pros and cons of each design will not be reviewed here; readers are referred to the cited literature for further information [171,174].

As the name suggests, a planar configuration has a flat appearance, which can be developed on a flexible conductive substrate (such as indium tin oxide coated on polyethylene terephthalate, ITO/PET) or directly on a fabric [179,180]. Numerous planar configured devices have been developed based on a tandem architecture, with a common electrode connecting the harvester and storage components. Jin et al. reported an organic solar cell/supercapacitor tandem planar strip developed through slitting a $5 \times 5 \text{ cm}^2$ flexible device with a medical scalpel [175]. They developed a silver metal-embedded PEDOT:PSS transparent conductive electrode (ME-TCE) as the current collector and common electrode for the tandem devices. By stacking one layer of organic solar cell with seven symmetrical supercapacitors in tandem format (Fig. 7b), the photocapacitor achieved a total efficiency of 5.0%.

Song et al. developed a tribo-electrochemical energizer on carbon nanotube (CNT)-casted cotton as the electrode, with nylon as the dielectric material and $\text{H}_3\text{PO}_4/\text{PVA}$ gel as the electrolyte [181]. They reported an increase in voltage and current output when the frequency rose from 1 to 7 Hz, with the supercapacitor yarn reaching 5 V after 4 min of vibration. In order to improve the stretchability of a planar device, Guo et al., developed a paper-based supercapacitor that was laser cut into a kirigami structure (Fig. 7c), where the paper was gold coated and graphite was deposited using a pencil drawing [176]. The TENG (comprising two pieces of silicone rubber separated by a silver nanowire film) was connected to the supercapacitor in tandem form through a rectifier. With a vibrational energy of 5 Hz, the energizer was in sustaining mode (no changes in voltage recorded) while the supercapacitor started to charge at 9 Hz distortion.

Lu et al. reported a flexible piezo-electrochemical energizer based on a PDMS substrate (PDMS/rGO-C/P(VDF-TrFE)/rGO-C/PDMS architecture) capable of reaching 0.45 V in 18 s when bent 90° [182]. Similarly, Aamir et al. developed a device on a gold-coated polyethylene terephthalate (PET) substrate, with MnO_2 -rGO as the electrodes and PVDF-rGO-ZnO composite as the separator, obtaining a maximum output voltage of 44 V under 10 N of compressive force and 10.34 mWh/kg worth of energy stored under palm pressure [183]. Krishnamoorthy et al. also developed a piezo-electrochemical energizer based on a highly conductive carbon cloth substrate, with siloxane sheets as the electrodes and ionogel@siloxane-PVDF as the separator [136]. The separation of both positive and negative ions in the ionogel toward the siloxane sheets electrodes under the influence of piezo-potential was proposed as the storage mechanism for this device. Under a compressive force of 10 N, the voltage rose from 105 to 180 mV within 250 s, while for a similar duration, 237 and 314 mV were achieved under 15–20 N. For micro-electronics, Cohn et al. utilized an underlying silicon wafer to fabricate a photo-electrochemical energizer, wherein a device architecture of FTO/mesoporous- TiO_2 /dye-molecules/ionolyte/etched-Si/ionic polymer/etched-Si offered a total efficiency of 2.1% with a working voltage of 0.64 V [184].

For wearable applications, self-powered energizers need to be developed into yarns/threads that can be woven or knitted into wearable fabrics. Wang et al. demonstrated a two-compartment photo-electrochemical energizer, wherein both dye-sensitized solar cells (Ti-wire/mesoporous- TiO_2 /N719-dye in a coaxial configuration) and a supercapacitor were connected through a common PEDOT:PSS electrode in parallel configuration, demonstrating a total efficiency of 5.1% with an ultralong stability of 1700 cycles (equivalent to 63 operation days) [185]. The resulting arrangement was sealed with hot melted glue, resulting in a 15 cm thread with a diameter of $\sim 3 \text{ cm}$, which is larger than typical clothing yarns ($\sim 10 \text{ }\mu\text{m}$). Mun et al. developed a separate piezoelectric nanogenerator (PENG) and supercapacitor (both in parallel configuration), which were then woven into a textile [186]. Carbon nanotubes arranged in parallel and twisted around silicone rubber were adopted for both PENG and supercapacitor, with the latter covered with solid electrolyte and encapsulated in silicone rubber. A voltage of 550 mV at 70% strain was generated when a strain force of 5.8 N was applied, while only 135 mV was retained after rectification.

Similar to Mun et al.'s work, Liu et al. fabricated a TENG/supercapacitor knitted textile, with Ni/Cu-coated polyester fiber as the core and polydimethylsiloxane (PDMS) as the shell for the TENG compartment [177]. The supercapacitor was fabricated with Ni-Co bimetallic oxyhydroxide and rGO/CNT, placed in parallel in PVA-KOH electrolyte (Fig. 7d). Bridged through a rectifier, the supercapacitor could be charged up to 2.4 V in 104 min at 3 Hz (requiring 370 and 161 min at 1 and 2 Hz, respectively). Dong et al. revised the design by developing a symmetrical supercapacitor wherein carbon fiber bundles/carbon nanofibers/PEDOT:PSS coaxial fibers were placed parallel to each other in $\text{H}_3\text{PO}_4/\text{PVA}$ electrolyte [187]. They reported no significant drop in electrochemical performance after numerous washing cycles. Yang et al. further improved the TENG/supercapacitor design into a single coaxial yarn/thread with an architecture of silicone rubber/carbon fiber/silicone rubber/supercapacitor (diameter $\sim 2 \text{ mm}$) [157]. The inner core of the supercapacitor had carbon fiber electrodes placed parallel to each other and enveloped by $\text{H}_3\text{PO}_4/\text{PVA}$ solid electrolyte. When four TENG/supercapacitor yarns were connected in series, the voltage of the device remained at 42.9 V under various motion frequencies, while the closed-circuit current increased from 0.19 to 0.51 μA at 1 and 2.5 Hz. Eventually, Kim et al. utilized all three configurations in fabricated photo-electrochemical energizer yarns/threads [178]. The device design involved coaxial type dye-sensitized solar cells wherein a Ti-wire/mesoporous- TiO_2 /N719-dye fiber was wrapped with a carbon nanotube counter electrode in a twisting manner (Fig. 7e). The carbon nanotube also functioned as the common electrode, with another carbon nanotube electrode placed parallel as the counter electrode of the supercapacitor. With LiTFSI/propylene carbon film as the solid electrolyte, this device showed an overall efficiency of 4.69%, with an excellent galvanostatic discharge time of 6 min at a current load of 200 μm .

6. Energy storage management

An energy storage module/pack always comes together with a battery management system (BMS) to ensure battery safety and optimum output performance. The main function of a BMS is to prevent overcharging and thermal runaway through balancing the battery's state-of-charge (SOC). Such protection is mostly achieved by controlling the amount of energy channeled into or out from each individual battery during charging and discharging. Recent studies adopting self-powered energizers have focused on investigating the workability of these energizers in a single application (for example, a sensor or light-emitting diode) as the proof-of-concept, showing promising results on the applicability of self-powered energizers for future IoT electronics. However, real-time wearable/micro appliances comprise a collection of electronics, such as data collectors, processing units, transfer or communication units, display screens, etc., which may require a package of self-powered energizers to supply adequate energy to drive these electronics. Under such circumstances, the questions are: (1) Is a BMS necessary for a self-powered energizer pack/module? (2) What would be the main function of a BMS in 3rd-ES technologies? and (3) What are the required modifications for a BMS to suit wearable/microelectronics?

Whether or not a BMS is needed to safeguard 3rd-ES devices depends on the amount of energy required to power the wearable/microelectronics. For implantable electronics, which can be powered and charged from a continuous energy source such as enzymatic catalysis of glucose in the blood stream or can involve a low power-consuming sensor, a single 3rd-ES battery would supply enough power. In this scenario, a BMS would not be required. However, for high power-consuming wearable electronics or 3rd-ES that rely on intermittent energy sources (light, mechanical, etc.), a BMS would be required to ensure optimal and stable power output. In order to mitigate the intermittency of ambient energy, an array of different electrochemical energizers could be utilized, with a BMS deciding the sequence of energy extraction when powering wearable electronics. In terms of preventing overcharging/thermal-runaway, considering the charging capability of self-powered energizers (mostly <

Table 1
Summary of self-rechargeable 3rd-ES technologies and their challenges.

Types	Source	Engineered component	Mode of storage	Storing mechanism	Challenges
Photo-electrochemical batteries	Illumination (light)	Electrode (anode, cathode)	Direct	Converting light to exciton > Exciton injection into electrode > Lithiation/delithiation	<ul style="list-style-type: none"> • Inconsistent illumination intensity. • Chemical reaction with charges (i.e., Li⁺) will alter the optical properties of light-absorbing materials. • Light source is unidirectional, severely affecting the performance efficiency.
Thermo/Pyro-electrochemical batteries	Temperature gradient	Redox electrolyte	Rectifier	Ion diffusion due to temperature gradient > Redox at the electrode surface > Charge transfer to electrode	<ul style="list-style-type: none"> • Difficulties in maintaining temperature gradient across short distance. • Heat dissipation through the protective casing. • Severe self-discharging during reduction of temperature gradient between electrodes.
Piezo-electrochemical batteries	Movement (bending, twisting, folding, pressing, etc.)	Separator, casing	Rectifier	Movement distorts separator > Piezo-potential generated > Charge diffusion driven by piezo-potential > Charge stored on surface or bulk of electrode	<ul style="list-style-type: none"> • Low charging rate due to small induced current. • AC pulse is generated instead of DC during straining and relaxation. • Device rectification limits the V_{Max} of the device. • Rigidity in protective casing and other components reduces piezo-performance.
Tribo-electrochemical batteries	Movement (contact)	Casing	Rectifier	Materials separation generates surface charges > Charges flow to electrode	<ul style="list-style-type: none"> • Pulse AC requires rectification for efficient charging. • Best device architecture unknown. • Impedance mismatch reduces charging efficiency.
Bio-electrochemical batteries	Bodily fluid (sweat, blood, tears, etc.)	Electrolyte	Direct	Bodily fluid completes the batteries > Enzymatic catalysis generates charges > Charge transfer to the electrode	<ul style="list-style-type: none"> • Low conductive salt concentration in electrolyte. • Short-term storage (sweat can easily evaporate).

2 V, based on previous publications), overcharging is not the main concern in 3rd-ES. Even though continuous development would further enhance the charging potential of self-powered energizers (> 2 V), adopting solid-state electrolytes capable of withstanding 5 V of working voltage would be sufficient to prevent the 3rd-ES from being damaged due to overcharging. Nevertheless, techniques to ensure the health of 3rd-ES technologies against accelerated degradation due to factors like overcharging or overdischarging, (dis)charging rate, operational temperature, etc. are crucial. Whether protecting a 3rd-ES can be achieved without a BMS strongly depends on establishing an understanding of the (dis)charging process — including the charging, discharging, and sustaining modes — of self-rechargeable energizers.

On the other hand, the requirement to instantaneously store intermittent energy sources has led to the adoption of the high-power-density EC as the main storage design for 3rd-ES. With the EC operating at temperature < 40 °C owing to its non-faradaic surface adsorption storage mechanism, thermal runaway is not a concern. We therefore project that the main function of the BMS for 3rd-ES will be monitoring and supplying constant power by controlling the power output or alternating between different ambient input sources. The health of these energizers will also need to be monitored to determine the need for maintenance or replacement. Certainly, the BMS needs to be simplified to enable its integration into wearable/microelectronics, keeping only its primary functionalities (detection and control) while other secondary features can be relinquished to external portable electronics (e.g., a smartwatch or smartphone) through IoT-like communication.

In other words, in the case of implantable electronics, the BMS for 3rd-ES will retain only data collection and transfer functionalities, while data interpretation/analysis as well as monitoring will be handled by external portable electronics. In terms of wearable electronics, a few companies (e.g., Monolithic Power System Inc., Texas Instruments Inc., Mouser Electronics Inc., etc.) have started designing miniaturized BMSs

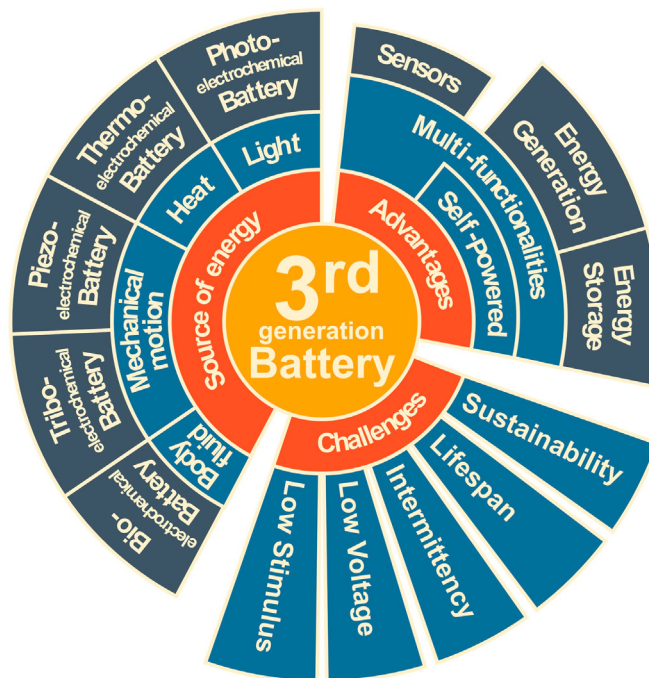


Fig. 8. Summary of tertiary energy storage. A few examples of tertiary energy storage that harvest ambient energy for power generation. Advantages include multifunctionality and the ability to self-power and be self-sustaining. The main challenges involve further enhancing the performance of tertiary energy storage technologies in various ways.

(smaller than $1 \times 1 \text{ cm}^2$) for smartwatches. However, the size of these miniaturized BMSs is still larger than the diameter of the thread, affecting its integration in yarn/thread electronics. Further, the current BMSs are not designed to be bent, folded, twisted, or washed, which are common experiences for wearable electronics. Following the transformation of energy storage technologies, a revolution in BMSs, in line with the IoT, is also anticipated. As discussed, 3rd-ES technologies will be accompanied by a simplified BMS with only primary detection and control features, while the energizer pack will communicate/synchronize with them through a central processing BMS and the data will be stored in the cloud for further analysis. Such transformations would offer a more simplified, miniaturized, or even flexible BMS for wearable/microelectronics.

7. Outlooks and future perspectives

In summary, we have discussed self-powered energizers in relation to several concepts to envisage possible candidates for 3rd-ES. According to the literature, these self-powered energizers can be separated into two main configurations: the tandem device, where energy harvesting is connected to storage through a common electrode; and the harvester-integrated two-terminal storage architecture. Tandem self-powered energizers were not discussed here, given that no modifications have been done on the storage compartment and the batteries are simply connected to an energy harvester through an external circuit or a common electrode.

In contrast, modifications have been carried out through materials engineering of the components within the storage device so that energy can be harvested and stored simultaneously within the energizers. Besides offering self-rechargeability, this modification retains a similar architecture to secondary energy storage devices (cathode/electrolyte + separator/anode), making device production and scale-up easy using already available production facilities. The 3rd-ES harvests ambient energies, such as light, heat, physical motion, biofluid, etc., for power generation, given their abundance and sustainability. A summary of their architectures/configurations is provided in Table 1.

Depending on the energy source, different components of the storage compartment are modified — the electrode for harvesting light, the electrolyte for harvesting heat and biofluids, and the separator for harvesting physical motion. Previous studies have demonstrated a few successful prototypes that could be used to drive sensors. However, unlike in testing situations, where controlled and constant stimuli are applied, ambient energies are intermittent and random, preventing 3rd-ES from achieving the reported power output. Under such circumstances, a BMS would be required to monitor and control the (dis)charging process to ensure constant and optimal performance from the 3rd-ES. The BMS could be designed to control the extraction of energy from an array of 3rd-ES that harvest energy from different ambient sources, thereby ensuring a constant supply of energy even though the sources are intermittent. Undoubtedly, further efforts are still required to develop a reliable 3rd-ES; a few points of concern are summarized in Fig. 8 and as follows.

Parasitic effect of protective casing. The inferior electrochemical performance of most 3rd-ES can be attributed mostly to the parasitic effect of the protective casing. As discussed above, the protective casing either dissipates heat through thermal conduction (for thermal-electrochemical energizers), or reduces mechanical stress due to its rigidity (for piezo-electrochemical energizers), or reduces light transmission due to its opacity (for photo-electrochemical energizers). These parasitic effects significantly hamper the efficiency of the energy conversion constituent, leading to low charging potential and current. Fabricating caseless electrochemical energizers would allow maximum performance from the energy conversion constituent but would also expose the energizers to external influences, causing electrode wear, electrolyte leakage, pollution by impurities, early failure, etc. Therefore, a protective casing needs to be engineered that inhibits thermal conduction across the casing and has increased

mechanical flexibility or transparency, depending on the targeted application. Further improving the sensitivity and harvesting efficiency of the energy conversion constituent under a small stimulus could be another route to further improve the electrochemical performance of 3rd-ES devices.

Low operating voltage. Most of the currently demonstrated energizers supply low voltage (in the range of 100–1000 mV with current in μA) compared to 3–4 V from a battery/supercapacitor, due to poor harvesting efficiency. This low voltage significantly reduces the energy density of the energizers and is insufficient to drive high-voltage applications, where numerous energizers connected in series are required. Further increasing the operational voltage of the 3rd-ES will be crucial for drawing upon the maximum potential of the storage compartment. Note that the charging potential is limited to the potential difference induced by the energy conversion constituent. In the case of photo-electrochemical energizers, a photoactive constituent with a voltage of 1.1 V would offer an operational voltage of only $< 1.1 \text{ V}$, considering the optimum energy level alignment and minute energy losses owing to charge recombination. In addition, the intensity of ambient energy is usually very low (residual heat $< 100 \text{ }^\circ\text{C}$; movement of $< 10 \text{ Hz}$), resulting in a much lower potential difference than what is reported for state-of-the-art pyro- or piezo-materials. An overhaul of the device design is required to further amplify the charging potential and thereby enhance the operational voltage.

Intermittency of ambient energy. Even though electrochemical capacitors can instantaneously store ambient energies while they are available, the intermittency of the ambient energies still presents a great obstacle to achieving a constant power supply from 3rd-ES devices. One of the approaches to this complication is to increase the energy density of the storage device. Instead of electrochemical capacitors, lithium-ion capacitors that possess improved energy and power density would be the favorable alternative. Besides this, considering the involvement of different constituents in harvesting different ambient energies, 3rd-ES can be designed in such a way that more than one ambient energy is harvested. A photo-vis-piezo-electrochemical energizer — a 3rd-ES with a photoactive electrode and a piezoelectric separator — is one example. Such energizers could generate and store energies from both light and physical motion, greatly mitigating the intermittency of ambient energies.

Lifespan. It is crucial for an energy storage device to outlast its application, to mitigate the inconveniences arising from deteriorating performance as well as energizer maintenance and replacement. Even though 3rd-ES has been developed based on mature 2nd-ES technologies, the integration of an energy conversion constituent requires the lifespan of the 3rd-ES to be reanalyzed. The cycling stability studies on 3rd-ES under constant washing, bending, rolling, folding, and twisting also provide vital information for real-time applications. In order to establish a reliable stability analysis of 3rd-ES, a standardized testing protocol is required. A protocol similar to what has been adopted for lithium-ion batteries can be followed, with additional conditions considered, such as exposure to detergent and ultra-violet radiation, chemical bleaching, interlayer detachment due to irregular distortion, rapid charge and discharge at different levels of state-of-charge, and so on.

Biocompatibility and sustainability. Considering the close proximity of wearable/implantable electronics to the human body, the biocompatibility and health concerns posed by these electronics need to be thoroughly analyzed and eliminated. Contents that are hazardous and present leakage concerns should be eliminated, which calls for the adoption of renewable materials and all-solid-state energizers. Undoubtedly, with sustainability becoming mainstream in future research and product development, the 3rd-ES is no exception, so either the energizers need to be constructed using renewable materials or a comprehensive recycling and circular economy needs to be developed for 3rd-ES.

Economic sustainability is yet another crucial factor to be considered while developing future energy storage technologies. The

fluctuating cost of transition metals (which are widely utilized in the electrodes of secondary batteries) was reported to significantly impact the final manufacturing cost of lithium-ion batteries [188]. Therefore, electrode materials that do not depend on mining operations and are naturally abundant, such as biomass carbon and polymeric materials, are more favorable for developing sustainable energy storage technologies.

Operational concerns. Overcharging, deep-discharging, and over-heating are a few of the critical concerns affecting the longevity of any energy storage device, including 3rd-ES. The stable performance and longevity of lithium-ion batteries were achieved through strict battery BMS monitoring. During operation, the BMS tracks the state-of-charge of the lithium-ion batteries by monitoring the amount of current flow in/out of the batteries. To prevent overcharging or deep-discharging, the BMS simply cuts off the battery connection to the external circuit. In contrast, the current or voltage input of a 3rd-ES device cannot be cut off in a similar manner, given that the source of its self-rechargeability originates from within the energizer. The only direct route to stop the charging process would be to eliminate the external stimuli. However, such preventive measures have not yet been discussed and should be investigated, considering their impact on the safety and longevity of 3rd-ES. Over-heating is another concern, as it would cause severe discomfort to the user, especially in the case of implantable microelectronic devices. The typical cooling system used to cool down lithium-ion batteries is inappropriate for implantable 3rd-ES, so alternative ways to cool down the 3rd-ES need to be devised.

Functionalities. Besides acting as the power supply, 3rd-ES devices can be utilized as sensors, adding more functionalities in a single device. With the help of artificial intelligence, the electrochemical performance and power output of a 3rd-ES device could be analyzed to monitor the user's health condition. Analyzing power output from bio-electrochemical energizers could offer instant details on blood glucose level, while implanting piezo-electrochemical energizers in the wall of blood vessels could be used to monitor blood pressure and pulse. More biomedical-orientated research would eventually lead to the use of 3rd-ES for the detection of diseases as well as cancerous tumors, allowing early treatment and higher success rates. Without a doubt, 3rd-ES can be regarded as the most promising technology capable of self-powering wearable/microelectronics for IoT appliances as well as constant 24/7 healthcare monitoring. Following existing and future endeavors with self-powered energizers, the ambitious goal of 3rd-ES overtaking the role of 2nd-ES in wearable/microelectronics can be anticipated.

Others (energy efficiency, cost, circularity, etc.). Several considerations, other than those detailed above, pertaining to the engineering and widespread sustainable deployability of 3rd-ES technologies lack traction. As discussed recently, newer technologies should consider the circularity of the materials, environmental footprint, social and environmental cost, in addition to materials/device functionality and device cost to enhance sustainability [189]. Therefore, significant questions on (i) the energy efficiency of multi-energy complementary charging, (ii) the cost and environmental factors of enabling access to these technologies for larger communities, (iii) minimizing the social risks (recycling, health hazards, etc.) of the technologies, and so forth need to be analyzed in depth for 3rd-ES technologies to be successful. Thus far, analyses of the performance of self-powered energizers have focused on the capability of the energizers to be self-recharged in the shortest possible time. However, there is no proper mechanism for calculating and reporting the energy efficiency. As discussed above, the overall electrochemical performance of these energizers depends heavily on the efficiency of the energy harvesting component. Therefore, improving the sensitivity of these components toward external stimuli is crucial for further improving the performance of these energizers. Regarding cost, this article has focused on promoting the development of 3rd-ES technologies but has not considered the hurdles to commercialization.

Author contributions

J. Ling and R. Jose proposed the concept. J. Ling wrote the original draft. C–C. Yang contributed to Section 3. R. Kunwar contributed to Section 5. I. I. Misnon, M. H. Ab Rahim, R. Jose, L. Li, and S. Peng co-edited the manuscript. S. Peng, C–C. Yang, and R. Jose supervised the project. All authors participated in manuscript discussion.

Competing financial interests

The authors declare no competing financial interests.

Declaration of competing interests

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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