Sustainable wearable energy storage devices self-charged by human-body bioenergy

Jian Lv1,2 | Jian Chen1,2 | Pooi See Lee1,2

1 School of Materials Science and Engineering, Nanyang Technological University, Singapore, Singapore
2 Singapore-HUJ Alliance for Research and Enterprise (SHARE), Nanomaterials for Energy and Energy Water Nexus (NEW), Campus for Research Excellence and Technological Enterprise, Singapore, Singapore

Correspondence
Pooi See Lee, School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore. Email: pslee@ntu.edu.sg

Abstract
Charging wearable energy storage devices with bioenergy from human-body motions, biofluids, and body heat holds great potential to construct self-powered body-worn electronics, especially considering the ceaseless nature of human metabolic activities. To bridge the gap between human-body bioenergy and storage of energy, wearable triboelectric/piezoelectric nanogenerators (TENGs/PENGs), biofuel cells (BFCs), thermoelectric generators (TEGs) have been designed to harvest energy from body-motions, biofluids, and body heat, respectively. Researchers have explored various strategies using bioenergy harvesters to charge wearable supercapacitors and batteries to relieve or even fully eliminate the recharging process from external power stations, thus, making wearable electronics more sustainable, autonomous, and user friendly. In this article, we review the advances in the design of sustainable energy storage devices charged by human-body energy harvesters. The progress in multifunctional wearable energy storage devices that cater to the easy integration with human-body energy harvesters will be summarized. Then, the focus is laid on the integrating strategies (single-cell strategy and separated-cell strategy), device design, materials selection, and characteristics of different self-charging human-body energy harvesting-storage systems. Finally, the challenges that impede the wide application of human-body energy harvesters charged supercapacitors/batteries and prospects will be discussed both from materials and structural design aspects.

KEYWORDS
human-body bioenergy, self-charging, sustainable, wearable energy storage devices

1 | INTRODUCTION

The wide applications of wearable sensors and therapeutic devices await reliable power sources for continuous operation.1–4 Electrochemical rechargeable energy storage devices, including supercapacitors (SCs) and batteries, have been intensively developed into wearable forms, to meet such a demand.5–8 Considering the curvilinear nature of the human body, safety concerns, and specific application scenarios, multiple functions, such as stretchability, self-healing, and transparent properties, thus, have been the centerpieces of research in wearable
However, most of the existing wearable energy storage devices exhibit low-energy density, on account of the limited thickness and area of the flexible devices. Meanwhile, the self-discharging nature of electrochemical energy storage, especially for SCs, inevitably drains the stored energy. A frequent recharging process with cumbersome wired power transmission from an immovable electrical grid is required to elongate the working periods, causing inconvenience to users. Integrating wearable energy harvesting devices with energy storage devices to form a self-sustainable power source has been an attractive route to replenish the consumed energy of the SCs/batteries, and thus, decrease the frequency of recharging or even enable a fully self-sustainable wearable electronics system.12

Since most wearable electronics are adapted to the human body, harvesting energy from the human body, including biomechanical, biofuel (glucose/lactate), and body heat energy using PENG/TENG, biofuel cells (BFCs), and thermoelectric generators (TEGs), respectively, has received considerable interest.13 Compared with the light-dependent wearable solar cells, human-body energy highly relies on human motions or continuous metabolic activities, thus, providing a reliable power source for wearable electronics. Meanwhile, wearable energy harvesters possess the advantages to integrate with various sensors for a self-powered sensing patch as they need to be mounted on the human body. This proof-of-concept design can be separated into two types. One is to use the output of the human-body energy harvesters to directly indicate the physiological intensity. The power, current, or voltage outputs of human body energy harvesters are proportional to the intensity of human physiological signals such as frequency of human motions,14 concentrations of lactate/glucose in sweat/blood,15 or temperature of the human body.16 Another way is to utilize a form of human-body energy harvester to provide energy for other biological signals or external stimuli, such as using the triboelectric nanogenerators (TENGs) to power a temperature sensor and chemical sensors.17,18 More specifically, the human-body energy harvesters can be possibly fabricated into a self-sustainable implantable device, to eliminate the requirement of the recharging process, and avoid further surgery for changing the energy source that would impart suffering, high cost, and risk to wearers.19 For example, implantable TENG and BFC have been demonstrated with the capability to power the implantable pacemakers.20–23 Even though the human-body energy harvesters implement on or in the human body are limited with lower energy generation, the miniaturized, flexible, and energy-saving developing trend of microelectronics technology is broadening the application of human-body energy.24–26

The merits of human-body energy harvesters stimulate the development of charging flexible SCs/batteries with energy converted from body motion, body heat, and biofuels to provide sustainable power sources for wearable or implantable devices.27–30 This design enables thin wearable SCs and batteries to be free of frequent recharging from immobile power stations. On the other side, integration with SC/battery could accumulate irregular energy from the human body and then deliver stable outputs for the performance of TENG/PENGs, BFCs, and TEGs that are affected by movement status and surrounding environment, greatly expanding the practical application of human-body energy harvesters.12,31 Most human-body energy harvesters are fabricated with conformability and mechanical compliance to have intimate contact with soft and curvilinear human tissues such as human skin, heart, and eyes. Thus, thin polymer films, tattoos, contact lens, and textiles have been used as platforms for wearable energy harvesters to not only function as traditional energy harvesters but also with specific properties such as comfort for wearing, biocompatibility, flexibility, stretch-ability, durability to washing, or ease of fabrication.32–35 To have a high-level integration with existing energy harvesters, energy storage devices need to have the same functionalities and compatible fabrication techniques with energy harvesters.

In this review, we summarize the recent progress on charging wearable electrochemical energy storage devices with different human-body bioenergy harvesters, including TENG/PENGs, which generate energy from human-body motion, BFCs extracting energy from biofluids and TEGs harvesting energy from body heat (Figure 1). First, the advances in multifunctional wearable energy storage devices that cater to the easy integration with
human-body energy harvesters will be shortly summarized. Then, the focus is laid on the integrating strategies (single-cell strategy and separated-cell strategy) for the self-charging human-body energy harvesting-storage system for wearable electronic devices. Charging wearable electrochemical energy storage devices with energy from the human body holds the potential to relieve or even eliminate the frequent recharging from stationary power stations. Meanwhile, wearable energy storage devices could buffer irregular or unstable outputs of human-body energy harvesters and subsequently release them as the constant power source. Lastly, the challenges that impede the wide application of human-body energy harvesters charged SCs/batteries and prospects will be discussed with perspectives given from the materials and structural design aspects.

2 WEARABLE ELECTROCHEMICAL ENERGY STORAGE DEVICES

Wearable SCs and batteries consisting of an anode and a cathode with a separator containing dissociated salts to enable ions transfer are two main types of electrochemical energy storing devices for wearable electronics. Flexibility is essential for devices to endure bending mechanical deformation. The current status quo of flexible power sources mainly focuses on the replacement of the brittle materials with flexible functional materials to endure the mechanical deformation such as recycling, bending, or stretching. For SCs, two different mechanisms are applied to fabricate electrical double-layer capacitors (EDLC) or pseudocapacitors. EDLCs store charge at the electrode/electrolyte interlayers by electrostatic double layers, while a surface or near-surface Faradic reaction which is reversible is involved in a pseudocapacitor. Pseudocapacitors show much higher energy density and capacitance than that of EDLCs, but their power density is lower, resulting from the slower surface redox or intercalation on electrodes.

Battery is a kind of transducer that converts electrical energy to chemical energy when charged from external power sources. In a charging and discharging cycle, the ions, such as lithium for lithium-ion batteries (LIB), transfer between bulk anode and cathode through an intercalation/deintercalation process to complete a reversible redox reaction. This process is controlled by the diffusion of ions in electrolyte and bulk electrodes, making the power density and charge-discharging rate of batteries lower than these of SCs. However, batteries exhibit much higher energy density, lower self-charging rates than SCs.

Among various battery systems, LIBs play a dominant role in the portable secondary battery market, owing to the superiorities in high voltage, high-energy density, low self-discharge, and long cycle life. However, the widespread adoption of wearable LIBs is hindered by concerns about safety issues and high costs. Various battery systems have been invented to replace LIBs. Sodium/potassium-ion batteries (SIBs/KIBs) involving similar Na+/K+ intercalation/deintercalation processes as Li+ were considered as the replacement of LIBs, due to the abundances of Na/K.38 The commercially used graphite anode in LIBs cannot be used for Na+/K+ intercalation. Wang and coworkers designed robust and monolayer hydrogen boride (HB) as the anode of KIBs. Beyond super-high areal capacity improved by the H vacancies (1138 mAh/g), the HB exhibited ultralow bending and high in-plane stiffness, making it an ideal material for the fabrication of wearable KIBs.39

Zinc ion batteries (ZIBs,) applying metallic zinc as the anode, have a high theoretical capacity (820 mAh/g), low electrochemical potential (−0.763 V versus SHE), resource abundance, low toxicity, and safe nature from aqueous nature. Various rechargeable ZIBs have been developed, including the reaction mechanisms, selection of cathode materials, performance improvement of Zn anode, and electrolytes innovations, dramatically boosting the application of ZIBs for wearable electronics.40 Ag-Zn batteries with comparable specific capacity with LIBs have been widely used in portable biomedical electronics. Lee and coworkers designed the first example of a stretchable Ag-Zn battery by embedding the silver nanowires into the PDMS elastomer as the current collectors and electroactive cathodes simultaneously.41 The Zn anodes were produced by electrodeposition of Zn on top of embedded Ag nanowires electrodes. The fabricated battery could maintain the performance at both relaxed and stretched states during 1000 cycles of 80% stretching, suggesting its great durability to severe mechanical deformations. Alkaline electrolytes enable ZIBs with high operation voltage, high capacity, and tolerance to high-current discharging, compared with the neutral or acidic electrolytes. Yin et al. developed a printed rechargeable AgO-Zn battery with a high capacity of 54 mAh/cm² and robust resiliency to mechanical deformation. The high capacity comes from the utilization of higher oxidation state oxide-AgO, whereas only Ag₂O is utilized in most of the Ag₂O-Zn batteries.42 This work presents a practical way for the fabrication of power sources for wearable electronics. The utilization of safer electrolyte may further widen the application of ZIBs, for example, a solid-state wearable and very safe ZIB utilizing gelatin and polyacrylamide (PAM)-based hierarchical polymer as the electrolyte, and α-MnO₂ nanorod/CNT as the cathode was fabricated by Li et al. in 2018.43 The electrolyte is produced by involving the grafting of PAM onto gelatin and the filling of gelatin chains in PAN (polyacrylonitrile) electrospinning networks.
The use of hazardous-free materials is also one important aspect of wearable batteries. Biocompatible and even biodegradable materials or fluids have been considered to replace the traditional electrodes or electrolytes. Bandodkar et al. designed a biocompatible battery using Mg as the anode and human sweat as the electrolyte. The fast sweat capture and storage was enabled by the utilization of a microfluidic channel fabricated using silicone and paper. The Mg battery was thin, flexible, and reliable for powering wireless epidermal sweat sensors and the heart rate sensor, suggesting the promising future of Mg batteries to serve as wearable power sources. Wang et al. imparted the stretchability to their “green” Mg battery (lemon juice as the electrolyte) by introducing the kirigami structure design. The Mg battery can endure bending, twisting and stretching, paving the way for the fabrication of “green” wearable power sources.

Endowing the electrochemical energy storages with flexibility/bendability is an initial step in the innovation of wearable power sources. When being used in more mechanically challenging scenarios, such as biointegrated devices, they are required to be able to endure harsher stretching deformations. Detailed review and discussion on wearable electrochemical energy storages are available in previous reviews. Herein, we focus on the specific aspects of harvesting bioenergy from human body for charging wearable energy storage.

3 ENERGY HARVESTING FROM THE HUMAN BODY

Biomechanical motions, body fluids, and body heat are rich power pools for renewable energy from the human body. To effectively extract bioenergy from the human body, TENG/PENG, BFCs, and TEGs with different working mechanisms, have been established. One challenge of human-body energy harvesters is the stable generation of electricity for wearable or implantable electronic devices in harsh working scenarios such as during the stretching for skin-worn harvesters, or the complicated physiological environment for implantable harvesters. Recent progress on advanced materials synthesis, fabrication techniques, and working mechanisms has dramatically speed up the practical applications of human-body energy harvesters.

3.1 TENG/PENG for mechanical energy harvesting

Nanogenerator, based on displacement current, is an emerging energy harvesting technology that efficiently converts ambient random mechanical energy into electricity for small electronics such as distributed sensors and wearable devices. In 2006, Wang et al. firstly reported a piezoelectric nanogenerator (PENG), which utilized ZnO nanowires to generate potential differences upon a strain. The working principle of PENGs is depicted in Figure 2A. The PENG is composed of a piezoelectric material that is sandwiched by the top and bottom electrodes. Under vertical strain, the piezoelectric material generates an electrostatic potential and induces the flow of electrons between the two electrodes. When the strain is released, a reversed current is formed by the backflow of the electrons. PENG is widely applied in self-charging units and self-powered sensors. To increase the current output, Gu et al. proposed a PENG with three-dimensional intercalation electrodes (Figure 2B). The multilayer structure created many boundary interfaces between the piezoelectric materials (Sm doped PMN-0.31PT NWs) and electrodes, which increased the total amount of polarization charges (1690 μC/m²) as well as the current density (290 μA/cm²). The PENG could charge a 1 μF capacitor very fast by harvesting walking energy.

In 2012, Fan et al. reported a flexible triboelectric nanogenerator (TENG), which has higher output and a wider choice of materials than PENG. The working mechanism of a TENG is based on the conjunction of triboelectrification and electrostatic induction (Figure 2C). A TENG has two dissimilar materials, which are positively and negatively charged respectively by triboelectrification. The relative movement of these two charged materials creates a potential difference and the flow of charge between two back electrodes. The TENG has four kinds of working modes: contact-separation, lateral sliding, single electrode, and free-standing mode, showing the versatility to scavenge energy from different kinds of mechanical movements like contacting, bending, pressing, sliding, and rotating. The flexible TENG is very suitable for biomechanical energy harvesting from low-frequency human motion. Xiong et al. proposed a textile-based wearable TENG involving the black phosphorus for the durable triboelectric electron-trapping coating to efficiently harvest body movement energy (Figure 2D). The black phosphorus protected by cellulose-derived hydrophobic nanoparticles makes the wearable TENG with excellent long-term water repellency and durability regardless of various extreme conditions, broadening the application of the ambient-sensitive materials in TENGs.

3.2 BFC for biochemical energy harvesting

BFCs are constructed to consume biomass for electricity generation through natural processes. Glucose and
lactate are two widely used fuels for implantable or skin-worn BFCs due to their abundance in blood and sweat, respectively.\textsuperscript{13,62–64} Figure 2E schematically shows the working mechanism of a typical glucose-oxygen BFC, comprising a glucose oxidase (GOx) immobilized anode to generate protons and electrons through glucose oxidation reaction, and a bilirubin oxidase (BOx) enzyme immobilized cathode to catalyze the oxygen reduction reaction.\textsuperscript{63} When the anode and cathode are connected by an external loading, electrons transfer from the GOx anode to the BOx cathode, and thus, current and power are generated. The current intensity is proportional to the biofuel concentration until the BFC is saturated. Major challenges of human-body BFCs are the stability of enzyme-based electrodes in dynamic surrounding environments (e.g., pH, temperature, oxygen levels, or humidity changes) and functional materials to manifest specific capability in different working places such as mechanical resiliency for skin-worn BFCs. The power density of human-body BFCs can reach several mW/cm\textsuperscript{2} and be able to power commercially available radio transmitters for the wireless communication between electronics and data receiver stations. For example, Bandodkar et al. reported a stretchable high-power-density epidermal BFC consuming lactate in human sweat through the combination of thick screen-printed CNT-based anode and cathode pellets and stretchable metal connection framework in an “island-bridge” configuration.\textsuperscript{1} During exercise, these BFCs could utilize the high areal surface to generate a high-power density of approximately 1 mW/cm\textsuperscript{2} and power a Bluetooth Low Energy (BLE) radio, as shown in Figure 2F. Recently, Yu et al. designed flexible epidermal BFCs with a high-power density of 3.5 mW/cm\textsuperscript{2} by integrating zero-(Pt-Co nanoparticles) to three-dimensional
(CNT network) nanomaterials in a highly conductive photolithographic Cu interconnection. The fabricated BFCs manifested a high-power density, conformable contact with human skin, and capability for powering wireless epidermal sensors (metabolic analytes and temperature), suggesting the great potential of sweat-based BFCs to power wearable electronic devices.

3.3 TEGs for biothermal energy harvesting

Released heat from the body accounts for the biggest proportion of energy provided by food and the mechanical efficiency of the body is only around 15-30%. Human body temperature is stabilized at 37°C through metabolism and, thus, enables the body heat to be a continuous energy source. Appropriately, 0.6-1.8 W power which is enough to power many wearable sensors could be generated if thermoelectric can harvest dissipated heat from one whole body (60-180 W) at a approximately 1% conversion efficiency. Wearable thermoelectric generators (TEGs) conformally contacting with human skin are designed to convert human body heat into electricity through the Seebeck effect. Figure 2G shows the cross-section of wrist-based TEGs having several P-type and N-type legs, copper strips, PDMS encapsulation, and a flexible thermal interphase layer (TIL) to enable the wearability of TEGs on curved skin. The differences between human skin and ambient temperature cause a stable heat flux flowing through the TEGs, thus, could generate the voltage between two legs. The maximization of conversion efficiency, intimacy TEG-body attachment, wearing convenience, low weight, and reliability are key factors that need to be solved when wearable TEGs are designed at different levels (materials, devices, and systems). Recently, Sun et al. reported the first example to wove selectively doped CNT fibers (Figure 2H) with a wrapping of acryllic fiber into stretchable π-type 3D fabric TEGs. The truly textile-based TEGs have an excellent stretchability of 80% from interlocked thermoelectric modules, a superior peak power density of 70 mW/m² at 44 K temperature difference, and compatibility with body movement. This work would greatly facilitate the development of textile-based TEGs to harvest energy from body heat. Wearable TEGs can also be used in augmented reality and virtual reality applications. A comprehensive review on the recent adoption of thermal technology for augmented reality and virtual reality can be found in a recent review. The working mechanism and output characteristics define the specific applications of each bioenergy harvesting technology. TENG/PENGs are flexible, simple in fabrication, and very efficient in harvesting the motion of the human body with low-frequency nature, making them suitable both for implantable and wearable use. The energy is generated in pulse mode with high voltage but low current. BFCs work like traditional fuel cells and can generate high-power density at the mW/cm² range and current density at around mA/cm² level in the presence of biofluids. However, the involvement of enzymes limited the performance stability in the prolonged operation. As the human body is a continuous source of heat, and nonbioactive materials are involved in the fabrication of TEGs, wearable TEGs are logically fit for nonstop energy harvesting. The energy generated by TEGs also can be high to the microwatt level. However, the amount of energy generated by a certain TEG highly relies on the temperature difference between the human body and the surrounding environment. Thus, it is still challenging to guarantee a stable output considering the varied surrounding temperature over a day. Also, the application of TEGs for implantable energy harvesting has rarely been reported for the minor temperature difference inside the human body. The details about the fabrication, characteristics, and challenges of wearable PENG/PENGs, BFCs, and TEGs have been fully presented in previous reviews.

4 HUMAN-BODY MOTIONS

4.1 PENG for mechanical energy harvesting

The direct conversion of mechanical energy into the chemical energy of a battery was first reported in 2014 by Zhang et al., known as a SCPU. A novel PVDF-PZT nanocomposite film was developed, serving as both the piezoelectric material of PENG and the separator of the battery. This all-in-one hybrid device design was compact and concise. Under strain, the piezoelectric potential of PVDF-PZT film driven ions to migrate through the film and incorporate
into the anode electrode. Following this work, the authors demonstrated a new all-solid-state SCPU (Figure 3A). The mesoporous PVDF-LiPF$_6$ film was used as the piezoseparator. The fabricated SCPU showed high power generation and high energy conversion/storage efficiency. Under periodic compressive deformation, the SCPU was quickly charged to 0.118 μAh within approximately 240 s. The SCPU was demonstrated in wearable power sources for sports bracelets and smart watches. Parida et al. reported a fast-charging SCPU that significantly shorten the charging time for near one order of magnitude (Figure 3B). The porous P(VDF-TrFE) film was impregnated with PMMA/PC/LiClO$_4$ gel electrolyte to act as the piezoelectric separator. Under strain, the P(VDF-TrFE) film generated a potential and induced an electric double layer at the carbon nanotube (CNT) electrodes, leading to fast adsorb and desorb ions. Although these kinds of all-in-one SCPU are compact, the power density is relatively low.

### 4.2 TENG for self-charging battery

The combination of high output TENG and high-energy density battery enables the fast charging and longtime operation of the SCPU. Zi et al. firstly reported a SCPU that combined a TENG and a LIB, as shown in Figure 3C. The arch shape TENG harvested energy from surrounding mechanical vibrations and simultaneously charged the LIB. The SCPU independently provided a constant current of 2 μA at 1.55 V voltage and continuously powered a UV sensor, while the full-charged LIB alone could only power the sensor for a few hours. The SCPU was mounted under a shoe to harvest walking energy, serving as a self-sustainable and portable power source. However, these SCPUs have poor stretchability because of using common polymer film and aluminum electrodes.

Fibers/yarns shape TENGs and batteries are more flexible and can be integrated into wearable textiles. Pu et al. reported a wearable SCPU based on textile TENG and flexible LIB belt (as shown in Figure 3D). A piece of common polyester fabric was coated with Nickle (Ni) to act as electrodes for the TENG, and the LiFePO$_4$ and Li$_4$Ti$_5$O$_12$ were coated on the Ni-cloth as the cathode and the anode of LIB. The SCPU had good flexibility and could be worn in different positions to harvest human-motion energy for powering a remote heartbeat meter. Besides, the Zn-ion battery (ZIB) was also combined with TENG to form a wearable all-fabric-based SCPU. The SCPU knitted into the pixel of a
flexible fabric substrate could harvest the energy of human finger motion and charge the battery for powering an electronic watch.

### 4.3 TENG for self-charging supercapacitor

A SC, especially the solid-state SC, is preferable for TENG energy storage because of the superior flexibility, reliability, and safety. For wearable devices, fiber and fabric provide a promising platform. Wang et al. reported a wearable SCPU consisting of all fiber-based SC and TENG for the first time, which was weaved on a coat to harvest the jogging energy. Besides, a highly integrated core-shell fiber-based SCPU was demonstrated, which had SC inside and TENG outside. In such a coaxial fiber, carbon fiber bundles were utilized as the electrode material for the TENG and SC (Figure 3E). The coaxial SCPU was knitted into a fabric to scavenge patting energy and power an electric watch. A washing test was conducted to verify the good launderability of the SCPU. The SCPU devices could also be constructed directly on textile. Cong et al. printed a super stretchable SCPU on the textile through a resist-dyeing-analogous method. The Ni and reduced graphene oxide were used as electrode of TENG and micro-SC, which could maintain excellent conductivity even at 600% tensile strain. (Figure 3F). The SC reached 50.6 mF/cm, while the output of TENG was 94.5 mW/m. It was demonstrated in powering a watch.

However, in the system scale, the impedance match between nanogenerator and battery/capacitor is very important for efficiency and lifetime. The pulsed high voltage and low current characteristics of nanogenerators influence the charging efficiency and the stability of the battery/capacitor. A power management system is preferred to bridge the energy generation and storage, which usually involves a step-down transformer and an AC-DC converter. Song et al. developed a power management and biosensors system on a flexible printed circuit board, which could transmit data to a mobile phone in real time. In the future, efforts are needed to improve the generator’s output, enhance the efficiency of the power management circuit, and develop suitable application systems.

### 5 HUMAN-BODY BIOFLUIDS CHARGED ENERGY STORAGE DEVICES

Utilizing energy from human-body biofluids to charge energy storage devices can be derived from the BFC-charged SCs due to their high-power density, safety, long cycling life, and high speed of the charging-discharging process. The charged SC can deliver much higher power than BFCs harvesting energy from human blood, sweat, tears, and mitigate the unstable outputs of BFCs caused by the variable levels of biofluids, thus, broadening the capabilities of biofluid energy to power wearable electronic devices. Until now, there are two configurations in integrating SCs and BFCs including a single-cell strategy that functionizes enzyme on capacitive electrodes or a separated-cell strategy in which two separated modules are connected by an external circuit.

#### 5.1 Single-cell strategy

The advance of highly conductive, superior capacitive, and electrochemically inert materials fostered the development of immobilizing enzymes on those materials to construct hybrid devices, called biosupercapacitors, with the function of harvesting energy and storing the harvested energy in the presence of biofluids. The biofluids serve as the electrolytes for both the SC modules and BFC modules. Double layer capacitive materials, such as CNTs and porous gold, and pseudocapacitive polymers, including conductive polymers (polypyrrole and polyaniline), redox polymers, and MnO₂, have been explored to endow traditional BFCs with the capability to store energy. The hybrid device could release electricity in a much higher power density than BFCs resulting from the fast charge-discharge rate of SCs. As shown in Figure 4A, a biosupercapacitor was constructed by Agnès et al. to wire GOx enzyme and laccase directly on two CNT matrixes as the anode and the cathode, respectively, for BFC setup. The high electrical conductivity, high specific surface of CNT matrixes enabled the storage of charge in the same device. Energy converted from biocatalytic reaction (glucose oxidation on anode and oxygen reduction on the cathode) can continuously charge the CNT matrix. Thanks to the fast discharging-charging nature of the CNT electrochemical double layer, the fabricated biosupercapacitor can release a high-power density of 15 mW/cm² at 0.5 V in a pulse mode for more than 40 000 cycles. The biosupercapacitor could recover itself after each discharge pulse through the energy generated from continued oxidation of glucose on the anode and oxygen reduction on the cathode.

Most of the reported biosupercapacitors involving the reduction of oxygen on the cathode. However, the concentration of dissolved oxygen in the biofluids is much lower than that of glucose, for example, only 0.14 mM oxygen in arterial blood and 0.08 mM in intestinal tissue, whereas 4.8 and 3.3 mM glucose in plasma and muscle, respectively. To mitigate the unstable deficiency of
oxygen for in vivo application, Xiao et al. utilized solid nanoporous gold/MnO$_2$ to replace enzymatic cathode based on oxygen reduction. During discharging, the fraction of Mn(IV) ($\sim$1.3%) accepts one electron and converts to insoluble Mn(III) and then the redistribution of surface Mn(III) and Mn(IV) in the bulk through the charge transfer causes the recovery of cathode potential in the reset step. Combining with a supercapacitive glucose dehydrogenase/redox polymer biocathode, the designed biosupercapacitor delivered 294 times higher power density than the continuous mode in N$_2$-bubbled 10 mM glucose solution, overcoming the limitation of oxygen supply in most biosupercapacitors.\textsuperscript{104}

The simple configuration of biosupercapacitor integrating two modules in one device can deliver high power output compared with classic BFC. However, the reported devices still utilize materials with limited flexibility, impeding the application of biosupercapacitors for wearable electronics. Another issue is about the shared electrolyte may constrain the performance of each module. The electrolyte with a high concentration of ions is preferred by SCs, but it is unrealistic in standard biofluids.

5.2 | BFC charge energy storage devices in a lateral connection

When BFCs and SCs are fabricated separately and then integrated on the same substrate, several merits can be reached: (1) the electrode materials and device configurations of each part can be optimized for better performance; (2) SC can be free from sharing the electrolyte with BFC, thus, specific and high-performance electrolytes can be used; (3) flexibility of integrating BFCs and SCs based on specific power requirements; (4) power released from SCs can be in not only a pulsed mode but also a continuous mode with high-power density. The advantages of charging energy storage by human-body BFCs in a lateral connection have encouraged the innovations of integrating two devices in a platform and connecting them through an external circuit.

Hou et al. developed an integrated system combining enzymatic BFCs extracting energy from glucose and SC storing harvested energy on the same substrates, including a piece of glass or flexible PET, for biofluid energy harvesting and storage, as shown in Figure 4B. The bioanode and biocathode of the BFC module were fabricated by...
immobilizing flavin adenine dinucleotide-glucose dehydrogenase for the oxidation of glucose and laccase for the reduction of oxygen on two MCNTs buckypapers, respectively. For the SC part, PVA-H$_3$PO$_4$ solid-state electrolyte was sandwiched by two MCNTs electrodes modified with pseudocapacitive PANI conductive polymer, inducing a much lower internal resistance than the two-in-one strategy. When two BFCs connected in-series were utilized to charge the SC, a 0.8 V charging voltage can be reached in SC and a maximum 608 µW/cm$^2$ can be delivered in the subsequent continuous discharging process with a current density of 0.8 mA/cm$^2$. This strategy allows for the versatile connection among BFCs and SCs, and thus, casts more possibility to power implantable or wearable electronic devices. A prototype of using the implantable glucose BFCs to charge SC and then powering the temperature sensor was developed by Bollella et al., as shown in Figure 4C. The energy accumulating devices, the SC was charged by a millimeter-scale implantable BFC with a size of 2 x 2 x 3 mm$^3$. Beyond the energy harvesting-storage system, they also designed a power management circuit to tune the power output from BFC-SC energy harvesting-storage system depending on the requirement of the temperature sensor system (including data memory and wireless data delivery). The complete system could work independently in the hemolymph of the slug which contains glucose, including energy extraction, sensing process, and wireless data read-out, demonstrating the great potential of BFC-SC to serve as a reliable power source.

The necessity of fabricating two modules separately can be further highlighted by a sweat-based biofluid energy conversion-storage system. Sweat-based BFCs scavenge lactate to generate and deliver electricity only in the presence of sweat. However, irregular perspiration of users leads to unstable sweat levels and lactate concentration, and thus, a constant power output is hard to be delivered. Lv et al. screen printed a hybrid stretchable BFC-SC system on two sides of a single spandex textile to harvest energy from lactate in sweat and then store harvested energy for subsequent use, as shown in Figure 4D. By formulating the stretchable CNT ink and MnO$_2$/CNT ink for the BFC and SC, respectively, and printing in a stretching durable serpentine structure, they realized the success of multiple-layer printing of integrated two stretchable modules on a single textile without deteriorating the softness of textiles. The integrated textile system was able to conform to human skin and endure repeated stretching deformation. When tested on the sweating subject’s arm, the SC was charged to 0.4 V from sweat BFC and still delivered power even after sweat was evaporated.

## 6 | HUMAN-BODY HEAT CHARGED ENERGY STORAGE DEVICES

As the human body is a constant pool of thermal energy and there always exists a temperature difference between the human body and the surrounding environment, charging wearable electrochemical energy storage devices with TEGs is a reliable measure for powering wearable electronics continuously. The temperature gap between the hot side and cold side of wearable TEGs is varied when humans stay in environments with different ambient temperatures and wind speeds. The electrochemical energy storage devices could store the unstable electrical energy produced by wearable TEGs and then release them as stable power sources. For traditional solid-state thermoelectric devices with p- and n-type semiconductors, the integration with energy storage could only be enabled by fabricating two modules separately on the same platform and then connected by conductive circuits. Newly developed ionic TEGs rely on the different thermodiffusion of ionic charge carriers in the presence of heat gradients and, thus, hold the attribute to be fabricated as two-in-one thermal energy harvesting and storage devices.

### 6.1 | Single-cell strategy

The SC could be simply charged by the temperature difference between the human body and ambient air by using two capacitive electrodes to sandwich a highly ionic conductive electrolyte, in which the ion movement can be driven by thermal flux. The Eastman entropies caused by ions solvation environment changes in variable temperatures and change of charge density at two electrode surfaces induced by the Soret effect result in simultaneous temperature-dependent potential difference and energy storage on two electrodes. The Soret effect is a phenomenon that the gradient of ion would be induced by the mobility difference of ions with the presence of temperature gradient. Kim et al. developed a human body thermal charged solid-state SC by sandwiching polystyrene sulfonic acid (PSSH) film through two symmetric highly capacitive electrodes containing graphene/CNT and PANI. The PSSH served as both the voltage generator and solid electrolyte. When one electrode was contacted with the human body, and another electrode was contacted with ambient air (5.3 K temperature difference for an in-vitro test), the H$^+$ diffused from hot electrode to cold electrode and PSS- moved less, causing the H$^+$ concentration on the cold electrode is much higher than that of the hot side. The H$^+$ gradient creates a much higher potential (8 mV/K) on the cold electrode than regular TEGs or thermocells.
FIGURE 5  Wearable energy storage devices are charged by energy harvested from human body heat. (A) The schematics and performance of a thermal charged supercapacitor (SC). Reproduced with permission. Copyright 2016, Wiley-VCH. (B) The photo image of the flexible cellulose ionic conductor and its mechanism for enhanced thermal voltage. Reproduced with permission. Copyright 2019, Springer Nature. (C) Photo image, schematics, and charging performance of a micro-SC charged by finger thermal energy when a finger touched the in-plane TEG. Reproduced with permission. Copyright 2020, Elsevier. (D) Photo image of a SC charged by TEGs on a T-shirt and the charging performance at different ambient temperatures. Reproduced with permission. Copyright 2017, IEEE

With the external connection, potential difference-induced electron flow caused the PANI oxidation and reduction on the hot electrode and cold electrode, respectively, to finish the charging procedure. After the removal of the temperature gradient, the H⁺ gradient gradually diminished and the previous hot electrode tuned to be approximately 0.038 V more positive than the cold electrode. The voltage change in the whole process is shown in Figure 5A, both the charging step and stored energy could power electronic devices.

The voltage output of the thermocharged SC is mainly determined by the gradient of ion concentrations on electrode surfaces at a certain temperature difference. An extremely high thermal gradient ratio, 24 mV/K, was achieved by using an aligned cellulosic membrane serving as an ion transfer chamber to enable the selective diffusion of sodium ions, as shown in Figure 5B. The aligned ion conductor was simply produced by filling the NaOH into the perpendicularly cut natural wood after the delignification process by highly concentrated NaOH. This cellulosic membrane contains oxidized chains of cellulose molecules to attract sodium ions to form the cellulose-Na complex and repel OH⁻ ions of NaOH electrolyte. Also, the density of negative charge on the cellulose nanofiber can be enhanced by the oxidation of 2,2,6,6-tetramethylpiperidine-1-oxyl. Both factors contribute to a high Soret coefficient. Additionally, the membrane is flexible and biocompatible, making it is suitable to harvest energy from the human body. This work provides a promising route for the fabrication of ionic thermocharged SC to harvest and store low-grade heat from the human body for wearable electronics.

6.2  TEGs charge energy storage devices in a lateral connection

The single-cell strategy for the human body heat harvesting-storage system suffers from the long charging time caused by slow ion diffusion of Soret effect, electrical leakage current, and self-discharging induced by external loading which is essential for the charging process. Charging SC by independent traditional wearable TEGs or thermocells is, thus, regarding as a promising tunnel
to reach a fast speed charging and a high discharging and charging ratio.112 Yang et al. integrated series-connected traditional TEGs, one in-planar micro-SC, and a metal pad to maximize the efficiency of heat transfer on the same substrate to harvest the thermal energy from a human finger, as shown in Figure 5C. The EDLC micro-SC contained CNT/graphene porous interdigitated electrodes and a H2PO4-PVA gel film as the electrolyte. When a human finger touched the ring shape metal pad, the heat transfer to the TEG component and the micro-SC can be charged by series-connected p-Ag2Te/n-Ag2Se TEG to the maximum potential within 10 s. The discharging and charging ratio of the integrated system was 97.6% at an 8.6 K temperature difference.113

Textile-based TEG-charged SC was developed to maximize the contact between wearable TEGs and human skin, ease the integration with wearable electronic circuits and sensors. Deng et al. integrated four TEG modules with one flexible SC on a T-shirt to harvest thermal energy from users (Figure 5D). The electricity generation capacity of TEGs was well studied by checking the power and voltage output in different body parts, motion states, environments, and wind speeds. At 5°C ambient temperature, four TEG modules containing around 800 thermocouples generated approximately 1 mW power. Once the TEG arrays connected with the SC at different ambient temperatures, fast charging was boosted, and the voltage of SC could reach a similar level with that of TEGs after 3-4 min. This work demonstrated the workability of TEGs and integrated TEGs-SC in different practical environments, paving the way for the massive utilization of TEGs-SC to power wearable electronic devices.108 A thermocell was also integrated on a T-shirt to charge a capacitor. The voltage of a single thermocell relying on temperature-dependent Fe(CN)63–/Fe(CN)64– redox reaction is much higher than that of traditional TEG, and thus, the capacitor could be charged to 2 mV after 1-2 s.114

7 | COMPENSATION FROM SOLAR ENERGY FOR THE HUMAN BODY-CHARGED ENERGY STORAGE DEVICES

Human beings are living on sunlight-radiated earth, thus, harvesting energy from sunlight is a good compensation for human-body energy to charge wearable electrochemical storage devices, especially considering each human-body energy harvester requires specific conditions to deliver the best power output. For example, only when a wearer metabolizes enough sweat containing a high concentration of lactate then epidermal lactate BFCs can display superior performance; continuous human movement is needed for wearable TENG to harvest mechanical energy. The compensation from sunlight can be enabled by either incorporating independent solar cells with bioenergy harvesters or designing all-in-one devices.

Wang and coworkers have combined TENG and solar cells to charge SCs and LIBs battery simultaneously to design sustainable power packages for wearable electronics since 2016.115-118 In one of their design (Figure 6A), a stretchable SC, a flexible TENG, and three fiber-shaped dye-sensitized solar cells (DSSCs) are integrated on a bracelet. The rectified TENG could harvest energy from body motion, be compensated by fiber-shaped DSSCs extracting energy from ambient, and then charge the wearable SC. Compared with the single TENG module (~100 s), the hybrid energy harvesters consumed only 43 s to charge the SC from 0 to 1.8 V in the presence of simulated sunlight, suggesting the compensative effect from fiber-shaped DSSCs. The practical application was shown by an electric watch that can work in both a bright and dark environment when it utilized a hybrid self-sustainable power bracelet as the power source.117

Combining BFCs and solar cells can harvest energy from human biofluids and sunlight irradiation simultaneously. The development of wearable systems that combine BFCs, solar cells, and energy storage devices is still not being well explored. However, previous reports about photoelectrochemical BFCs can instruct utilizing both energies generated by BFCs and solar cells to charge wearable electrochemical energy-storage systems. This kind of BFCs fabricated by coupling biocatalysts with photoactive materials, thus, solar energy can be harvested by BFCs,119-128 as shown in Figure 6B. The open-circuit potential of photoelectrochemical BFC can be around approximately 1 V which is higher than that of solely BFC and solar cells. The shortage lies in the low-power density and the optimizations in material design and enzyme/semiconductor conjunction will significantly enhance the efficiency of hybrid devices.119

The energy output of TEGs is highly related to the temperature difference. Apart from integrating solar cells with TEGs to charge wearable energy storage devices, the sunlight also can be used to increase the temperature difference for TEGs through a layer of the light absorber to fabricate solar TEGs. The light absorber can produce heat by converting the solar irradiation and then transfer the concentrated heat to the legs of TEGs through a highly thermal-conductive substrate, as shown in Figure 6C.129-131 Jung et al. simplified the system by printing the TEG legs onto the thin solar absorber made of five-period Ti/MgF2 superlattice film (~ 500 nm). By doing so, the temperature difference was increased to 20°C under solar irradiation.132 The energy storage devices could be fastly charged by solar TEGs, especially in outdoor places.
FIGURE 6 Compensation from solar cells for the human body energy harvesters to charge wearable energy storage devices. (A) The schematics and charging performance (current and voltage) of a stretchable supercapacitor charged by both a TENG and a solar cell. Reproduced with permission. 117 Copyright 2019, Elsevier. (B) The schematics of the photoelectrochemical fuel cells. Reproduced with permission. 119 Copyright 2016, Wiley-VCH. (C) The schematics of the solar irradiation for increasing the temperature difference between the hot side and cold side. Reproduced with permission. 131 Copyright 2011, Springer Nature

8 | CONCLUSION AND PERSPECTIVE

Charging flexible electrochemical energy storage devices by human-body energy (body motion, heat, and biofluids) is becoming a promising method to relieve the need of frequent recharging, and, thus, enable the construction of a self-sustainable wearable or implantable system including sensing, therapy, and wireless data transmission. Electrochemical energy storage devices can accumulate the irregular or unstable harvested energy for use as stable power sources for wearable or implantable electronics. To be well-integrated with human-body energy harvesters, wearable SCs and batteries need to be conformal to the soft human body or organs. Therefore, multifunctionalities, such as stretchability, self-healing capability, and transparency, are endowed to newly developed electrochemical energy storage devices. 46,133–135 Based on the characteristics and mechanisms of energy harvesters (PENGs/TENGs, BFCs, and TEGs), two strategies are utilized either by single-cell strategy or by connecting through external circuits to design different human-body energy harvesting-storage systems. The single-cell strategy integrates the capability of energy harvesting and charges storage in one pair of electrodes, simplifying the device construction, while divided modules enable the performance maximizations of each module and flexibility of connection depending on the power consumption of electronic devices. Beyond the human-body energy, sunlight energy can be a versatile compensation in the presence of sunlight for human body energy to charge electrochemical energy storage devices. The human-body charged SCs/batteries have been demonstrated to be promising for powering wearable electronics.

The practical application of the human-body energy harvesting-storage system is still encountering several challenges, even though the conceptual progress in this field has been achieved. The most obvious challenge is that the stored energy in electrochemical energy storage devices from the human body is still far below that of the traditional cable charging method, thus, only wearable electronic devices with low energy consumption can be powered. 136 Also, most of the energy storage modules in reported systems relied on capacitive SCs, because batteries need stronger power sources to charge. SCs are suffering from a faster self-discharging nature comparing with batteries, impeding the subsequent use of the stored energy. This challenge is mainly attributed to the low power efficiency of human-body energy harvesters and low integration efficiency.

The progress in materials science and device structural design would enable the elevated performance of human-body energy harvesters and electrochemical energy storage devices to minimize the impedance/voltage...
mismatch between two modules and increase energy output. Meanwhile, integrating different types of energy harvesters generating energy simultaneously from body motion, biofluids, and body heat together would increase the power generation by fully harvesting human-body energy, and weaken the influence of human activities and surroundings on the performance of single-energy harvesters. For example, a textile-based microgrid system has been constructed by integrating TENGs and epidermal BFCs on one textile platform to simultaneously extract energy from human-body motions and sweat stimulated by body exercise, and then to deliver more energy to wearable energy storage devices. Two energy harvesters alleviated the dependence of a single harvester on the subject’s exercise status. Also, the system can compensate the limitation of BFC coming from the delay in perspiration and of the TENGs coming from the lack of motion, and thus, elongates the operation for powering a wearable chemical sensor from a 10-min exercise to over 30 min, exhibiting the great prospects in combining hybrid energy harvesters for the charging of energy storage devices. Other challenges, including the compatible and cheap fabrication for different components, tunable energy capacity depending on the specific energy consumption, and multifunctional performance, such as high stretchability and self-healing behavior of the whole integrated system, are also impeding the wide application of human-body energy harvesting storage. Materials selection, mechanism exploration, device structural design, and electronic circuit optimization are four aspects that can be considered to eliminate the shades in the development of human-body self-sustainable energy systems. The growing focus on wearable health care monitoring, therapies, and human-machine interfaces would attract joint efforts from material scientists, chemists, and electronics experts to develop practical human body-system self-powered electronics.

ACKNOWLEDGMENTS
Jian Lv and Jian Chen contributed equally to this work. This work was supported by the National Research Foundation, Prime Minister’s Office, Singapore, under its Campus for Research Excellence and Technological Enterprise (CREATE) program.

CONFLICT OF INTEREST
The authors declare no conflict of interest.
[Correction added on 29 June 2021, after first online publication: Conflict of Interest section has been added.]

REFERENCES
1. Cai G, Wang J, Qian K, Chen J, Li S, Lee PS. Extremely stretchable strain sensors based on conductive self-healing dynamic cross-links hydrogels for human-motion detection. Adv Sci. 2017;4:1600190.
2. Kim J, Campbell AS, de Ávila BEF, Wang J. Wearable biosensors for healthcare monitoring. Nat Biotechnol. 2019;37:389-406.
3. Lv J, Kong C, Yang C, et al. Wearable, stable, highly sensitive hydrogel-graphene strain sensors. Beilstein J Nanotechnol. 2019;10:475-480.
4. Gao D, Parida K, Lee PS. Emerging soft conductors for bioelectronic interfaces. Adv Funct Mater. 2019;30:1907184.
5. Dong L, Xu C, Li Y, et al. Flexible electrodes and supercapacitors for wearable energy storage: a review by category. J Mater Chem A. 2016;4:4659-4685.
6. Zhou G, Li F, Cheng HM. Progress in flexible lithium batteries and future prospects. Energ Environ Sci. 2014;7:1307-1338.
7. Tan P, Chen B, Xu H, et al. Flexible Zn- and Li-air batteries: recent advances, challenges, and future perspectives. Energ Environ Sci. 2017;10:2056-2080.
8. Chen S, Qiu L, Cheng HM. Carbon-based fibers for advanced electrochemical energy storage devices. Chem Rev. 2020;120:2811-2878.
9. Park S, Tan AWM, Wang J, Lee PS. Coaxial Ag-base metal nanowire networks with high electrochemical stability for transparent and stretchable asymmetric supercapacitors. Nanoscale Horizons. 2017;2:199-204.
10. Park S, Thangavel G, Parida K, Li S, Lee PS. A Stretchable and self-healing energy storage device based on mechanically and electrically restorative liquid-metal particles and carboxylated polyurethane composites. Adv Mater. 2019;31:1-10.
11. Gong X, Yang Q, Zhi C, Lee PS. Stretchable energy storage devices: from materials and structural design to device assembly. Adv Energy Mater. 2020;2003308. https://doi.org/10.1002/aenm.202003308
12. Pu X, Hu W, Wang ZL. Toward wearable self-charging power systems: the integration of energy-harvesting and storage devices. Small. 2018;14:1-19.
13. Dagdeviren C, Li Z, Wang ZL. Energy harvesting from the animal/human body for self-powered electronics. Annu Rev Biomed Eng. 2017;19:85-108.
14. Chen X, Parida K, Wang J, et al. A stretchable and transparent nanocomposite nanogenerator for self-powered physiological monitoring. ACS Appl Mater Interfaces. 2017;9:42200-42209.
15. Jeerapan I, Sempionatto JR, Pavinaotto A, You JM, Wang J. Stretchable biofuel cells as wearable textile-based self-powered sensors. J Mater Chem A. 2016;4:18342-18353.
16. Zhang F, Zang Y, Huang D, Di CA, Zhu D. Flexible and self-powered temperature-pressure dual-parameter sensors using microstructure-frame-supported organic thermoelectric materials. Nat Commun. 2015;6:1-10.
17. Chen X, Ren Z, Guo H, Cheng X, Zhang H. Self-powered flexible and transparent smart patch for temperature sensing. Appl Phys Lett. 2020;116:043902.
18. Song Y, Min J, Yu Y, et al. Wireless battery-free wearable sweat sensor powered by human motion. Sci Adv. 2020;6:9842.
19. Jiang D, Shi B, Ouyang H, Fan Y, Wang ZL, Li Z. Emerging implantable energy harvesters and self-powered implantable medical electronics. ACS Nano. 2020;14:6436-6448.
20. Ouyang H, Liu Z, Li N, et al. Symbiotic cardiac pacemaker. Nat Commun. 2019;10:1-10.
21. Li N, Yi Z, Ma Y, et al. Direct powering a real cardiac pacemaker by natural energy of a heartbeat. ACS Nano. 2019;13:2822-2830.
22. Holade Y, Macvittie K, Conlon T, et al. Pacemaker activated by an abiotic biofuel cell operated in human serum solution. *Electroanalysis*. 2014;26:2445-2457.

23. Zheng Q, Shi B, Fan F, et al. In vivo powering of pacemaker by breathing-driven implanted triboelectric nanogenerator. *Adv Mater*. 2014;26:5851-5856.

24. Yeknami AF, Wang X, Imani S, et al. A 0.3V biofuel-cell-powered glucose/lactate biosensing system employing a 180 nW 64 dB SNR passive $\delta$ADC and a 920MHz wireless transmitter. *Dig Tech Pap—IEEE Int Solid-State Circuits Conf*. 2018;61:284-286.

25. Hayashi K, Arata S, Murakami S, Nishio Y, Kobayashi A, Nitsu K. A 6.1-nA fully integrated CMOS supply modulated OOK transmitter in 55-nm DDC CMOS for glassless-free, self-powered, and fuel-cell-embedded continuous glucose monitoring contact lens. *IEEE Trans Circuits Syst I Express Briefs*. 2018;65:1360-1364.

26. ElAnsary M, Soltani N, Kassiri H, et al. 50-nW Opamp-less $\Delta \Sigma$-modulated bioimpedance spectrum analyzer for electrochemical brain interfacing. *IEEE J Solid-State Circuits*. 2020;1-13. Published online.

27. Dong K, Wang YC, Deng J, et al. A highly stretchable and washable all-yarn-based self-charging knitting power textile composed of fiber triboelectric nanogenerators and supercapacitors. *ACS Nano*. 2017;11:9490-9499.

28. Hou H, Xu Q, Pang Y, et al. Efficient storing energy harvested by triboelectric nanogenerators using a safe and durable all-solid-state sodium-ion battery. *Adv Sci*. 2017;4:1-5.

29. Kim SL, Lin HT, Yu C. Thermally chargeable solid-state supercapacitor. *Adv Energy Mater*. 2016;6:1-7.

30. Lv J, Jeerapan I, Tehrani F, et al. Sweat-based wearable energy harvesting-storage hybrid textile devices. *Energy Environ Sci*. 2018;11:3431-3442.

31. Falk M, Shleev S. Hybrid dual-functioning electrodes for combined ambient energy harvesting and charge storage: towards self-powered systems. *Biosens Bioelectron*. 2019;126:275-291.

32. Wu H, Huang YA, Xu F, Duan Y, Yin Z. Energy harvesters for wearable and stretchable electronics: from flexibility to stretchability. *Adv Mater*. 2016;28:9881-9919.

33. Jia W, Valdés-Ramírez G, Bandodkar AJ, Windmiller JR, Wang J. Epidermal biofuel cells: energy harvesting from human perspiration. *Angew Chemie Int Ed*. 2013;52:7233-7236.

34. Kim J, Cha E, Park JU. Recent advances in smart contact lenses. *Adv Mater Technol*. 2020;5:1-17.

35. Chen G, Li Y, Bick M, Chen J. Smart textiles for electricity generation. *Chem Rev*. 2020;120:3668-3720.

36. Chen J, Lee PS. Electrochemical supercapacitors: from mechanism understanding to multifunctional applications. *Adv Energy Mater*. 2020;31:2003311.

37. Yu Z, Tetard L, Zhai L, Thomas J. Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. *Energy Environ Sci*. 2015;8:702-730.

38. Chen J, Chua DHC, Lee PS. The advances of metal sulfides and in situ characterization methods beyond li ion batteries: sodium, potassium, and aluminum ion batteries. *Small Methods*. 2020;4:1-26.

39. Xiang P, Chen X, Xiao B, Wang ZM. Highly flexible hydrogen boride monolayers as potassium-ion battery anodes for wearable electronics. *ACS Appl Mater Interfaces*. 2019;11:8115-8125.

40. Li H, Ma L, Han C, et al. Advanced rechargeable zinc-based batteries: recent progress and future perspectives. *Nano Energy*. 2019;62:550-587.

41. Yan C, Wang X, Cui M, et al. Stretchable silver-zinc batteries based on embedded nanowire elastic conductors. *Adv Energy Mater*. 2014;4:1301396.

42. Yin L, Scharf J, Ma J, et al. High performance printed AgO-Zn rechargeable battery for flexible electronics. *Joule*. 2021;5:228-248.

43. Li H, Han C, Huang Y, et al. An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte. *Energy Environ Sci*. 2018;11:941-951.

44. Bandodkar AJ, Lee SP, Huang I, et al. Sweat-activated biocompatible batteries for epidermal electronics and microfluidic systems. *Nat Electron*. 2020;3:554-562.

45. Wang Z, Li X, Yang Z, et al. Fully transient stretchable fruit-based battery as safe and environmentally friendly power source for wearable electronics. *EcoMat*. 2021;3:e012073.

46. Mackanic DG, Kao M, Bao Z. Enabling deformable and stretchable batteries. *Adv Energy Mater*. 2020;10:2001424.

47. Sumboja A, Liu J, Zheng WG, Zong Y, Zhang H, Liu Z. Electrochemical energy storage devices for wearable technology: a rationale for materials selection and cell design. *Chem Soc Rev*. 2018;47:5919-5945.

48. Li H, Tang Z, Liu Z, Zhi C. Evaluating flexibility and wearability of flexible energy storage devices. *Joule*. 2019;3:613-619.

49. Liu Z, Li H, Shi B, Fan Y, Wang ZL, Li Z. Wearable and implantable triboelectric nanogenerators. *Adv Funct Mater*. 2019;29:1808820.

50. Fan FR, Tang W, Wang ZL. Flexible nanogenerators for energy harvesting and self-powered electronics. *Adv Mater*. 2016;28:4283-4305.

51. Guo Z, Zhao Y, Ding Y, et al. Multi-functional flexible aqueous sodium-ion batteries with high safety. *Chem*. 2017;7(2):348-362.

52. Siddique ARM, Mahmud S, Heyst BV. A review of the state of the science on wearable thermoelectric power generators (TEGs) and their existing challenges. *Renew Sustain Energy Rev*. 2017;73:730-744.

53. Bahk JH, Pang H, Yazawa K, Shakouri A. Flexible thermoelectric materials and device optimization for wearable energy harvesting. *J Mater Chem C*. 2015;3:10362-10374.

54. Bandodkar AJ, Wang J. Wearable biofuel cells: a review. *Electroanalysis*. 2016;28:1188-1200.

55. Wannapob R, Vagin MY, Jeerapan I, Mak WC. Pure Nanoscale morphology effect enhancing the energy storage characteristics of processable hierarchical polypyrrole. *Langmuir*. 2015;31:11904-11913.

56. Jeerapan I, Ma N. Challenges and opportunities of carbon nanomaterials for biofuel cells and supercapacitors: personalized energy for futuristic self-sustainable devices. *C—J Carbon*. 2019;5:62.

57. Wang ZL. On Maxwell’s displacement current for energy and sensors: the origin of nanogenerators. *Mater Today*. 2017;20:74-82.

58. Wang ZL, Song J. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science* (80-). 2006;312:242-246.

59. Gu L, Liu J, Cui N, et al. Enhancing the current density of a piezoelectric nanogenerator using a three-dimensional intercalation electrode. *Nat Commun*. 2020;11:1-9.
60. Fan FR, Tian ZQ, Lin Wang Z. Flexible triboelectric generator. *Nano Energy*. 2012;1:328-334.

61. Xiong J, Cui P, Chen X, et al. Skin-touch-actuated textile-based triboelectric nanogenerator with black phosphorus for durable biomechanical energy harvesting. *Nat Commun*. 2018;9:1-9.

62. Chen G, Li Y, Bick M, Chen J. Smart textiles for electricity generation. *Chem Rev*. 2020;120:3668-3720.

63. Jeerapan I, Sempionatto JR, Wang J. On-body bioelectronics: wearable biofuel cells for bioenergy harvesting and self-powered biosensing. *Adv Funct Mater*. 2019;1906243:1-18.

64. Bandodkar AJ. Review—wearable biofuel cells: past, present and future. *J Electrochem Soc*. 2017;164:H3007-H3014.

65. Bandodkar AJ, You J-M, Kim N-H, et al. Soft, stretchable, high power density electronic skin-based biofuel cells for scavenging energy from human sweat. *Energy Environ Sci*. 2017;10:1581-1589.

66. Yu Y, Nassar J, Xu C, et al. Biofuel-powered soft electronic skin with multiplexed and wireless sensing for human-machine interfaces. *Sci Robot*. 2020;5:eaaa7946.

67. Winter DA. *Biomechanics and Motor Control of Human Movement*. New York, NY: John Wiley & Sons; 2009.

68. Riemer R, Shapiro A. Biomechanical energy harvesting from human motion: theory, state of the art, design guidelines, and future directions. *J Neuroeng Rehabil*. 2011;8:1-13.

69. Hyland M, Hunter H, Liu J, Veety E, Vashaee D. Wearable thermoelectric generators for human body heat harvesting. *Appl Energy*. 2016;182:518-524.

70. Kim CS, Yang HM, Lee J, et al. Self-Powered wearable electrocardiography using a wearable thermoelectric power generator. *ACS Energy Lett*. 2018;3:501-507.

71. Francisco L, De Pascali C, Sglavo V, Grazioli A, Masieri M, Siciliano P. Modelling, fabrication and experimental testing of an heat sink free wearable thermoelectric generator. *Energy Convers Manage*. 2017;145:204-213.

72. Kim SJ, We JH, Cho BJ. A wearable thermoelectric generator fabricated on a glass fabric. *Energy Environ Sci*. 2014;7:3959-1965.

73. Wang Y, Shi Y, Mei D, Chen Z. Wearable thermoelectric generator for harvesting heat on the curved human wrist. *Appl Energy*. 2017;205:710-719.

74. Nozariasbmarz A, Collins H, Dsouza K, et al. Review of wearable thermoelectric energy harvesting: from body temperature to electronic systems. *Appl Energy*. 2020;258:114069.

75. Sun T, Zhou B, Zheng Q, Wang L, Jiang W, Snyder GJ. Stretchable fabric generates electric power from woven thermoelectric fibers. *Nat Commun*. 2020;11:572.

76. Parida K, Bark H, Lee PS. Emerging thermal technology enabled augmented reality. *Adv Funct Mater*. 2021;2007952. https://doi.org/10.1002/adfm.202007952

77. Zhang Y, Zhang Y, Xue X, et al. PVDF-PZT nanocomposite film based self-charging power cell. *Nanotechnology*. 2014;25:105401.

78. He H, Fu Y, Zhao T, et al. All-solid-state flexible self-charging power cell basing on piezoelectrolyte for harvesting/storing body-motion energy and powering wearable electronics. *Nano Energy*. 2017;39:590-600.

79. Parida K, Bhavanasi V, Kumar V, Wang J, Lee PS. Fast charging self-powered electric double layer capacitor. *J Power Sources*. 2017;342:70-78.

80. Wang S, Lin ZH, Niu S, et al. Motion charged battery as sustainable flexible-power-unit. *ACS Nano*. 2013;7:11263-11271.

81. Liu X, Zhao K, Wang ZL, Yang Y. Unity convoluted design of solid li-ion battery and triboelectric nanogenerator for self-powered wearable electronics. *Adv Energy Mater*. 2017;7:1-8.

82. Pu X, Li L, Song H, et al. A self-charging power unit by integration of a textile triboelectric nanogenerator and a flexible lithium-ion battery for wearable electronics. *Adv Mater*. 2015;27:2472-2478.

83. Wang Z, Ruan Z, Ng WS, et al. Integrating a triboelectric nanogenerator and a zinc-ion battery on a designed flexible 3d spacer fabric. *Small Methods*. 2018;2:1800150.

84. Luo J, Fan FR, Jiang T, et al. Integration of micro-supercapacitors with triboelectric nanogenerators for a flexible self-charging power unit. *Nano Res*. 2015;8:3934-3943.

85. Jiang Q, Wu C, Wang Z, et al. MXene electrochemical microsupercapacitor integrated with triboelectric nanogenerator as a wearable self-charging power unit. *Nano Energy*. 2018;45:266-272.

86. Shi X, Chen S, Zhang H, Jiang J, Ma Z, Gong S. Portable self-charging power system via integration of a flexible paper-based triboelectric nanogenerator and supercapacitor. *ACS Sustain Chem Eng*. 2019;7:18657-18666.

87. Guo H, Yeh MH, Lai YC, et al. All-in-one shape-adaptive self-charging power package for wearable electronics. *ACS Nano*. 2016;10:10580-10588.

88. Wang J, Li X, Zi Y, et al. A flexible fiber-based supercapacitor-triboelectric-nanogenerator power system for wearable electronics. *Adv Mater*. 2015;27:4830-4836.

89. Yang Y, Xie L, Wen Z, et al. Coaxial triboelectric nanogenerator and supercapacitor fiber-based self-charging power fabric. *ACS Appl Mater Interfaces*. 2018;10:42356-42362.

90. Cong Z, Guo W, Guo Z, et al. Stretchable coplanar self-charging power textile with resist-dyeing triboelectric nanogenerators and microsupercapacitors. *ACS Nano*. 2020;14:5590-5599.

91. Pankratov D, Blum Z, Shleev S. Hybrid electric power biodevices. *ChemElectroChem*. 2014;1:1798-1807.

92. Shleev S, González-Arribas E, Falk M. Biosupercapacitors. *Curr Opin Electrochem*. 2015;226-233.

93. Narvaez Villarrubia CW, Soavi F, Santoro C, et al. Self-feeding paper based biofuel cell/self-powered hybrid μ-supercapacitor integrated system. *Biosens Bioelectron*. 2016;86:459-465.

94. Xiao X, Conghaile P, Leech D, Ludwig R, Magner E. A symmetric supercapacitor/biofuel cell hybrid device based on enzyme-modified nanoporous gold: an autonomous pulse generator. *Biosens Bioelectron*. 2017;90:96-102.

95. Pankratov D, Shen F, Ortiz R, et al. Fuel-independent and membrane-less self-charging biosupercapacitor. *Chem Commun*. 2018;54:11801-11804.

96. Kizling M, Draminska S, Stolarczyk K, et al. Biosupercapacitors for powering oxygen sensing devices. *Bioelectrochemistry*. 2015;106:34-40.

97. Pankratov D, Blum Z, Suyatin DB, Popov VO, Shleev S. Self-charging electrochemical biocapacitor. *ChemElectroChem*. 2014;1:343-346.

98. Alsouab S, Ruff A, Conzuelo F, et al. An intrinsic self-charging biosupercapacitor comprised of a high-potential bioanode and a low-potential biocathode. *Chempluschem*. 2017;82:576-583.
136. Yu H, Li N, Zhao N. How far are we from achieving self-powered flexible health monitoring systems: an energy perspective. *Adv Energy Mater*. 2020;11:2002646.

137. Katic J, Rodriguez S, Rusu A. A high-efficiency energy harvesting interface for implanted biofuel cell and thermal harvesters. *IEEE Trans Power Electron*. 2018;33:4125-4134.

138. Liu H, Fu H, Sun L, Lee C, Yeatman EM. Hybrid energy harvesting technology: from materials, structural design, system integration to applications. *Renew Sustain Energy Rev*. 2021;137:110473.

139. Yin L, Kim KN, Lv J, et al. A self-sustainable wearable multi-modular E-textile bioenergy microgrid system. *Nat Commun*. 2021;12:1-12.

140. Bandodkar AJ, You JM, Kim NH, et al. Soft, stretchable, high power density electronic skin-based biofuel cells for scavenging energy from human sweat. *Energy Environ Sci*. 2017;10:1581-1589.

**How to cite this article:** Lv J, Chen J, Lee PS. Sustainable wearable energy storage devices self-charged by human-body bioenergy. *SusMat*. 2021;1:285–302. [https://doi.org/10.1002/sus2.14](https://doi.org/10.1002/sus2.14)