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Hybrid dual-functioning electrodes for combined ambient energy harvesting and charge storage: Towards self-powered systems

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ABSTRACT

In the last few years, there have been an increasing number of reports where different energy harvesters are directly combined with charge storing devices, based on dual-function electrodes able to convert and store electrical energy in the same volume. This includes (bio)fuel cells harvesting chemical energy, (bio)solar cells harvesting solar energy, tribo- and piezoelectric devices harvesting mechanical energy, and thermoelectrics harvesting thermal energy, which now have been intimately combined with batteries and electrochemical capacitors. These new types of hybrid electric devices show great promise especially for the design of self-powered electronics where an integrated hybrid power system is preferable to separated ones, capable of scavenging ambient energy and simultaneously store it and in this way increasing the efficiency and enabling further miniaturization. This paper details the recent emergence of hybrid energy systems, reviewing the progress made using widely different energy harvesting techniques, which have so-far not been described in a single body of work.

1. Introduction

The harvesting and storage of ambient energy for portable, wearable and implantable applications, such as smart electronics and wearable micro- and nano-sensors, is now attracting a significant research interest (Bandodkar and Wang, 2016; Fan et al., 2016; Wen et al., 2016). Enormous efforts are being devoted to create multifunctional micro-systems in a wide variety of applications, e.g. chemical/biomolecular sensing, environmental monitoring, health monitoring, portable/wearable biomedical devices and personal electronics (Diamond et al., 2008; Hu et al., 2011; Messer et al., 2006; Soh et al., 2015; Takei et al., 2015; Yamamoto et al., 2016). Development of portable electronic devices have also moved towards light, thin and integrated small-scale devices (Bandodkar and Wang, 2016; Gao et al., 2016; Guo et al., 2016; Kim and Rogers, 2008; Kim et al., 2017; Patel et al., 2012). With the development of wireless sensor nodes for such a wide range of applications, there is a rising need for an autonomous power sources, where adapting and scaling down conventional energy systems is not easily done (Lukatskaya et al., 2016). Relying solely on battery power for such systems is in many cases not a suitable solution, as batteries contain a finite amount of energy and would need to be replaced or somehow recharged. A significant research effort is therefore being directed towards developing self-powered, wireless and autonomous systems, where ambient energy harvesters are very promising as energy sources for small-scale electronic devices and can provide simplicity and ease of handling of such systems (Knight et al., 2008; Paradiso and Starner, 2005).

Recent developments in micro- and nanotechnologies have resulted in a rapid growth of self-sufficient autonomous platforms, with various methods available for harvesting energy from locally available sources e.g. deploying thermoelectric, piezoelectric, photovoltaic and biofuel cells (BFCs) (Bandodkar and Wang, 2016; Fan et al., 2016; Wen et al., 2016; Yang et al., 2012). The power output of these energy harvesters is however typically quite low, ranging from μW to mW, which is an issue in their implementation in autonomous systems. Ambient energy harvesters typically provide power and voltage output lower than what is required to charge conventional batteries and supercapacitors. Having separate energy harvesting and charge storing elements also limits the possibilities to design miniature and flexible devices, which e.g. is crucial for implantable devices.

There is now a recent trend to directly combine energy harvesters with charge storing elements within one and the same unit, increasing the efficiency of the devices and enabling the creation of miniature systems (Chen et al., 2013; Fan et al., 2016; Pan et al., 2016; Pankratov et al., 2014a). These new types of hybrid electric devices, made up of dual-functioning elements for combined energy harvesting and storage, show great promise, especially in many applications of self-powered electronics where an integrated hybrid power system is preferable to

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separated ones. This have become a very hot research topic in the last couple of years with a multitude of different energy-harvesting hybrids, all from thermoelectric, solar, piezoelectric and fuel cell (FC) hybrid devices being reported so far (Agnes et al., 2014; Ramadoss et al., 2015; Sun et al., 2014; Zhao et al., 2016).

Several different recent reviews have described some examples of hybrid devices, but this have so far been as just a small part of a larger theme, such as wearable devices, or only dealing with a few specific types of energy harvesters used for hybrid devices (Luo et al., 2017; Pu et al., 2017; Zhong et al., 2017). We here therefor focus this review on the recent progress made in the development specifically of hybrid devices. While based on widely different energy harvesting techniques, the different hybrid devices share many commonalities, which have so far not been described in a single body of work.

1.1. Hybrid dual-function devices

As the word "hybrid" is used in various contexts, it is appropriate to start with defining in more detail what we actually mean herein. Hybrid is used to classify a wide range of different system, but by using the term hybrid we focus on the recent development of dual-functioning electrodes, specifically combining energy harvesting with energy storage within the same system using double-feature electrodes. Dual-function or double feature electrodes are special type of electrodes, which are able to convert certain type of energy into electric energy, and, simultaneously, are able to store electric energy in the same volume, used for conversion (Pankratov et al., 2014a).

A brief overview of the different harvesting systems employed to design hybrid devices is presented in Table 1, where a wide range of energy harvesters can be used to generate power form ambient energy sources. This includes (bio)fuel cells harvesting chemical energy, photovoltaics harvesting solar energy, piezoelectric devices harvesting mechanical energy, and thermoelectrics harvesting thermal energy, all of which can be designed for flexible, miniature self-powered devices. While the power that can be scavenged from such systems typically is quite low, current micro-sensor systems can be designed with a low power requirement, with values in the range of microwatts to milliwatts but where individual components can be down to even nanowatts (Morimura et al., 2014; Nikolic et al., 2014). Moreover, in many practical examples, e.g. biomedical monitoring of an important analyte, a sampling rate of once every few minutes is generally sufficient. As illustrated in Fig. 1, this enables power that is being generated/harvested to be accumulated in the hybrid battery/capacitor during the downtime operation, to be released during active mode, which can also help to mitigate power output swings. It is thus highly beneficial for low-power energy harvesters, as well as energy harvesters based on irregular or intermittent sources, to be able to store and accumulate energy.

Hybridization creates a novel platform in the development of energy

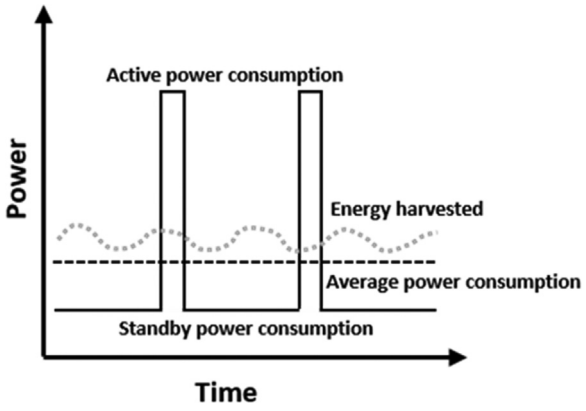

Fig. 1. Example of an energy harvester operating continuously and storing the accumulated charge, which is then delivered to the application when switched on in short active modes of high power consumption.

materials and enables unique advantages of low weight, flexibility and miniaturization. Typically, a self-powered device will consist of an energy harvesting system, e.g. a piezoelectric generator or a FC, connected to a separate battery or capacitor, possibly via a power conditioning circuit such as rectifier circuit or a voltage pump. This part is then connected via a power management unit to the end application, such as a sensor/radio device, to realize a functional device (Fig. 2), all connected through external wires. This reduces the level of integration and incurs additional Ohmic losses, resulting in bulkier systems and energy lost at the external connections. By designing a hybrid device, the energy harvesting and energy storing units can instead be combined into one unit, making the design of self-powered autonomous systems more straight forward. Either relying on different types of capacitance based on reversible charge-transfer reactions and/or electric double-layer capacitance, as in electrochemical capacitors (ECs), or built in together with a battery, continuously replenishing self-sufficient autonomous electric devices can be realized. Such a system is ideally suited for remote, wearable or implantable devices, where ambient energy harnessed by e.g. a wearable solar cell or an implantable BFC can be used to supply a sensor system with power. In particular, hybrid systems show great promise for powering of low-power micro-systems for a wide range of applications, to extend the life-time or completely replace batteries and power systems, where batteries simply are not feasible (Pankratov et al., 2014a; Wang and Wu, 2012).

1.2. Electrochemical capacitors

Most of the so far reported hybrid devices employ ECs, using a wide variety of different super-capacitive materials. Designing materials that combine ECs with different energy harvesters provides an innovative

Table 1
Overview of different ambient energy harvesters for hybrid devices.

Energy source	Energy harvester	Description
Chemical	(Bio)fuel cell	Harvesting energy from a wide variety of fuels Enzymatic, microbial and nonbiogenous catalysts DC output
Solar	(Bio)photovoltaics	Harvesting energy from solar radiation Dye sensitized, perovskite and bio-solar cells DC output
Mechanical	Piezoelectric/(Triboelectric)	Harvesting energy from vibrations and movement Wurtzite and other blend structures, piezoelectric separators AC output
Thermal	Thermoelectric/(Pyroelectric/Thermopower waves)	Harvesting energy from temperature gradient/(temperature fluctuations/ignited fuel) Based on thermally induced capacitive effect DC/AC output

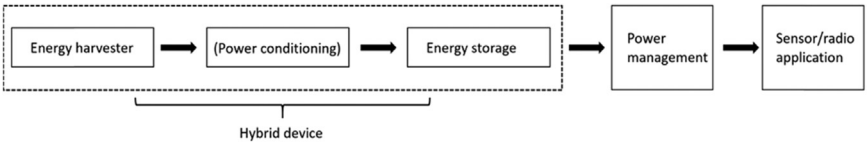

Fig. 2. Typical scheme of components needed to implement an energy harvester, where hybridization significantly simplifies the system.

solution, allowing harnessing of ambient energy and delivering high-power pulses, which is very attractive for the operation of many miniature autonomous devices. This can greatly enhance the power output from the energy harvester/EC hybrid, and have indeed been used to increase the instantaneous power output by several orders of magnitude (vide infra). Incorporating super capacitive elements, e.g. nanostructured carbon and conductive polymers (vide infra), thus allow for miniaturization and integration into a wide variety of energy harvesters and functional devices (Liu et al., 2016; Ng et al., 2015; Pankratov et al., 2014a; Soavi et al., 2016). ECs have been discussed in detail elsewhere in several extensive recent reviews, but a short description is appropriate here due to the prevalent role ECs play in the development of hybrid devices (Dubal et al., 2015; González et al., 2016; Liu et al., 2016; Wang et al., 2012; Wang et al., 2016b; Yu et al., 2015).

ECs can store comparatively large amounts of electric energy (much more than regular capacitors but less than batteries), reaching capacitance values as high as several thousands of farads g^{-1}, with high power density (up to 15 kW kg^{-1}), fast charging, and long life cycles, while the energy density of an EC is lower than a battery (Kötz and Carlen, 2000 ;Chen and Dai, 2014; Simon and Gogotsi, 2008; Wang et al., 2012; Yu et al., 2015). The operating voltages of EC vary generally from below 1.2 V for aqueous systems (due to the dielectric breakdown of water) up to 3 V and above for organic electrolytes and ionic liquids. The capacitance of ECs mainly arises from surface reactions of electrode materials, with a capacitive part stemming from reversible adsorption/desorption of ions at the electrode/electrolyte interface and a pseudocapacitive part originating from surface faradic redox reactions.

ECs are often divided on the basis on their main storage mechanisms into electrochemical double-layer capacitors (EDLC) and pseudo-capacitors (as illustrated in Fig. 3) (Simon and Gogotsi, 2008; Wang et al., 2012). Moreover, based on the composition of electrode materials that make up a complete EC, devices can be divided into symmetric ECs, asymmetric ECs, and hybrid ECs. Symmetric supercapacitors are typically composed of two identical EC-type electrodes, whereas asymmetric supercapacitors are composed of two different EC-type electrodes (in regards to loading, material etc.). Hybrid supercapacitors feature asymmetric electrodes of different nature that are charged/discharged specifically via different electrostatic and faradic modes, integrating one EDLC and one pseudocapacitor. One advantage of such a design is that by assembling asymmetric and hybrid ECs, the cell voltage of the device can be increased.

EDLCs typically consist of various carbonaceous materials of very large surface area, such as carbon nanotubes (CNTs), activated carbon and graphite-based materials, where the capacitance arises from the charge separation at the electrode/electrolyte interfaces, thus storing/delivering charge by an electrostatic process (Li and Wei, 2013; Simon and Gogotsi, 2008; Wang et al., 2016b). Carbon is attractive due to its abundance, non-toxicity, high chemical stability, good electronic conductivity, and high specific surface area. An EDLC composed of carbon-based materials generally exhibit excellent cycling stability, fast kinetics and high power density due to the rapid sorption and desorption of ions and enormous charge capacity, although the specific capacitance (and energy density) is rather low. To make a good EC, a carbon material should have high specific surface area with good electrolyte accessibility to the pores, and much of the recent development in the area focuses on optimizing the porous structure and controlling the morphology of the material (Li and Wei, 2013). Another way to improve the capacitive properties is to introduce surface functionalization, typically nitrogen, boron, phosphorus, and sulfur (Chen et al., 2012; Paraknowitsch and Thomas, 2013; Wang et al., 2008). These can improve the material by introducing redox reactions, provide electron donor/acceptor, and improve wettability. The addition of conductive polymers and transition metal oxides with pseudo-capacitance within the carbon material can also enhance the overall capacitance of the electrode materials (Wang et al., 2016b).

Pseudo-capacitance arises from rapid reversible faradaic reactions occurring at or near solid electrode surfaces (reversible adsorption, redox reactions, and reversible electrochemical doping–dedoping), which typically contain transition metal oxides, nitrides and polymers, possessing a much higher specific capacitance than carbon materials

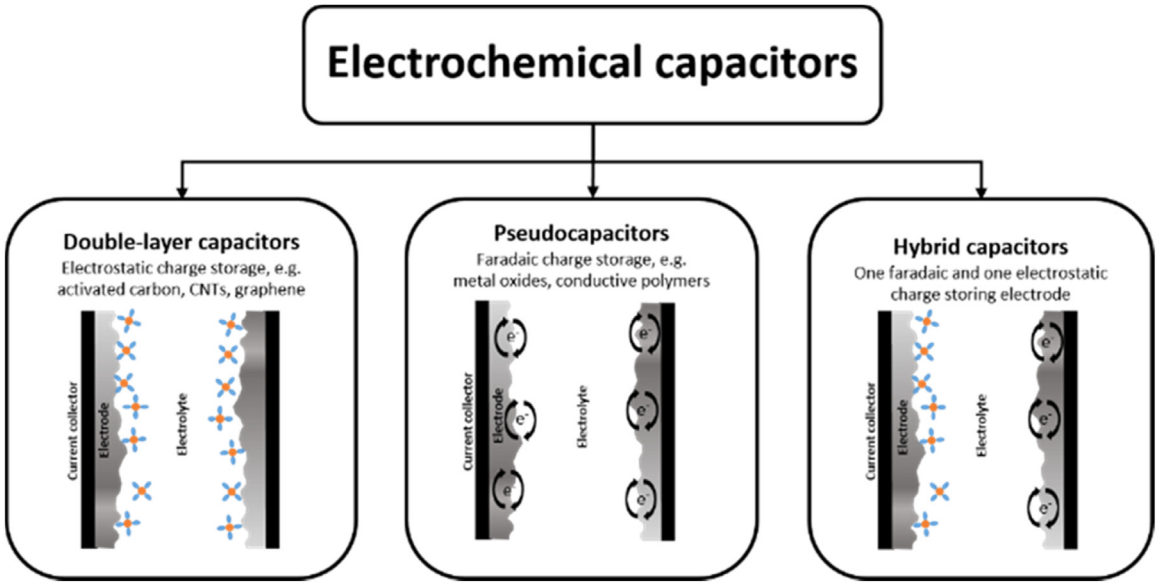

Fig. 3. Schematic of the main charge storing mechanism of ECs, based on EDLC (left), faradaic reactions (middle), or a mixture (right).

with a relatively high surface area and comparatively high energy density (Conway and Pell, 2003). The charge storing in pseudocapacitors is similar to batteries, with the major difference that batteries are limited by ion diffusion within the active material, whereas pseudocapacitos are not controlled by diffusion processes. Pseudocapacitive electrodes generally display a linear dependence of the charge stored with the charging potential within the window of interest, originating from electron-transfer mechanisms instead of solely relying on the accumulation of ions as in an EDLC. Transition metal oxides (e.g. RuO_2, MnO2, IrO_2, V_2O_5, SnO_2) have a high specific capacitance and energy density and can promote efficient redox reactions, however, generally confer a high cost (Wang et al., 2012). Conducting polymers, such as poly(pyrrole) (PPy), poly(3,4ethylenedioxythiophene) (PEDOT) and poly(aniline) (PANI), offer capacitive behavior through redox reactions that occur at the surface and throughout the bulk polymer. They have good intrinsic conductivity, adjustable redox activity through chemical modification, and they are particularly attractive due to their low cost compared to more expensive metal oxides, providing a lightweight and flexible material (Bryan et al., 2016; Huang et al., 2016; Sun et al., 2015; Wang et al., 2016a). A downside with using conducting polymers is that swelling and shrinking may occur during intercalation and deintercalation, leading to possible structural deterioration at the molecular or nano-scale, which reduces cycling stability (Bryan et al., 2016; Wang et al., 2016a). Conductive polymers and metal oxides are often composited with different carbon structures to improve the cycling stability and capacitive properties, significantly enhancing the charge storing capability owing to improved ion diffusion rates and increased surface contact area (Snook et al., 2011; Zhi et al., 2013). Moreover, the capacitive properties of redox polymers, where a transition metal is coupled to a polymer backbone, have been utilized in electrochemical capacitors (Knoche et al., 2016; Pankratov et al., 2016; Yu et al., 2012). Furthermore, biofilms of different bacteria and specifically bound virus particles have been investigated for their capacitive properties (Ieropoulos et al., 2005; Lee et al., 2009; Malvankar et al., 2012).

Apart from the electrode material itself, the electrolyte is of great importance due to the ionic conductivity and charge compensation on both electrodes of the cell (Zhong et al., 2015). The temperature coefficient and the conductivity chiefly determine the ESR of a supercapacitor, and the ionic concentration of the electrolyte should match the needs of the electrical double layer and the faradaic reactions. Aqueous electrolytes offer higher ionic concentration, lower resistance and much higher ionic conductivity than organic electrolytes, but suffer from a much lower potential window. For a hybrid device, it is important that the electrolyte is compatible with the energy harvester and the intended application (e.g. implanted or flexible/foldable device).

At present, the development of ECs has mostly been separated from energy harvesters. However, many different energy harvesters incorporate different polymers or carbon structures, and several examples have now recently been demonstrated where the support material takes on the function of both energy harvesting and energy storing (vide infra). With the recent interest in developing flexible, stretchable, transparent and miniature electronic devices, research efforts have been directed towards designing nanocarbon-based and supercapacitors based on flexible, micro-, stretchable, compressible, and transparent electrode materials(Bandodkar and Wang, 2016; Guo et al., 2016; Hu et al., 2016; Liu et al., 2016; Pu et al., 2016; Pu et al., 2015; Zhong et al., 2014). CNTs can be assembled in arrays, sponges and fibres, and when arranged so that electrolyte can diffuse in the structure, make superior EC (Pint et al., 2011; Zhong et al., 2013). Freestanding CNT and carbon micro-fiber films often have a porous structure, high conductivity and excellent tensile strength, and can be supported on flexible substrates such as CF paper and cloth (Hu et al., 2009; Zhang et al., 2015). Graphene can by the addition of spacer molecules be arranged to a flexible and porous structure with good ion penetration, suitable for EC, and combined with various supports to create flexible and foldable ECs (El-Kady et al., 2016; Kim et al., 2013). Flexible materials can also be designed by combining CNTs with different conducting polymers (Peng et al., 2008). Liquid electrolytes may be used to design such flexible capacitors, with a potential problem of sealing the device, but solid and gel electrolytes may also be employed (Liu et al., 2016). These types of materials are very useful in the design of hybrid devices, which can be incorporated in the design of a wide range of energy harvesters, taking advantage of easily processable and flexible carbon based materials and polymers to create dual functioning electrodes of superior performance. The choice of supercapacitor parameters, such as resistance, capacitance, and leakage current, is of course crucial to successful operation of the hybrid system, and should be optimized for the intended energy harvester.

2. Hybrid energy harvesting/charge storing devices

A detailed specification of each type of energy harvester used in hybrids is not within the scope of this review, instead our focus is to highlight examples of how these widely different harvesting techniques can be combined with materials for charge storing, in turn detailing examples of chemical, solar, mechanical and thermal hybrids. In addition to pure hybrid devices, we also highlight some examples of different integrated devices e.g. based on layered structures or three-electrode systems.

2.1. Chemical energy harvester hybrids

FCs are commonly combined with external charge storing components, e.g. Li-ion batteries, improving their performance (Conway and Pell, 2003; Jarvis et al., 1999; Khaligh and Li, 2010). ECs have also been combined with FCs, allowing for easier implementation and the potential to increase the efficiency (Morin et al., 2014). However, up until the last few years, no devices had taken advantage of double-feature electrodes to design hybrid devices.

Shleev et al. recently reported on a hybrid fuel cell device based on double-feature electrodes, using ascorbate as fuel (Pankratov et al., 2014c). A schematic representation of the device and operation of the FC is shown in Fig. 4. Ascorbate was oxidized at a PANI/CNT modified electrode, with the concomitant reduction of oxygen at a platinum nanoparticle/PPy/CNT modified electrode. The charge generated from the FC was stored in the capacitive conductive polymer/CNT composite, operating as an EC. While the power generated from the FC by itself was very modest, generating just a few $\mu W\,cm^{-2}$, by letting it charge the EC and operating the device in pulsed mode, the power output could be increased by over two orders of magnitude. The device was not optimized, e.g. employing p-type polymers for the charge storing of both the positive and negative electrode. Moreover, the cycling stability was not investigated, with a charging time of over 1 h. However, the hybrid device illustrates the huge potential in combining a low-power FC with an EC, where utilization of dual-functioning electrodes can greatly enhance the usefulness of the device as a power supply.

Apart from regular FCs, a good example of the benefit that can be attained by designing dual functioning electrodes is seen when combining EC with BFCs. BFCs are a special type of FCs, which employ biological catalysts instead of more conventional non-biogenous catalysts. The biocatalyst can be a microorganism, as in microbial FCs, which use whole living cells to extract power from different fuels and oxidants, or an enzyme, as in enzymatic FCs, which instead employ isolated redox enzymes directly (Bullen et al., 2006; Calabrese Barton et al., 2004). One drawback of BFCs is that they normally suffer from poor stability due to the limited lifetime of the catalyst and an inability to fully oxidize fuels. However, the stability can be improved by e.g. immobilizing the enzyme in a suitable matrix and fuel efficiency can be increased by co-immobilizing several biocatalysts (Zhu et al., 2014; Falk et al., 2014). Another problem for the practical application of BFCs is that the power output tends to be quite low, ranging from a few

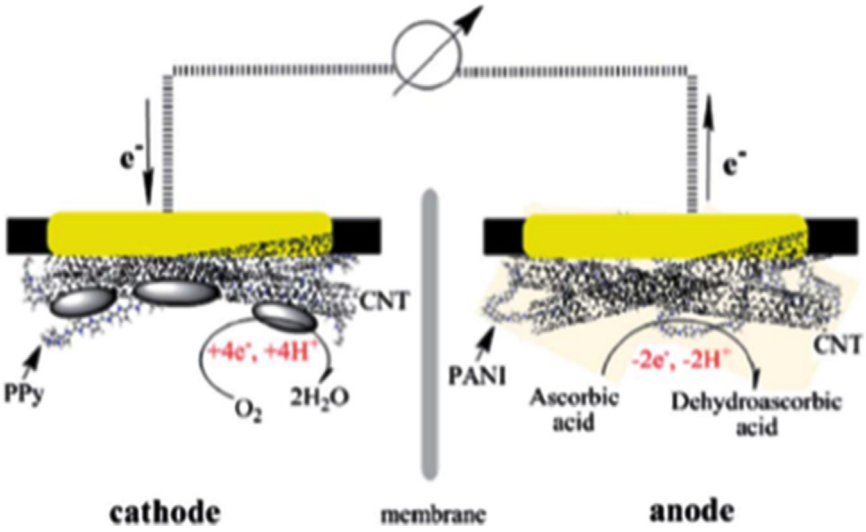

Fig. 4. Illustration of a membrane-based hybrid FC/EC, combining an ascorbate/oxygen FC with an EC. Reprinted with permission from Pankratov et al. (2014b).

μW cm^{-2} up to a maximum of a few mW cm^{-2}, depending on the fuel and circumstances it is being operated. This is several orders of magnitude lower power output compared with conventional FCs using high-energy fuels, which severely limits the implementation of BFCs as power source (Calabrese Barton et al., 2004; Logan and Rabaey, 2012). Several niche applications can still be envisaged, such as e.g. power sources for wearable or implantable low-power miniature systems harvesting energy from fuel available at the site of operation (Bandodkar and Wang, 2016; Calabrese Barton et al., 2004). The low power output of BFCs makes incorporation with ECs highly beneficial for the device performance. Indeed, there are many examples of separate capacitors being combined with BFCs in the literature (Dewan et al., 2009; Hanashi et al., 2014; Hanashi et al., 2009; Skunik-Nuckowska et al., 2014; Wang et al., 2015a). However, by directly hybridizing a BFC with an EC, the device performance can be significantly enhanced (Deeke et al., 2012). Hybridization also has the advantage of allowing miniaturization and simplification of the design compared with coupling to an external EC. Moreover, the charging times could be adapted to the generally low current provided by the BFC (Soavi et al., 2016). Furthermore, many BFCs employ different carbonaceous materiel, taking advantage of the large surface area and good electrical properties to increase catalyst load and thus performance of the energy harvester, where the support also can function as an excellent EC. As the voltage output of a single BFC generally is well below 1 V, voltage amplifiers would be incorporated to charge external commercial energy storage components. Using a hybrid BFC is thus a more efficient, simple and cheap way of harvesting energy, which mitigates the need of additional electronics management, and operating the device in a pulsed mode can significantly enhance the power output of the device. However, it is only until quite recently hybrid BFC/charge storing deices have been discovered (Pankratov et al., 2014b), or, better to say, disclosed (Pankratov et al., 2014a).

One of the earliest instances of a BFC using a dual-functioning electrode was reported by Deeke et al. (2012), who integrated a capacitive component of activated carbon and polymer within the bioanode of a microbial FC. The authors used charging pulses of 5 min and discharging pulses of 20 min, where from the discharge charge could be attributed to the stored charge in the capacitive anode and the continuously generated charge by the anode, as illustrated in Fig. 5. This concept was later further expanded on by the same authors (Deeke et al., 2015; Deeke et al., 2013). Lv et al. (2012) instead incorporated RuO_2 layer in the anode design and could in this way considerable increase the performance compared with an unmodified anode. The group of Atanassov utilized the inherent capacitive features of microbial FC electrodes and added an additional third EC electrode coupled with the cathode in a single chamber membrane-less design to create a self-charging device able to harvest energy from wastewater (Santoro et al., 2016). The device was capable of generating peak power of 8.4 mW cm^{-2}, which is the highest performance achieved by a microbial FC system. The same group also illustrated that by optimizing size and design of the system components, the volumetric power output could be increased manifold (Houghton et al., 2016).

Pankratov et al. were the first to report on a complete hybrid BFC/EC, where both electrodes consisted of double-feature electrodes (Pankratov et al., 2014b). The hybrid device is illustrated in Fig. 6a. The BFC part was based on gold nanoparticles modified electrodes using cellobiose dehydrogenase (CDH, an enzyme capable of oxidizing different sugars) on the anodic side, and bilirubin oxidase (BOx, a multicopper oxidase, which is able to reduce molecular oxygen) on the cathodic side. The opposite side of the electrode functioned as ECs, being modified with supercapacitive PANI/CNT composite. The device was capable of delivering a power of 1.2 mW cm^{-2} when operated in a pulsed mode, which was over 2 orders of magnitude greater than using the just enzymatic FC alone in a continuous mode. The capacitor was fully charged within 2 h, reaching a cell voltage of 0.4 V. The device performance could foreseeably be improved e.g. by not using a symmetric EC based on a p-doped polymer and adapting the capacitor to the BFC output, but clearly demonstrated the huge potential in designing a hybrid enzymatic FC/EC for otherwise low-power output systems. The self-charging mediator free concept was also employed to design flexible and transparent devices using different glucose-oxidizing enzymes on ITO-nanoparticle modified electrodes, with the potential application as power sources for electronic contact lenses (Bobrowski et al., 2018; González-Arribas et al., 2017b).

The device described by Pankratov et al. did not use the same electrode material both as a main capacitive component, as well as a support for immobilization of biocatalysts layer for the FC. This approach have however been employed in several of the recently reported hybrid BFCs. Agnes et al. (2014) demonstrated a hybrid device using CNTs, taking advantage of both the suitability of CNTs as an immobilization matrix for enzymes as well as the short charging time and high capacitance of the material functioning as an EC. The device constituted compressed pellets of MWCNTs combined with either glucose oxidase (GOx) or laccase (Lc), as shown in Fig. 6b. The electrodes were soaked in sugar and oxygen-containing fuel for 3 days to reach an equilibrium concentration throughout the porous CNT matrix and obtain complete charging of the capacitance. The mobility through and inaccessibility of the pours structure, reducing the specific surface area,

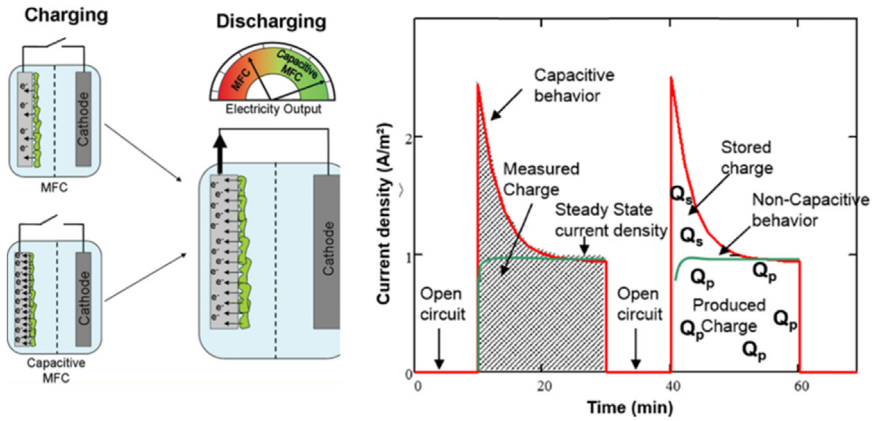

Fig. 5. Scheme of charging/discharging and theoretical discharge graph of a capacitive anode of a microbial FC, with charge originating from the stored capacitive part (peak) and the produced charge by the anode from the steady-state operation. Reprinted with permission from Deeke et al. (2012).

was not further investigated. The open circuit potential reached roughly 800 mV and the device was able to deliver around 20 mW cm^{-3} in pulsed mode, the highest power output of any reported enzymatic FC. The device could deliver power pulses of 2 mW for 10 ms every 10 s, at least for 5 days, representing 40,000 charge–discharge cycles.

Kizling et al. reported on a conducting polymer hybrid, where a PPy-modified cellulose was used as a matrix for fructose dehydrogenase (FDH) enzyme, and the large effective surface area functioned both as a catalyst layer and as a supercapacitor. The anode was combined with a carbon paper/CNT/Lc based cathode and used in a flow BFC/EC hybrid (Kizling et al., 2015a, 2015b). A paper-based supercapacitive glucose/air enzymatic FC assembled into a capillary driven microfluidic system was described by Narvaez Villarrubia et al. (2016). The cathode, made of a catalytic layer of BOx on buckypaper, was modified with teflonized carbon black as hydrophobic gas diffusion layer to promote the flow of oxygen to the catalytic sites. The anode, made of NAD-dependent glucose dehydrogenase (GDH) mediated by methylene green immobilized in a CNT/chitosan matrix, was supplied with glucose by the capillary flow. The device took advantage of the capacitive properties of the bioelectrodes, where the power output was maximally improved by over an order of magnitude when the device was operated in a pulsed mode. However, the overall cell capacitance was limited by the rather low capacitance of the cathode. The power output of different pulses and different current and pulse times of the hybrid device, together with a Ragone plot showing values of Epulse and Ppulse for complete discharges at different currents is shown in Fig. 7.

Instead of using conductive polymers or carbonaceous materials as capacitive components, a higher specific capacitance can be achieved by using redox polymers. Redox polymers can also function as efficient mediators in BFCs (Gallaway and Calabrese Barton, 2008; Rinaldi et al., 2008). Knoche et al. reported on a hybrid device based on redox polymers used in this manner, improving the capacitive performance of the device. The glucose/oxygen hybrid BFC/EC constituted FAD-GDH and CNTs immobilized within a dimethyl-ferrocene modified linear poly(ethylenimine) redox polymer on carbon felt, combined with a cathode of BOx immobilized with MWCNTs (Knoche et al., 2016). The hybrid device had a high specific capacitance of 300 ± 100 F g^{-1}, with an OCP of 0.6 ± 0.2 V and reached a maximum power of 10 ± 2 mW cm^{-3} when operated in pulsed mode. Pankratov et al. (2016) recently showed another glucose/oxygen BFC/EC hybrid device based on redox polymer, where the EC part was based on symmetric electrodes employing an osmium redox polymer, aptly named “Nernstian biosupercapacitor. Like the other hybrid BFCs the device generated electricity by oxidizing glucose with concomitant reduction of O2 utilizing biocatalysts, while the charge generated was stored in the symmetric capacitive parts of the electrodes with the OCV at the end of the charging process being defined by the Nernst equation (hence the name). The charged device had a cell voltage of around 0.4 V, and by taking advantage of the capacitive properties of the redox polymer the steady state power could be enhanced by roughly an order of magnitude. Similarly, Xiao et al. (2017b) recently reported on a hybrid BFC where FAD-GDH and BOx were immobilization with electrodeposited PEDOT and an osmium bipyridine redox polymer on de-alloyed nanoporous gold. By operating the device in a pulsed mode the meagre output of the original BFC of around 1 μW cm^{-2} was increased over 4 hundred-fold. The author also developed an oxygen-independent version of the previously reported BFC, where the enzyme-based cathode was exchanged to a solid-state nanoporous gold-manganese dioxide cathode, with a similar performance as the BFC (Xiao et al., 2017a). In this way oxygen limitation, in particular for implanted devices, could

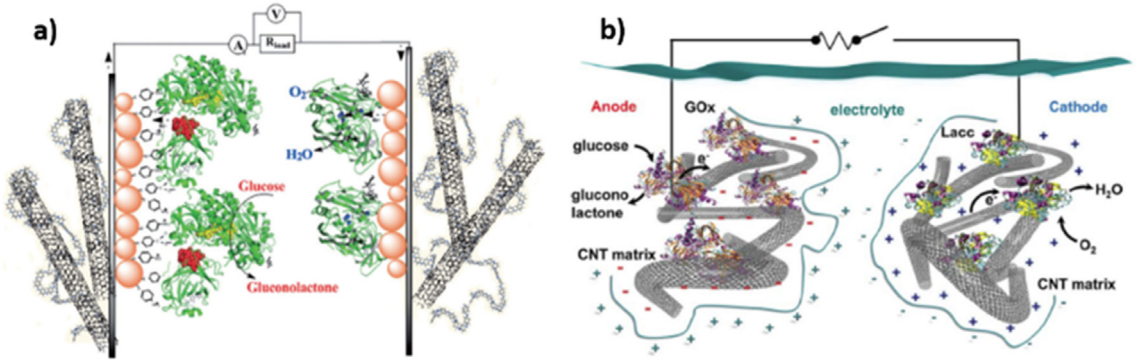

Fig. 6. Schematic representations of a self-charging glucose/oxygen hybrid enzymatic FC/EC devices. a) EC made of PANI/CNTs composite combined with CDH/BOx modified AuNPs. b) EC/FC composed of CNT/enzyme matrix. Reprinted with permission from Pankratov et al. (2014b) (a) and Agnes et al. (2014) (b).

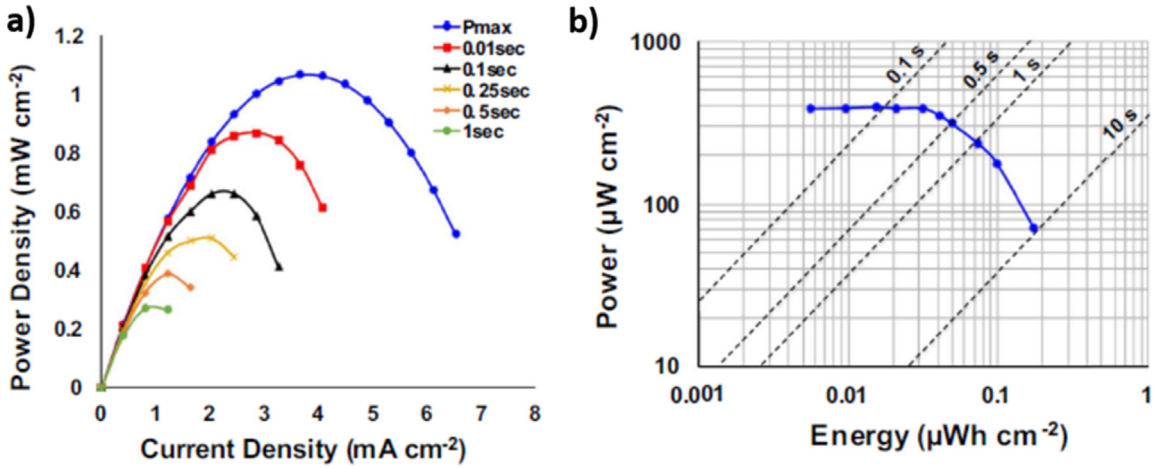

Fig. 7. a) Power curves at different current pulses and b) Ragone plot hybrid BFC/EC. Reprinted with permission from Narvaez Villarrubia et al. (2016).

be avoided.

2.2. Solar energy harvester hybrids

The concept of a "photocapacitor" was proposed about ten years ago and now a variety of different photo-batteries and photo-supercapacitors have been developed (Jones, 2016; Miyasaka and Murakami, 2004). Due to the low efficiencies of the solar cell parts (mainly traditional DSSC and organic hybrid solar cells) and the low capacity of the storage part, these tandem devices still exhibit much lower performance than employing independent power packs. Much recent effort has been devoted towards integrating the energy conversion and storage devices into hybrid units for highly-efficient, light-weight and portable devices (Kim et al., 2015a; Pan et al., 2016, 2014; Wen et al., 2016).

A DSSC is a photoelectrochemical device in which dye sensitizers generate electrons upon light absorption between a dye-adhered metal oxide surface compartment and hole-conducting electrolyte. DSSCs have the prospect of cheap large-scale production but still suffer rather low power conversion efficiencies (8–13%). Several integrated photo-supercapacitor devices based on DSSC have been reported recently, however mostly comprising three-electrode devices with a DSSC photoanode, a shared counter electrode and a current collector of the supercapacitor in conjunction with two electrolytes (Ng et al., 2015). An external circuit, such as a diode switch, is required to connect the solar cell to the capacitor during energy harvesting cycle and prevent the capacitor discharge through the DSSC. The first example of an "energy-storable dye sensitized solar cell" was introduced in 2004 by Nagai and Segawa, using a PPy electrode together with a dye sensitized electrode (Nagai and Segawa, 2004). The electrode configuration is shown in Fig. 8a, comprising one compartment part of the DSSC and another compartment part of the charge–storage electrode. The device exhibited an energy density less than 0.3 mW h cm^{-2} and self-discharge time of less than 10 min, with a rather low energy storage efficiency of 22%. A variety of different such systems have thereafter been reported. Xu et al. (2014) presented stack-integrated photo-supercapacitor using a three-electrode sandwich structure, composed of a DSSC and an EC built on bi-polar anodic titanium oxide nanotube arrays delivering an overall photoelectric conversion and storage efficiency up to 1.64%, with a maximum energy storage efficiency of 51.60%. Cohn et al. utilized a three-electrode architecture of integrated, solid-state DSSC-supercapacitor system using an individual silicon wafer, produced using conventional semiconductor manufacturing processes, as a multi-functional energy storage and conversion unit. The silicon wafer simultaneously performed the charge transfer role of a DSSC as well as the double-layer charge storage role of an EC, yielding a total device efficiency of 2.1% (Cohn et al., 2015).

Instead of using a supercapacitor as the charge storing part, Guo et al. developed a power pack with a series-wound DSSC and a lithium ion battery on the same Ti foil with double-sided TiO_2 nanotube arrays. The device design and charging mechanism is shown in Fig. 8b. The upper part is the DSSC, with the nanotube array collecting electrons generated upon irradiation. The bottom parts constitute the Li ion battery, where Li ions are inserted in the nanotube array anode, storing the charge. Three solar cells were used tandem to provide enough voltage to charge the battery, which was charged to about 3 V in roughly 8 min with a discharge capacity is about 38.89 μA h under the discharge density of 100 μA and a total energy conversion and storage efficiency of 0.82% (Guo et al., 2012). Another example of a DSSC-battery hybrid was developed by Yu et al. (2014), which used triiodide/iodide redox shuttle to couple a dye-sensitized titanium dioxide photoelectrode with the oxygen electrode for the photo assisted charging of a lithium–oxygen battery.

While using a three-electrode system reduces internal resistive losses it still involves two energy conversion steps, limiting the level of integration. Further integration can be achieved by employing active parts shared between the energy conversion and charge storage, realizing both energy harvesting and storage in one device with the same material and structure. Sun et al. (2014) recently reported on such a dual-functioning DSCC-EC hybrid device, using wire-shaped titanium modified with titanium dioxide nanotubes and wound with a MWCNT/PANI-fiber with incorporation of a redox electrolyte containing an I^{3-}/I^{-} redox ion couple. The device and mechanism of operation is shown in Fig. 9. Briefly, photoelectrons are generated under illumination and injected into the conduction band of titanium dioxide, I^{3-} is reduced to I^{-} catalyzed at the CNT and I^{-} then regenerate the dye. The same device can also function as an electric double-layer capacitor to store electrical energy, where the CNT fiber adopts the dual role of catalyzing the reaction in the DSSC and storing charges as an EC. The device exhibited an energy conversion efficiency of 6.58% and a specific capacitance of 2.13 mF cm^{-2}. Such a wire-shaped device show promise as e.g. a flexible energy textile. The same group also reported on a fiber device using a similar concept, but based on eutectic melts for the photoconversion to provide higher thermal and mechanical stability (Chen et al., 2014).

Another example of a solar dual-functioning hybrid device was presented by Takshi et al. (2015) The researchers employed a composite film of PEDOT-PSS with a dye deposited on an indium tin oxide electrode combined with a porous activated carbon electrode and methyl viologen electrolyte. The composite film functioned both as photoactive electrodes and charge storage.

While DSSCs allows for integration with charge storing units, the efficiency of the DSSC is quite low. Organic-inorganic metal halide PSC,

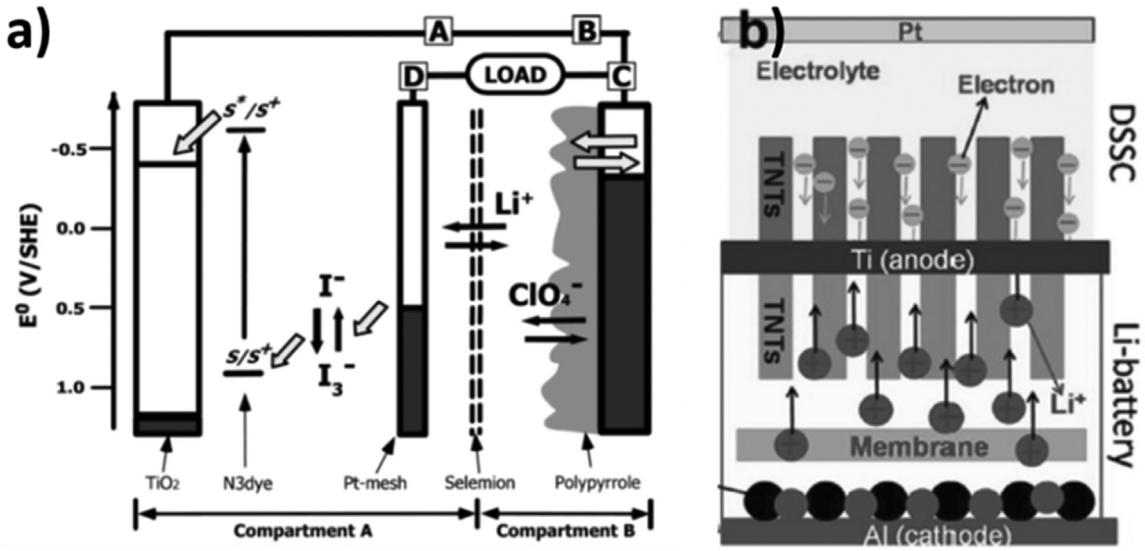

Fig. 8. a) Outline of the mechanism of a three-electrode energy-storable DSSC, where white arrows represent electron transfer and black arrows represents ion diffusion. b) Working principle of DSSC (top) integrated with a Li-ion battery (bottom). Reprinted with permission from Nagai and Segawa (2004) (a) and Guo et al. (2012) (b).

employing a perovskite structured compound as the light-harvesting active layer, could potentially be a good substitute for DSSCs due to low-processing-cost materials and high efficiencies (Chen et al., 2015b; Collavini et al., 2015). The fundamental technology for PSC is solid-state sensitized solar cells, with efficiencies attainable over 20%, but liquid-based PSCs receives little attention due to stability issues from dissolution of the perovskite (Park, 2015). This also limits the ease with which cells can be hybridized. However, a one-year stable PSC was recently reported (Grancini et al., 2017), moreover, there are also few recent examples where PSCs have been integrated with lithium-ion batteries and ECs to design self-chargeable units. Du et al. (2015) combined a flexible self-stacked solvated graphene supercapacitor with a PSC, suggesting its use in the applications of storing solar energy and flexible electronics, such as portable and wearable personal devices. Xu et al. showed a powerpack of integrated organometallic PSC with a polypyrrole-based supercapacitor, whereas Xu et al. demonstrated the integration of PSC with lithium ion batteries (Xu et al., 2015a, 2015b). However, these devices were not hybrids but integrated separate charge storing and energy harvesting entities. A single unit device was recently reported by Zhou et al. (2016), describing a self-powered photovoltachromic supercapacitor, created by stacking a PSC with a MoO3/Au/MoO3 transparent electrode and electrochromic supercapacitor in a layered structure. Such a design e.g. have a great potential as self-powered smart windows. In this way, the transmittance could be tuned while at the same time storing the harvested energy by the solar cell. This configuration allowed for both a wide range for tunable transmittance and seamless integration of energy conversion and storage. A printable PSC with a supercapacitor integrated through a common PEDOT-carbon bridge was recently reported by Xu et al. (2016). The device design is illustrated in Fig. 9d, where FTO glass was screen printed with TiO2 and ZrO2 and electrodeposited with anion-doped PEDOT. Perovskite was then filled in the porous structure and combined with a PEDOT-carbon counter electrode, using stabilizer-containing isopropanol as electrolyte to protect the perovskite. The photogenerated electrons and holes from the excited perovskite are transferred to and electrochemically stored in the PEDOT EC, and under visible light illumination the capacitor could be charged to 0.70 V in 7 s. The hybrid device had a maximum overall efficiency of 4.70% with a high energy storage efficiency of 73.77%.

A general problem with the so far reported integrated/hybrid devices is the low overall efficiency, often just a few percent. This can be attributed to the typically relatively low efficiency of the solar energy capturing part, in combination with energy losses incurred upon energy storage due to resistance losses and low integration level, leaving plenty of room for improvement. In a recent report by Liang et al. (2018), the authors presented a layered device with perovskite integrated with

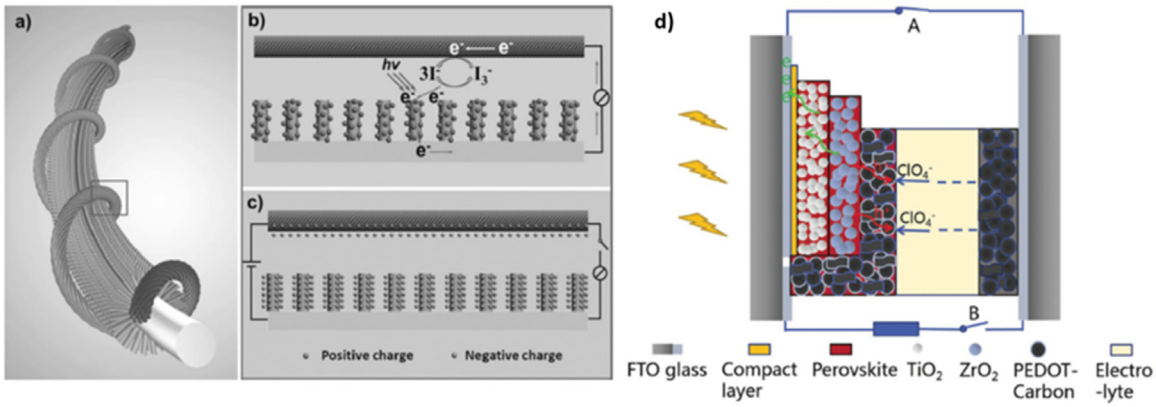

Fig. 9. (a) Structure of wire-shaped solar hybrid (b) along with the working mechanism as DSSC (c) and EC. (d) Schematic and mechanism of PSC integrated with an EC. Reprinted with permission from Sun et al. (2014) (a–c) and Collavini et al. (2015) (d).

nanocarbon-based supercapacitor. The device showed an overall energy efficiency with a maximum of 7.1%. Liu et al. (2017) able to reach a total efficiency of over 10%, where the authors combined a silicon nanowire/PEDOT:PSS solar cell with a polypyrrol supercapacitor, where the layered integrated device reached a total energy conversion efficiency of 10.5%.

Apart from more traditional photovoltaic cells, significant research effort has been devoted towards developing bio-solar cells. Bio-solar cells are based on the photosynthesis in plants, algae and microorganisms, where solar energy is used to convert carbon dioxide and water into oxygen and carbohydrates. Electrodes have been designed that employ electrochemically active bacteria or algae, as well as using isolated chloroplasts, thylakoids and individual photosystems, integrating photosynthetic and electrochemically active organisms to generate in situ green electricity or fuel, such as e.g. hydrogen (Ciesielski et al., 2008; Kirchhofer et al., 2015; Pinhassi et al., 2016; Strik et al., 2011; Wei et al., 2016). The bio-solar cells reported so far are comparatively low-energy producing devices with a low efficiency, where the power density and biocatalyst stability require large improvements before the technology can be considered for practical application, with estimates of reaching around 3% efficiency (McCormick et al., 2015). Quite similar to BFCs, but using solar radiation instead of fuel to generate electrical energy, integrated hybrid devices can be created by incorporating supercapacitive elements with charge-generating elements of photosensitive cells and organelles, somewhat mitigating the low power-output of the device.

Little attention has been focused on proteins instinctive capacitor-like behaviors and the capacitor-like behavior of the plasma membrane. Nevertheless, Rao et al. (2014) designed a light-powered biocapacitor system integrated with a photo-induced proton-pump protein proteorhodopsin (pR) and a modified alumina nanochannel. After exposure to light and the pR proton-pump had been charged, the nanochannel resistance worked against the transmembrane ion current with dynamic potential, and promoted capacitor discharging. A first hybrid biosolar device was recently reported by the research group of Shleev, combining nanostructured indium tin oxide as charge-storing electrodes with biological catalysts generating electricity from light to create a self-charging solar hybrid device (González-Arribas et al., 2017a). As shown in Fig. 10, by modifying one electrode with thylakoid membranes and the other with BOx, an enzyme capable of oxidizing oxygen to water, electrical energy was generated upon illumination, without the use of any additional mediators, and stored in the capacitive electrodes modified with indium tin oxide nanoparticles. While the performance of the solar energy harvester was quite poor, with a power output of around 50 $\mu W\,m^{-2}$ and a low stability, with a specific capacitance of the electrodes were around 0.2 $mF\,cm^{-2}$, by operating the device in a pulsed mode roughly a hundred-fold increase in power output was obtained (in a similar fashion to several of the previously described chemical energy harvesters). Another self-charging bio-solar cell was also reported very recently, employing thylakoid membranes together with osmium polymer to harvest the solar energy and gold nanoparticles modified electrodes as a separate current collector and EC to store the generated charge (Pankratova et al., 2017). Similar to the previously reported solar biosupercapacitor, the power output of the device was just a few microwatts per cm^{-2}, but through combination with the supercapacitive nanoparticle-modified surface, a five-fold increase in the power output during pulse operation was possible.

2.3. Mechanical energy harvesters hybrids

A significant research effort has been devoted into the development of self-powered devices using mechanical energy harvesters, with a lot of work performed especially by the research group Zhong Lin Wang, who were the first to report on the idea of using a nanogenerator energy harvester based on nanowire arrays (Wang and Song, 2006). Since then there have been many reports on triboelectric and piezoelectric nanogenerators, which also have been summarized in several recent reviews (Fan et al., 2016; Kang et al., 2016; Park et al., 2016; Wang and Wu, 2012; Zheng et al., 2017). These energy harvesters can be designed using flexible materials for e.g. wearable electronics, implantable electronics and self-powered sensors, with a peak power output of up to 500 $W\,m^{-2}$ for some of the recently reported devices (Fan et al., 2016; Guo et al., 2016; Hu et al., 2016; Hwang et al., 2015; Luo et al., 2015; Pu et al., 2016; Pu et al., 2015; Song et al., 2015; Zhong et al., 2014). In addition as a power source for low-power applications, networks of triboelectric energy harvesters have also been proposed for large-scale power applications, harvesting energy form the movement of the ocean (Chen et al., 2015a; Wang, 2014).

Due to the nature of how the electricity is generated, where vibrations cause a repeatedly applied strain/release or contact with a variable frequency and irregular amplitude of a pulsed AC output, vibrational energy harvesters cannot be directly used to drive electronic devices in most situations. Typically, a power conditioning unit is combined with the vibrational energy harvester, where the output AC current is converted to DC current by employing a rectifier circuit. The energy harvester can then be combined with an energy storing unit. The intermittent nature of operation of mechanical energy harvesters makes integrating capacitors or batteries very beneficial. Indeed, many

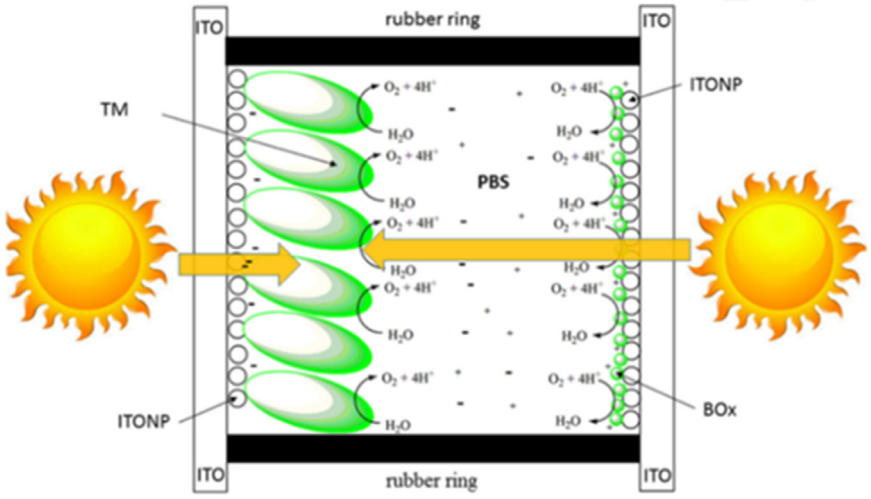

Fig. 10. Schematic of the first reported bio-solar/EC hybrid, based on thylakoid membranes to harvest the solar radiation and nanoparticles-modified surface to store the charge. Reprinted with permission from González-Arribas et al. (2017a).

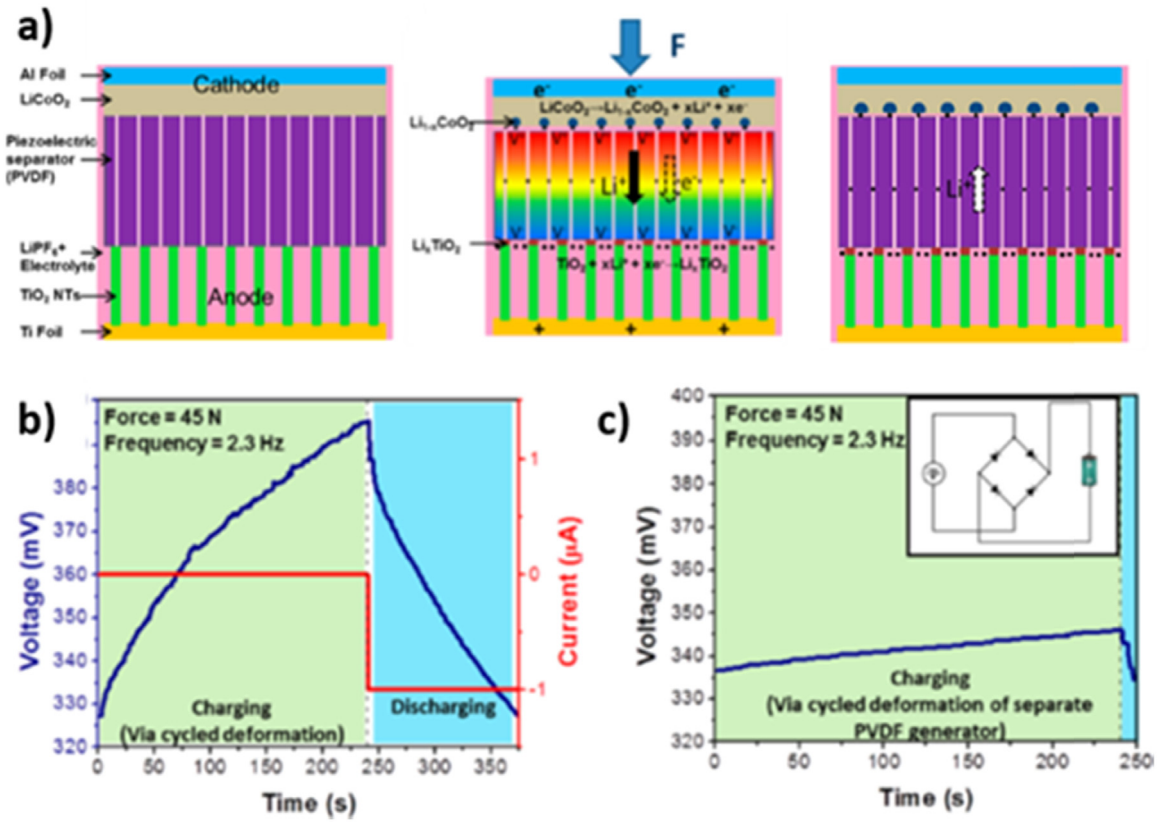

Fig. 11. a) Schematic of the charging of a piezoelectric/Li-ion battery hybrid. b) Self-charging and discharging of the hybrid device and c) a separate piezoelectric energy harvester and Li-ion battery. Reprinted with permission from Xue et al. (2012).

different reports have shown incorporating separate energy harvester and energy storage, with even combined solar-vibrational energy harvesters with supercapacitors being designed (Dong et al., 2017; Jiang et al., 2018; Li et al., 2018; Luo et al., 2015; Pu et al., 2015; Shi et al., 2016; Wen et al., 2016; Zi et al., 2016).

Instead of using two combined but physically separated units, a few reports have recently described hybrid mechanical energy harvester/energy storage devices. Being able to omit the use of a rectifier between the vibrational harvester and the energy storage device enables a higher integration density and reduces unnecessary energy losses (Wang, 2017) The first such mechanical-energy storing hybrid was reported by Xue et al. (2012). The group presented a self-charging Li-ion battery by integrating a piezoelectric separator of poly(vinylidene fluoride) (PVDF) instead of the usual polyethylene separator, letting the piezoelectric potential from the separator drive the diffusion of Li ions, with a LiCoO2 cathode, TiO2 nanotube anode and LiPF6 electrolyte. The device was then packed in a coin cell. A schematic illustration of the mode of operation is shown in Fig. 11a, where a piezopotential is created when a compressive stress is applied onto the cell, with the positive polarity at the cathode side and negative piezopotential at the anode, driving Li ions from the cathode to the anode and charging the device. Charging ceases when chemical equilibrium is re-established and when the applied force is released the piezoelectric field disappears, breaking the electrostatic equilibrium and allowing a portion of the Li ions to diffuse back to the cathode. The system then reaches a new equilibrium and a cycle of self-charging is completed. The performance of the hybrid device was compared with using a separate battery and piezo generator with a rectifier, yielding a much higher efficiency in the integrated system (Fig. 11b and c). The overall efficiency was rather low however, mainly attributed to the rigid coin cell absorbing most of the mechanical energy with low flexibility and poor straining of the piezoelectric material. The performance could be improved by employing a flexible device design allowing for larger deformation and separately by employing a highly porous PVDF membrane to optimize the piezoelectric separator (Kim et al., 2015b; Xing et al., 2014; Xue et al., 2014).

Instead of integrating the mechanical energy harvester with a battery, an EC can be integrated within the device. The research group of Wang also reported on a flexible, light-weight self-charging piezo/EC hybrid device, using MnO2 nanowires as positive and negative electrodes of a supercapacitor with a PVDF-ZnO film as piezoelectric separator (Ramadoss et al., 2015). A schematic of the device is illustrated in Fig. 12, along with data showing the self-charging process under continuous palm impact. The operation of the device as a self-powered system was elegantly demonstrated by letting the piezo-supercapacitor hybrid power an LED upon tapping the device with the palm. Another flexible piezo-supercapacitor hybrid was recently reported by Song et al. (2015). A PVDF film was used as piezoelectric energy harvester, which was coated with a gel electrolyte of polyvinyl alcohol/sulphuric acid and sandwiched between anodically pretreated carbon cloth electrodes. While a reversed piezoelectric filed is created when the compressive force is removed, the magnitude is much smaller than that during compression, and successful charging of piezo hybrid devices could be realized.

Very recently Yang et al. (2018) described an electrokinetic mechanical hybrid device. Electrokinetic energy harvesting is based on the fact that as electrolyte solution flows into a capillary tube with surface charges, the surface charges give rise to a repulsive force to the co-ions and attract excess counter ions near the tube surface. Yang used this effect to design a hybrid device, illustrated in Fig. 13, which was composed of two identical carbon nanotube/titanium electrodes, separated by a piece of anodic aluminum oxide nanochannels membrane. The hybrid device was charged by pressure-driven electrolyte flowing through the nanochannels. As electrolyte flowed through the membrane

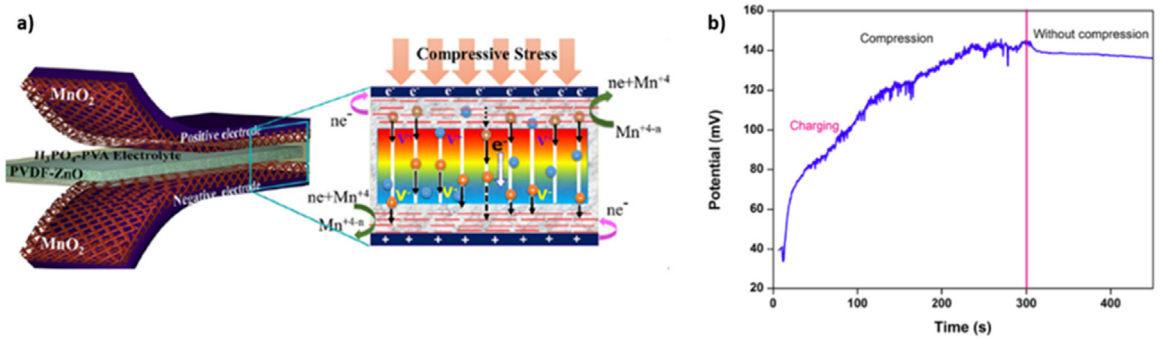

Fig. 12. a) Schematic and illustration of a self-charging piezoelectric/EC hybrid device. b) Self-charging under the compression of a human palm. Reprinted with permission from Ramadoss et al. (2015).

nanochannels under pressure a potential was induced via the electrokinetic effect, which was used to charge the CNT/Ti capacitor electrodes by connecting an external load. The hybridization of the device eliminated need of typical electrokinetic devices of maintaining a continuous pressure across the nanochannels, as the energy directly could be stored within the same device.

2.4. Thermal energy harvester hybrids

Thermoelectric energy harvesters generally rely on the Seebeck effect and are based on solid-state energy converters, however, the thermally induced capacitive effect can also be used to harvest energy (the so-called Soret effect) (Hyuck et al., 2013; Lim et al., 2016). This temperature dependence of surface ion density has been utilized for thermal-to-electric energy conversion by designing thermally chargeable supercapacitors based on different nanoporous carbon supercapacitors, capable of storing the generated charge within the same device (Hyuck et al., 2013; Qiao et al., 2008; Wang et al., 2015b). In brief, the devices consist of two supercapacitor electrodes sandwiching an ionic thermoelectric with as high ionic Seebeck coefficient as possible. The charging of the supercapacitor by thermally driven ion diffusion occurs as the ionic conductor contains a mobile cation and a relatively immobile anion, and when a temperature gradient is applied a buildup of mobile cation will occur at the cold electrode through thermodiffusion, generating a thermopotential. Upon connecting a load between the capacitive electrodes, oxidation and reduction will occur at the hot and cold electrodes, charging the supercapacitor.

A recent thermoelectric supercapacitor hybrid based on thermodiffusion was reported by Zhao et al. (2016). The authors employed a liquid state polymeric electrolyte to charge a CNT-based supercapacitor under a temperature gradient, which was then stored in the hybrid device as the temperature gradient was removed. The charging/discharging of the device is illustrated in Fig. 14. Establishing a temperature gradient across the two electrodes leads to an ionic thermovoltage and thermoelectric charging of the EC follows. After completed charging, the heating is turned off and charge is stored in the EC, which then can be discharged. The polymer electrolyte was based on polyehtyleneoxide treated by sodium hydroxide, containing rather immobile polymeric anions and mobile sodium cations, and showed a high ionic Seeback coefficient of 11.1 mV K^{-1} and a relatively low thermal conductivity, albeit the electrical conductivity was rather low (8.13×10^{-3} S m^{-1}). Kim et al. (2016) also recently reported on a thermally chargeable supercapacitor, instead employing a solid state ionic conductor. The device was based on two PANI-deposited graphene and CNT films sandwiching polystyrene sulfonic acid as a solid electrolyte, containing mobile hydrogen and rather immobile PSS, which when the humidity was above 70% displayed both high ionic Seeback coefficient (8 mV K^{-1}, which dropped at lower humidity)) and good electrical conductivity (9 S m^{-1}). These types of hybrid thermoelectric-supercapacitor devices have the advantage of being based on flexible, printable supercapacitors and show promise for powering of wearable, portable and implantable bioelectronics devices using waste heat naturally occurring to charge the devices. Due to the high ionic Seeback coefficient, a relatively small temperature gradient is sufficient to

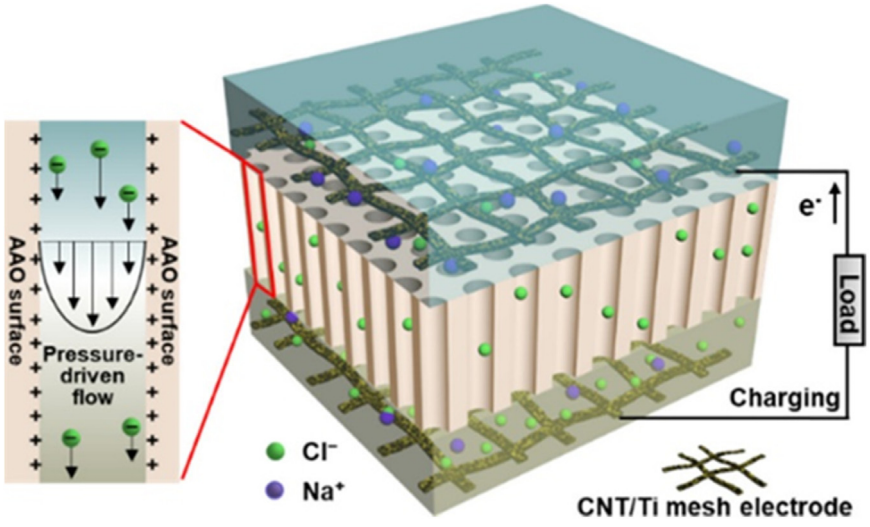

Fig. 13. Example of an electrokinetic energy harvesting hybrid device, utilizing pressure driven flow to generate charge which is stored on the capacitive electrodes. Reprinted with permission from Yang et al. (2018).

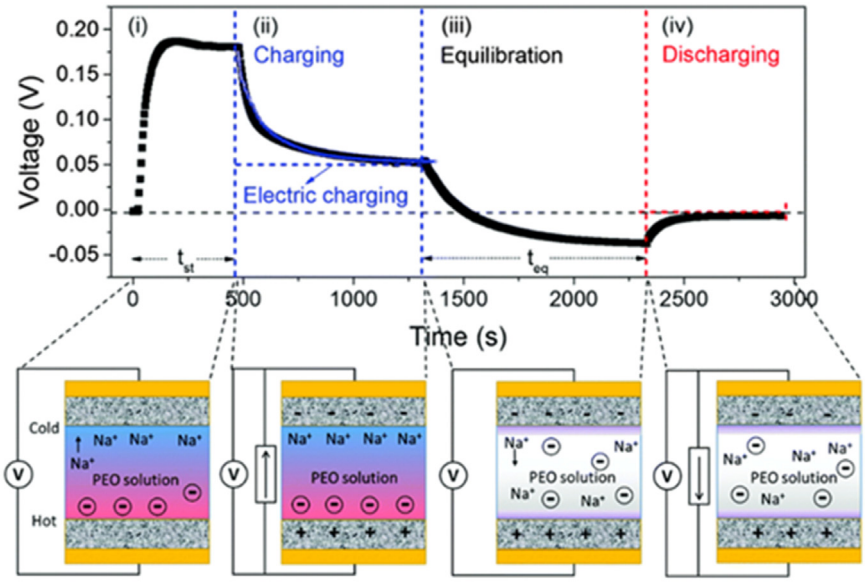

Fig. 14. Charging and discharging cycle of a thermoelectric/EC hybrid. Reprinted with permission from Zhao et al. (2016).

charge the capacitor with to a useful level. The same group recently also demonstrated a thermally chargeable supercapacitor based on GO, with intercalated sulfate ions to improve the conductivity of the material (0.4 S m^{-1} at 70% RH), reaching a thermopower of close to 6 mV K^{-1} at 70% RH (Kim et al., 2018). The device could be batch-fabricated using laser irradiation, suggesting a route for mass manufacturing.

Apart from relying on the Seeback effect to harvest thermal energy, energy harvesters can also be designed utilizing the pyroelectric effect of certain materials. Pyroelectric materials can be found in applications for infrared sensing, but has lately garnered significant interest as energy harvesting materials (Bowen et al., 2014; Lingam et al., 2013). Pyroelectric energy harvesters have quite a lot of common with piezoelectric energy harvesters, as certain piezoelectric materials constituting anisotropic solids will generate a spontaneous polarization upon temperature fluctuations. If the material's dimensions also change upon the temperature fluctuations, strain will be induced resulting in an additional contribution of piezoelectrically induced charges. Pyroelectric energy harvesters thus rely on temperature fluctuations, dT/dt, in contrast to thermoelectric materials, which rely on a temperature gradient, dT/dx. Like with piezoelectric energy harvesters, this will give rise to an AC current and would generally need a rectifier circuit to harness the energy. Pyroelectric energy harvesters could be very useful in an environment where the temperature is uniform, but fluctuates. One example of was presented by Wang et al., employing the pyroelectric and semiconductor properties of ZnO nanowires (Yang et al., 2012). Pyroelectric energy harvesters have also been combined with piezoelectric and solar energy harvester, and also used to power separate energy storage devices (Lee et al., 2014; Yang et al., 2013). However, no pyroelectric charge-storing hybrids have been reported so far, but pyroelectric hybrid devices should in principle be able to draw similar benefits as piezoelectric hybrid devices.

Instead of using a thermoelectric energy harvester using ambient heat to generate power, fuel can be directly burned and converted to electrical energy using thermopower wave generators as a high energy density source. This was first reported in 2010 by the group of Michal Strano (Choi et al., 2010). A thermopower wave is a self-propagating chemically driven wave, triggered by ignition, traveling along the length of a thermally and electrically conductive conduit, such as a carbon nanowire or a nanotube. The thermal conduit conducts heat faster than the fuel itself, coupling back to the fuel and generating a soliton, which produces a concomitant electrical pulse of disproportionately high specific power. Being a relatively new discovery, thermopower wave devices typically have energy conversion efficiencies well below 1% with most of the energy being lost to the environment, although recent reports show efficiencies in excess of 1% (Mahajan et al., 2016). Recently, Shin et al. (2016) incorporated a thermopower wave with a, letting consecutive thermopower waves charge a supercapacitor. A schematic of the device is shown in Fig. 15, which was composed of supercapacitors constituting a pair of layered structures consisting of a nickel electrode, a MnO2 layer and a PVA electrolyte gel neighboring a chemical fuel layer of nitrocellulose. Multiple TWs in the layered structures were ignited to accumulate and store energy inside the supercapacitor. The induced voltage originated from thermoelectricity driven by the temperature difference existing across the thermal conduit and the transient chemical potential gradient, arising because of the chemical potential difference existing across the conduit. The potential gradient attracted sodium ions from the electrolyte to the MnO2 layer, where adsorption of sodium ions successively reduced the MnO2, and the potential differences between the anions and cations in the electrolyte gel resulted in the formation of an electrical double layer on the MnO2 surface, charging the supercapacitor. With the incorporation of an EC, the energy of the thermopower wave could thus be stored directly within the device.

3. Summary and conclusions

A shortcoming of ambient energy harvesters is that electricity generation is highly dependent on local availability and typically intermittent in nature, requiring the use of separate charge storing elements. This have limited the use of such devices, but the development of hybrid energy harvesting/charge storing have opened the possibility to bypass the intermediate step of electricity generation, which represents a more efficient, compact, and cost-effective approach. This would allow devices to be deployed in the design of self-powered autonomous systems. However, the development of hybrid systems is still in its infancy, where current research studies in this area are mostly focused on proof-of concept studies. Much work remains to optimize the different parts, efficiently integrating the two, but a lot of crossover can be seen in the efforts of developing different energy harvesting hybrids, which show the viability of dual-functioning electrodes.

Hybrid technologies have so far mainly focused on of four general types of energy harvesters: (1) Chemical, as in (B)FCs, (2)(Bio)solar, (3) Mechanical, as in PENG, and (4) Thermal. Briefly looking at each in turn, (1) the development of hybrid (B)FC/EC devices have

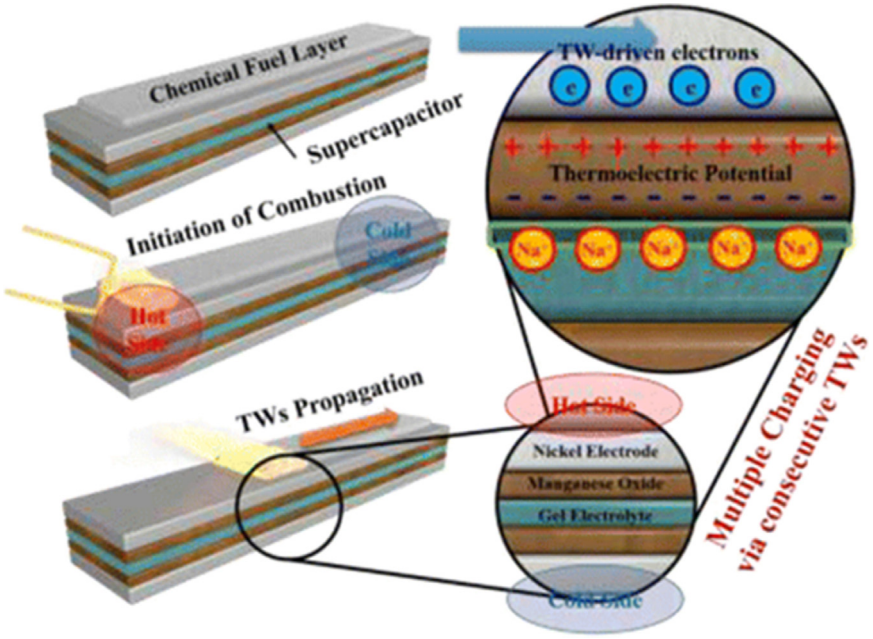

Fig. 15. Schematic of the working principle of a thermopower wave/EC hybrid system. Reprinted with permission from Shin et al. (2016).

demonstrated new possibilities for otherwise low-power systems, where integration with EC is a particularly promising direction to obtain a usable power level, e.g. for wearables or implantable devices. A deep level of integration allows for significant miniaturization and simplification of the device and by operating in pulsed mode the power output can be increased several orders of magnitude. While the devices reported so far has not been optimized in terms of e.g. capacitance vs. FC performance and device design (such as electrolyte, size and distance of electrodes), greater improvements and new applications are expected as the development of hybrid systems draws more attention. (2) The development of different hybrid solar cell technologies is a good way to mitigate the intermittent nature of the energy source, and while the overall efficiencies of the hybrid devices developed so far are insufficient, rapid improvements have been made in storage and total efficiency over the last few years. Combining DSSC, PSCs and even biosolar cells, all based on different mechanisms of converting the solar radiation to electrical energy, directly with charge storing elements enables new possibilities for the technologies, such as self-sufficient wearable, lightweight energy supplies. (3) Mechanical hybrid devices allow local irregular and mostly low-frequency vibrational energy to be stored and used in self-powered applications, where the elimination of the use of rectification circuit greatly enhances the integration level of the energy harvesting/storage system. Devices are versatile in terms of materials choice and structure design, enabling the design of flexible and wearable devices, and could foreseeably be improved e.g. by incorporating new nanostructured materials with high pseudocapacitive behavior and specific capacitance, as well as incorporating highly porous piezoelectric separators. (4) The development of hybrid thermoelectric/charge storage hybrid devices show great promise as a flexible, portable power source. While the technology is very new, rapid large improvements have been made within the last years. By utilizing the Soret effect to charge an integrated supercapacitor, small temperature gradients, such as a wearable device would be exposed to, could realistically be used to power low-power electronics. The development of pyroelectric and thermopower wave devices also provides interesting possibilities for self-powered charge-storing units. By properly configuring thermoelectric devices for maximum power output via effective heat transfer as well as optimizing the integration with charge-storing component, self-powered units harvesting ambient heat could be realized.

To improve current hybrid devices a large research effort is needed in studies regarding materials optimization and structural design, to make scaled-up fabrication and practical applications feasible. In particular, low energy transfer efficiency from the harvesting to storage devices of the early reported prototypes is a reoccurring issue, which require proper voltage matching as well as matching the capacities and impedances of the energy-storage with the energy harvester. Optimizing the materials used as electrode materials, separators, electrolytes, etc. both in regards to the energy harvester as well as the energy storage part is highly important. The mechanical performances of the materials need to be carefully investigated in order to allow wearable devices to be designed, and in addition, the safety aspect of materials used is of outmost importance for the safe operation of the device, especially when in contact with the human body. However, the massive increase in attention for hybrid devices with a rapidly increasing number of reports in scientific literature is set to propel the development, enabling hybrid devices incorporated in self-powered autonomous devices to become a reality in the future.

3.1. Future perspectives

With the ongoing trend to develop integrated systems for miniature electronics, our surroundings, homes and even bodies are becoming more intimately connected to electronic devices (Chu et al., 2017; Lukatskaya et al., 2016; Selvan and Mohamed Ali, 2016). Hybridization of power harvesting devices harnessing ambient energy with charge storing materials could play a key role in making such systems self-sustaining and self-powered. An example of where hybrid energy harvesting/charge storing systems could be employed in such a manner is shown in Fig. 16, where hybridization allows an easier route for miniature, more efficient systems to be designed. This could be a mechanical or solar hybrid incorporated into clothing, a flexible thermal hybrid or a wearable/implantable fuel cell hybridized with energy storage. Taking advantage of dual-functioning materials have already allowed the construction of different early prototype hybrid systems, where energy harvesting and charge storing can occur within the same volume. This could then be used for e.g. powering of some sensor, allowing for a seamless design of self-powered autonomous systems. Furthermore, different energy harvesters could be combined to enable using different energy sources within the same hybrid device (Wen

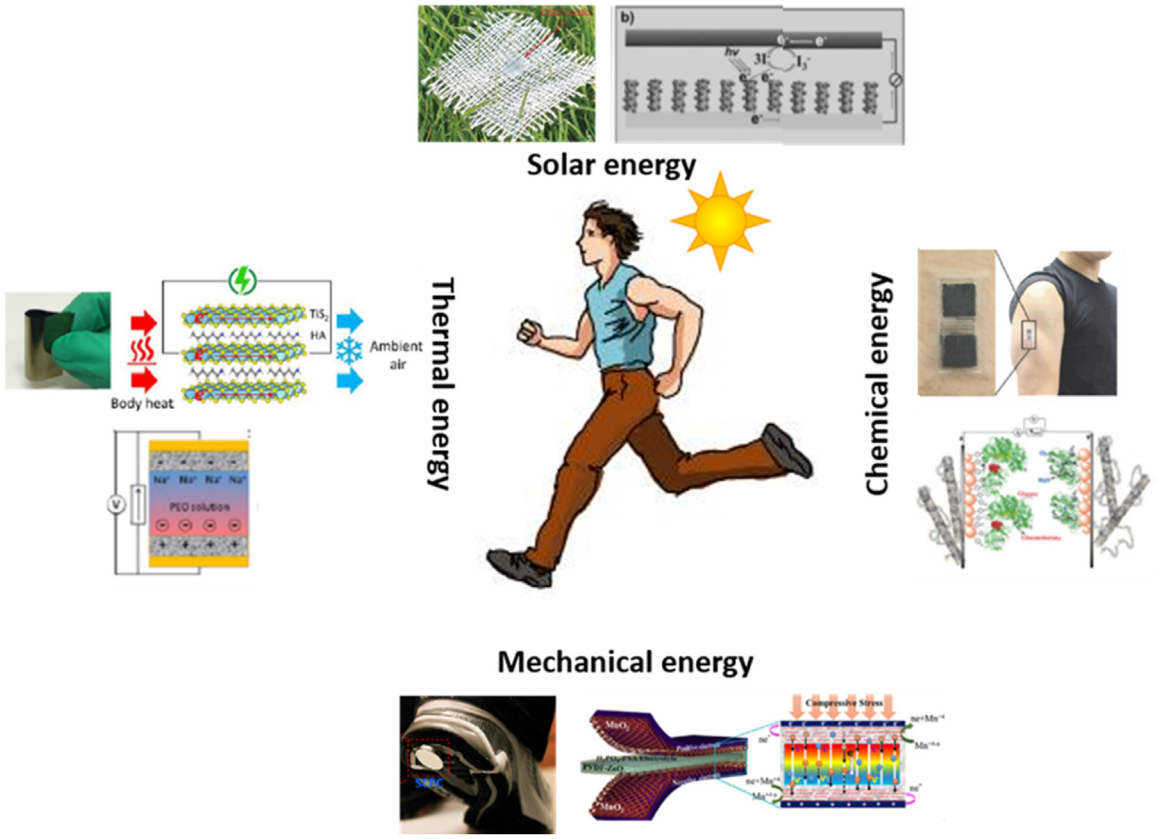

Fig. 16. Examples of hybrid devices for wearable applications. Images of devices adapted with permission from Bandodkar and Wang (2016), Pan et al. (2014), Pankratov et al. (2014b), Ramadoss et al. (2015), Sun et al. (2014), Wan et al. (2016), Xue et al. (2012), Zhao et al. (2016).

et al., 2016).

While reports of hybrid devices so far have focused on miniature/wearable devices, the use of dual-functioning materials could also be highly beneficial in the design of larger systems. For example, dual-functioning hybrid devices could be a way to achieve practical electrification in off-grid remote locations, e.g. combining solar cells with integrated charge storing. Furthermore, hybrid devices could lead to further development of electrochemical power sources with high energy and power, for implementation e.g. in electrical vehicles or smart-grid energy storage.

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Conflicts of interest

There are no conflicts to declare.

References

Agnes, C., Holzinger, M., Le Goff, A., Reuillard, B., Elouarzaki, K., Tingry, S., Cosnier, S., 2014. Supercapacitor/biofuel cell hybrids based on wired enzymes on carbon nanotube matrices: autonomous reloading after high power pulses in neutral buffered glucose solutions. Energy Environ. Sci. 7 (6), 1884–1888.

Bandodkar, A.J., Wang, J., 2016. Wearable biofuel cells: a review. Electroanalysis 28 (6), 1188–1200.

Bobrowski, T., González Arribas, E., Ludwig, R., Toscano, M.D., Shleev, S., Schuhmann, W., 2018. Rechargeable, flexible and mediator-free biosupercapacitor based on transparent ITO nanoparticle modified electrodes acting in μM glucose containing buffers. Biosens. Bioelectron. 101, 84–89.

Bowen, C.R., Taylor, J., LeBoulbar, E., Zabek, D., Chauhan, A., Vaish, R., 2014. Pyroelectric materials and devices for energy harvesting applications. Energy Environ. Sci. 7 (12), 3836–3856.

Bryan, A.M., Santino, L.M., Lu, Y., Acharya, S., D'Arcy, J.M., 2016. Conducting polymers for pseudocapacitive energy storage. Chem. Mater. 28 (17), 5989–5998.

Bullen, R.A., Arnot, T.C., Lakeman, J.B., Walsh, F.C., 2006. Biofuel cells and their development. Biosens. Bioelectron. 21 (11), 2015–2045.

Calabrese Barton, S., Gallaway, J., Atanassov, P., 2004. Enzymatic biofuel cells for implantable and microscale devices. Chem. Rev. 104 (10), 4867–4886.

Chen, J., Yang, J., Li, Z., Fan, X., Zi, Y., Jing, Q., Guo, H., Wen, Z., Pradel, K.C., Niu, S., Wang, Z.L., 2015a. Networks of triboelectric nanogenerators for harvesting water wave energy: a potential toward blue energy. ACS Nano 9 (3), 3324–3331.

Chen, L.-F., Zhang, X.-D., Liang, H.-W., Kong, M., Guan, Q.-F., Chen, P., Wu, Z.-Y., Yu, S.-H., 2012. Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors. ACS Nano 6 (8), 7092–7102.

Chen, T., Dai, L., 2014. Flexible supercapacitors based on carbon nanomaterials. J. Mater. Chem. A 2 (28), 10756–10775.

Chen, T., Yang, Z., Peng, H., 2013. Integrated devices to realize energy conversion and storage simultaneously. ChemPhysChem 14 (9), 1777–1782.

Chen, W., Wu, Y., Yue, Y., Liu, J., Zhang, W., Yang, X., Chen, H., Bi, E., Ashraful, I., Grätzel, M., Han, L., 2015b. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. Science 350 (6263), 944.

Chen, X., Sun, H., Yang, Z., Guan, G., Zhang, Z., Qiu, L., Peng, H., 2014. A novel "energy fiber" by coaxially integrating dye-sensitized solar cell and electrochemical capacitor. J. Mater. Chem. A 2 (6), 1897–1902.

Choi, W., Hong, S., Abrahamson, J.T., Han, J.-H., Song, C., Nair, N., Baik, S., Strano, M.S., 2010. Chemically driven carbon-nanotube-guided thermopower waves. Nat. Mater. 9 (5), 423–429.

Chu, B., Burnett, W., Chung, J.W., Bao, Z., 2017. Bring on the bodyNET. Nature 549.

Ciesielski, P.N., Scott, A.M., Faulkner, C.J., Berron, B.J., Cliffel, D.E., Jennings, G.K., 2008. Functionalized nanoporous gold leaf electrode films for the immobilization of photosystem I. ACS Nano 2 (12), 2465–2472.

Cohn, A.P., Erwin, W.R., Share, K., Oakes, L., Westover, A.S., Carter, R.E., Bardhan, R., Pint, C.L., 2015. All silicon electrode photocapacitor for integrated energy storage and conversion. Nano Lett. 15 (4), 2727–2731.

Collavini, S., Völker, S.F., Delgado, J.L., 2015. Understanding the outstanding power conversion efficiency of perovskite-based solar cells. Angew. Chem. Int. Ed. 54 (34), 9757–9759.

Conway, B.E., Pell, W.G., 2003. Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices. J. Solid State Electrochem. 7 (9), 637–644.

Deeke, A., Sleutels, T.H.J.A., Donkers, T.F.W., Hamelers, H.V.M., Buisman, C.J.N., Ter Heijne, A., 2015. Fluidized capacitive bioanode as a novel reactor concept for the microbial fuel cell. Environ. Sci. Technol. 49 (3), 1929–1935.

Deeke, A., Sleutels, T.H.J.A., Hamelers, H.V.M., Buisman, C.J.N., 2012. Capacitive

bioanodes enable renewable energy storage in microbial fuel cells. Environ. Sci. Technol. 46 (6), 3554–3560.
Deeke, A., Sleutels, T.H.J.A., Heijne, A.T., Hamelers, H.V.M., Buisman, C.J.N., 2013. Influence of the thickness of the capacitive layer on the performance of bioanodes in microbial fuel cells. J. Power Sources 243, 611–616.
Dewan, A., Beyenal, H., Lewandowski, Z., 2009. Intermittent energy harvesting improves the performance of microbial fuel cells. Environ. Sci. Technol. 43 (12), 4600–4605.
Diamond, D., Coyle, S., Scarmagnani, S., Hayes, J., 2008. Wireless sensor networks and chemo-/biosensing. Chem. Rev. 108 (2), 652–679.
Dong, K., Wang, Y.-C., Deng, J., Dai, Y., Zhang, S.L., Zou, H., Gu, B., Sun, B., Wang, Z.L., 2017. A highly stretchable and washable all-yarn-based self-charging knitting power textile composed of fiber triboelectric nanogenerators and supercapacitors. ACS Nano 11 (9), 9490–9499.
Du, P., Hu, X., Yi, C., Liu, H.C., Liu, P., Zhang, H.-L., Gong, X., 2015. Self-powered electronics by integration of flexible solid-state graphene-based supercapacitors with high performance perovskite hybrid solar cells. Adv. Funct. Mater. 25 (16), 2420–2427.
Dubal, D.P., Ayyad, O., Ruiz, V., Gomez-Romero, P., 2015. Hybrid energy storage: the merging of battery and supercapacitor chemistries. Chem. Soc. Rev. 44 (7), 1777–1790.
El-Kady, M.F., Shao, Y., Kaner, R.B., 2016. Graphene for batteries, supercapacitors and beyond. Nat. Rev. Mater. 1, 16033.
Falk, M., Shleev, S., Narváez Villarrubia, C.W., Babanova, S., Atanassov, P., 2014. Biological Fuel Cells for Biomedical Applications. Enzymatic Fuel Cells. John Wiley & Sons, Inc., Hoboken, New Jersey, pp. 422–450.
Fan, F.R., Tang, W., Wang, Z.L., 2016. Flexible nanogenerators for energy harvesting and self-powered electronics. Adv. Mater. 28 (22), 4283–4305.
Gallaway, J.W., Calabrese Barton, S.A., 2008. Kinetics of redox polymer-mediated enzyme electrodes. J. Am. Chem. Soc. 130 (26), 8527–8536.
Gao, W., Emaminejad, S., Nyein, H.Y.Y., Challa, S., Chen, K., Peck, A., Fahad, H.M., Ota, H., Shiraki, H., Kiriya, D., Lien, D.-H., Brooks, G.A., Davis, R.W., Javey, A., 2016. Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis. Nature 529 (7587), 509–514.
González-Arribas, E., Aleksejeva, O., Bobrowski, T., Toscano, M.D., Gorton, L., Schuhmann, W., Shleev, S., 2017a. Solar biosupercapacitor. Electrochem. Commun. 74, 9–13.
González-Arribas, E., Bobrowski, T., Di Bari, C., Sliozberg, K., Ludwig, R., Toscano, M.D., De Lacey, A.L., Pita, M., Schuhmann, W., Shleev, S., 2017b. Transparent, mediator- and membrane-free enzymatic fuel cell based on nanostructured chemically modified indium tin oxide electrodes. Biosens. Bioelectron. 97, 46–52.
González, A., Goikolea, E., Barrena, J.A., Mysyk, R., 2016. Review on supercapacitors: technologies and materials. Renew. Sustain. Energy Rev. 58, 1189–1206.
Grancini, G., Roldán-Carmona, C., Zimmermann, I., Mosconi, E., Lee, X., Martineau, D., Narbey, S., Oswald, F., De Angelis, F., Graetzel, M., Nazeeruddin, M.K., 2017. One-year stable perovskite solar cells by 2D/3D interface engineering. Nat. Commun. 8, 15684.
Guo, H., Yeh, M.-H., Lai, Y.-C., Zi, Y., Wu, C., Wen, Z., Hu, C., Wang, Z.L., 2016. All-in-one shape-adaptive self-charging power package for wearable electronics. ACS Nano.
Guo, W., Xue, X., Wang, S., Lin, C., Wang, Z.L., 2012. An integrated power pack of dye-sensitized solar cell and Li battery based on double-sided TiO2 nanotube arrays. Nano Lett. 12 (5), 2520–2523.
Hanashi, T., Yamazaki, T., Tanaka, H., Ikebukuro, K., Tsugawa, W., Sode, K., 2014. The development of an autonomous self-powered bio-sensing actuator. Sens. Actuators B: Chem. 196, 429–433.
Hanashi, T., Yamazaki, T., Tsugawa, W., Ferri, S., Nakayama, D., Tomiyama, M., Ikebukuro, K., Sode, K., 2009. BioCapacitor—a novel category of biosensor. Biosens. Bioelectron. 24 (7), 1837–1842.
Houghton, J., Santoro, C., Soavi, F., Serov, A., Ieropoulos, I., Arbizzani, C., Atanassov, P., 2016. Supercapacitive microbial fuel cell: characterization and analysis for improved charge storage/delivery performance. Bioresour. Technol. 218, 552–560.
Hu, K., Xiong, R., Guo, H., Ma, R., Zhang, S., Wang, Z.L., Tsukruk, V.V., 2016. Biotactile sensors: self-powered electronic skin with biotactile selectivity (Adv. Mater. 18/2016). Adv. Mater. 28 (18) (3414-3414).
Hu, L., Choi, J.W., Yang, Y., Jeong, S., La Mantia, F., Cui, L.-F., Cui, Y., 2009. Highly conductive paper for energy-storage devices. Proc. Natl. Acad. Sci. USA 106 (51), 21490–21494.
Hu, Y., Zhang, Y., Xu, C., Lin, L., Snyder, R.L., Wang, Z.L., 2011. Self-powered system with wireless data transmission. Nano Lett. 11 (6), 2572–2577.
Huang, Y., Li, H., Wang, Z., Zhu, M., Pei, Z., Xue, Q., Huang, Y., Zhi, C., 2016. Nanostructured polypyrrole as a flexible electrode material of supercapacitor. Nano Energy 22, 422–438.
Hwang, G.-T., Byun, M., Jeong, C.K., Lee, K.J., 2015. Flexible piezoelectric thin-film energy harvesters and nanosensors for biomedical applications. Adv. Healthc. Mater. 4 (5), 646–658.
Hyuck, L., Weiyi, L., Xi, C., Yu, Q., 2013. Effects of ion concentration on thermally-chargeable double-layer supercapacitors. Nanotechnology 24 (46), 465401.
Ieropoulos, I., Greenman, J., Melhuish, C., Hart, J., 2005. Energy accumulation and improved performance in microbial fuel cells. J. Power Sources 145 (2), 253–256.
Jarvis, L.P., Atwater, T.B., J. Cygan, P., 1999. Fuel cell/electrochemical capacitor hybrid for intermittent high power applications. J. Power Sources 79 (1), 60–63.
Jiang, Q., Wu, C., Wang, Z., Wang, A.C., He, J.-H., Wang, Z.L., Alshareef, H.N., 2018. MXene electrochemical microsupercapacitor integrated with triboelectric nanogenerator as a wearable self-charging power unit. Nano Energy 45, 266–272.
Jones, K., 2016. In: Ameta, Suresh C., Ameta, Rakshit (Eds.), Solar Energy Conversion and Storage. Photochemical Modes. Chromatographia 79 (1209-1209).
Kang, M.-G., Jung, W.-S., Kang, C.-Y., Yoon, S.-J., 2016. Recent progress on PZT based piezoelectric energy harvesting technologies. Actuators 5, 1.
Khaligh, A., Li, Z., 2010. Battery, ultracapacitor, fuel cell, and hybrid energy storage systems for electric, hybrid electric, fuel cell, and plug-in hybrid electric vehicles: state of the art. IEEE Trans. Veh. Technol. 59 (6), 2806–2814.
Kim, B.J., Kim, D.H., Lee, Y.-Y., Shin, H.-W., Han, G.S., Hong, J.S., Mahmood, K., Ahn, T.K., Joo, Y.-C., Hong, K.S., Park, N.-G., Lee, S., Jung, H.S., 2015a. Highly efficient and bending durable perovskite solar cells: toward a wearable power source. Energy Environ. Sci. 8 (3), 916–921.
Kim, D.-H., Rogers, J.A., 2008. Stretchable electronics: materials strategies and devices. Adv. Mater. 20 (24), 4887–4892.
Kim, J., Kumar, R., Bandodkar, A.J., Wang, J., 2017. Advanced materials for printed wearable electrochemical devices: a review. Adv. Electron. Mater. 3 (1), 1600260 (n/a).
Kim, S.L., Hsu, J.-H., Yu, C., 2018. Intercalated graphene oxide for flexible and practically large thermoelectric voltage generation and simultaneous energy storage. Nano Energy 48, 582–589.
Kim, S.L., Lin, H.T., Yu, C., 2016. Thermally chargeable solid-state supercapacitor. Adv. Energy Mater. 6 (18), 1600546 (n/a).
Kim, T., Jung, G., Yoo, S., Suh, K.S., Ruoff, R.S., 2013. Activated graphene-based carbons as supercapacitor electrodes with macro- and mesopores. ACS Nano 7 (8), 6899–6905.
Kim, Y.-S., Xie, Y., Wen, X., Wang, S., Kim, S.J., Song, H.-K., Wang, Z.L., 2015b. Highly porous piezoelectric PVDF membrane as effective lithium ion transfer channels for enhanced self-charging power cell. Nano Energy 14, 77–86.
Kirchhofer, N.D., Rasmussen, M.A., Dahlquist, F.W., Minteer, S.D., Bazan, G.C., 2015. The photobioelectrochemical activity of thylakoid bioanodes is increased via photocurrent generation and improved contacts by membrane-intercalating conjugated oligoelectrolytes. Energy Environ. Sci. 8 (9), 2698–2706.
Kizling, M., Draminska, S., Stolarczyk, K., Tammela, P., Wang, Z., Nyholm, L., Bilewicz, R., 2015a. Biosupercapacitors for powering oxygen sensing devices. Bioelectrochemistry 106 (Part A), 34–40.
Kizling, M., Stolarczyk, K., Kiat, J.S.S., Tammela, P., Wang, Z., Nyholm, L., Bilewicz, R., 2015b. Pseudocapacitive polypyrrole–nanocellulose composite for sugar-air enzymatic fuel cells. Electrochem. Commun. 50, 55–59.
Knight, C., Davidson, J., Behrens, S., 2008. Energy options for wireless sensor nodes. Sensors 8, 12.
Knoche, K.L., Hickey, D.P., Milton, R.D., Curchoe, C.L., Minteer, S.D., 2016. Hybrid glucose/O_2 biobattery and supercapacitor utilizing a pseudocapacitive dimethylferrocene redox polymer at the bioanode. ACS Energy Lett. 1 (2), 380–385.
Kötz, R., Carlen, M., 2000. Principles and applications of electrochemical capacitors. Electrochim. Acta 45 (15–16), 2483–2498.
Lee, J.-H., Lee, K.Y., Gupta, M.K., Kim, T.Y., Lee, D.-Y., Oh, J., Ryu, C., Yoo, W.J., Kang, C.-Y., Yoon, S.-J., Yoo, J.-B., Kim, S.-W., 2014. Highly stretchable piezoelectric-pyroelectric hybrid nanogenerator. Adv. Mater. 26 (5), 765–769.
Lee, Y.J., Yi, H., Kim, W.-J., Kang, K., Yun, D.S., Strano, M.S., Ceder, G., Belcher, A.M., 2009. Fabricating genetically engineered high-power lithium-ion batteries using multiple virus fenes. Science 324 (5930), 1051.
Li, S., Zhang, D., Meng, X., Huang, Q.-A., Sun, C., Wang, Z.L., 2018. A flexible lithium-ion battery with quasi-solid gel electrolyte for storing pulsed energy generated by triboelectric nanogenerator. Energy Storage Mater. 12, 17–22.
Li, X., Wei, B., 2013. Supercapacitors based on nanostructured carbon. Nano Energy 2 (2), 159–173.
Liang, J., Zhu, G., Lu, Z., Zhao, P., Wang, C., Ma, Y., Xu, Z., Wang, Y., Hu, Y., Ma, L., Chen, T., Tie, Z., Liu, J., Jin, Z., 2018. Integrated perovskite solar capacitors with high energy conversion efficiency and fast photo-charging rate. J. Mater. Chem. A 6 (5), 2047–2052.
Lim, H., Shi, Y., Qiao, Y., 2016. Thermally chargeable supercapacitor working in a homogeneous, changing temperature field. Appl. Phys. A 122 (4), 443.
Lingam, D., Parikh, A.R., Huang, J., Jain, A., Minary-Jolandan, M., 2013. Nano/micro-scale pyroelectric energy harvesting: challenges and opportunities. Int. J. Smart Nano Mater. 4 (4), 229–245.
Liu, L., Niu, Z., Chen, J., 2016. Unconventional supercapacitors from nanocarbon-based electrode materials to device configurations. Chem. Soc. Rev. 45 (15), 4340–4363.
Liu, R., Wang, J., Sun, T., Wang, M., Wu, C., Zou, H., Song, T., Zhang, X., Lee, S.-T., Wang, Z.L., Sun, B., 2017. Silicon nanowire/polymer hybrid solar cell-supercapacitor: a self-charging power unit with a total efficiency of 10.5%. Nano Lett. 17 (7), 4240–4247.
Logan, B.E., Rabaey, K., 2012. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337 (6095), 686.
Lukatskaya, M.R., Dunn, B., Gogotsi, Y., 2016. Multidimensional materials and device architectures for future hybrid energy storage. Nat. Commun. 7, 12647.
Luo, B., Ye, D., Wang, L., 2017. Recent progress on integrated energy conversion and storage systems. Adv. Sci. 4 (9), 1700104.
Luo, J., Fan, F.R., Jiang, T., Wang, Z., Tang, W., Zhang, C., Liu, M., Cao, G., Wang, Z.L., 2015. Integration of micro-supercapacitors with triboelectric nanogenerators for a flexible self-charging power unit. Nano Res. 8 (12), 3934–3943.
Lv, Z., Xie, D., Yue, X., Feng, C., Wei, C., 2012. Ruthenium oxide-coated carbon felt electrode: a highly active anode for microbial fuel cell applications. J. Power Sources 210, 26–31.
Mahajan, S.G., Liu, A.T., Cottrill, A.L., Kunai, Y., Bender, D., Castillo, J., Gibbs, S.L., Strano, M.S., 2016. Sustainable power sources based on high efficiency thermopower wave devices. Energy Environ. Sci. 9 (4), 1290–1298.
Malvankar, N.S., Mester, T., Tuominen, M.T., Lovley, D.R., 2012. Supercapacitors based on c-type cytochromes using conductive nanostructured networks of living bacteria. ChemPhysChem 13 (2), 463–468.
McCormick, A.J., Bombelli, P., Bradley, R.W., Thorne, R., Wenzel, T., Howe, C.J., 2015. Biophotovoltaics: oxygenic photosynthetic organisms in the world of

bioelectrochemical systems. Energy Environ. Sci. 8 (4), 1092–1109.
Messer, H., Zinevich, A., Alpert, P., 2006. Environmental monitoring by wireless communication networks. Science 312 (5774), 713.
Miyasaka, T., Murakami, T.N., 2004. The photocapacitor: an efficient self-charging capacitor for direct storage of solar energy. Appl. Phys. Lett. 85 (17), 3932–3934.
Morimura, H., Oshima, S., Matsunaga, K., Shimamura, T., Harada, M., 2014. Ultra-low-power circuit techniques for mm-size wireless sensor nodes with energy harvesting. IEICE Electron. Express 11 (20) (20142009-20142009).
Morin, B., Van Laethem, D., Turpin, C., Rallières, O., Astier, S., Jaafar, A., Verdu, O., Plantevin, M., Chaudron, V., 2014. Direct hybridization fuel cell – ultracapacitors. Fuel Cells 14 (3), 500–507.
Nagai, H., Segawa, H., 2004. Energy-storable dye-sensitized solar cell with a polypyrrole electrode. Chem. Commun. 8, 974–975.
Narvaez Villarrubia, C.W., Soavi, F., Santoro, C., Arbizzani, C., Serov, A., Rojas-Carbonell, S., Gupta, G., Atanassov, P., 2016. Self-feeding paper based biofuel cell/self-powered hybrid μ-supercapacitor integrated system. Biosens. Bioelectron. 86, 459–465.
Ng, C.H., Lim, H.N., Hayase, S., Harrison, I., Pandikumar, A., Huang, N.M., 2015. Potential active materials for photo-supercapacitor: a review. J. Power Sources 296, 169–185.
Nikolic, G., Stojcev, M., Stamenkovic, Z., Panic, G., Petrovic, B., 2014. Wireless sensor node with low-power sensing. Facta Univ. Ser.: Electron. Energ. 27 (3), 435–453.
Pan, S., Ren, J., Fang, X., Peng, H., 2016. Integration: an effective strategy to develop multifunctional energy storage devices. Adv. Energy Mater. 6 (4), 1501867 (n/a).
Pan, S., Yang, Z., Chen, P., Deng, J., Li, H., Peng, H., 2014. Wearable solar cells by stacking textile electrodes. Angew. Chem. Int. Ed. 53 (24), 6110–6114.
Pankratov, D., Blum, Z., Shleev, S., 2014a. Hybrid electric power biodevices. ChemElectroChem 1 (11), 1798–1807.
Pankratov, D., Blum, Z., Suyatin, D.B., Popov, V.O., Shleev, S., 2014b. Self-charging electrochemical biocapacitor. ChemElectroChem 1 (2), 343–346.
Pankratov, D., Conzuelo, F., Pinyou, P., Alsaoub, S., Schuhmann, W., Shleev, S., 2016. A nernstian biosupercapacitor. Angew. Chem. Int. Ed. 55 (49), 15434–15438.
Pankratov, D., Falkman, P., Blum, Z., Shleev, S., 2014c. A hybrid electric power device for simultaneous generation and storage of electric energy. Energy Environ. Sci. 7 (3), 989–993.
Pankratova, G., Pankratov, D., Hasan, K., Åkerlund, H.-E., Albertsson, P.-Å., Leech, D., Shleev, S., Gorton, L., 2017. Supercapacitive photo-bioanodes and biosolar cells: a novel approach for solar energy harnessing. Adv. Energy Mater. 1602285 (n/a).
Paradiso, J.A., Starner, T., 2005. Energy scavenging for mobile and wireless electronics. IEEE Pervasive Comput. 4 (1), 18–27.
Paraknowitsch, J.P., Thomas, A., 2013. Doping carbons beyond nitrogen: an overview of advanced heteroatom doped carbons with boron, sulphur and phosphorus for energy applications. Energy Environ. Sci. 6 (10), 2839–2855.
Park, K.-I., Jeong, C.K., Kim, N.K., Lee, K.J., 2016. Stretchable piezoelectric nanocomposite generator. Nano Converg. 3 (1), 12.
Park, N.-G., 2015. Perovskite solar cells: an emerging photovoltaic technology. Mater. Today 18 (2), 65–72.
Patel, S., Park, H., Bonato, P., Chan, L., Rodgers, M., 2012. A review of wearable sensors and systems with application in rehabilitation. J. Neuroeng. Rehabil. 9 (1), 21.
Peng, C., Zhang, S., Jewell, D., Chen, G.Z., 2008. Carbon nanotube and conducting polymer composites for supercapacitors. Prog. Nat. Sci. 18 (7), 777–788.
Pinhassi, R.I., Kallmann, D., Saper, G., Dotan, H., Linkov, A., Kay, A., Liveanu, V., Schuster, G., Adir, N., Rothschild, A., 2016. Hybrid bio-photo-electro-chemical cells for solar water splitting. Nat. Commun. 7, 12552.
Pint, C.L., Nicholas, N.W., Xu, S., Sun, Z., Tour, J.M., Schmidt, H.K., Gordon, R.G., Hauge, R.H., 2011. Three dimensional solid-state supercapacitors from aligned single-walled carbon nanotube array templates. Carbon 49 (14), 4890–4897.
Pu, X., Hu, W., Wang Zhong, L., 2017. Toward wearable self-charging power systems: the integration of energy-harvesting and storage devices. Small 14 (1), 1702817.
Pu, X., Li, L., Liu, M., Jiang, C., Du, C., Zhao, Z., Hu, W., Wang, Z.L., 2016. Wearable self-charging power textile based on flexible yarn supercapacitors and fabric nanogenerators. Adv. Mater. 28 (1), 98–105.
Pu, X., Li, L., Song, H., Du, C., Zhao, Z., Jiang, C., Cao, G., Hu, W., Wang, Z.L., 2015. A self-charging power unit by integration of a textile triboelectric nanogenerator and a flexible lithium-ion battery for wearable electronics. Adv. Mater. 27 (15), 2472–2478.
Qiao, Y., Punyamurtual, V.K., Han, A., Lim, H., 2008. Thermal-to-electric energy conversion of a nanoporous carbon. J. Power Sources 183 (1), 403–405.
Ramadoss, A., Saravanakumar, B., Lee, S.W., Kim, Y.-S., Kim, S.J., Wang, Z.L., 2015. Piezoelectric-driven self-charging supercapacitor power cell. ACS Nano 9 (4), 4337–4345.
Rao, S., Lu, S., Guo, Z., Li, Y., Chen, D., Xiang, Y., 2014. A light-powered bio-capacitor with nanochannel modulation. Adv. Mater. 26 (33), 5846–5850.
Rinaldi, A., Mecheri, B., Garavaglia, V., Licoccia, S., Di Nardo, P., Traversa, E., 2008. Engineering materials and biology to boost performance of microbial fuel cells: a critical review. Energy Environ. Sci. 1 (4), 417–429.
Santoro, C., Soavi, F., Serov, A., Arbizzani, C., Atanassov, P., 2016. Self-powered supercapacitive microbial fuel cell: the ultimate way of boosting and harvesting power. Biosens. Bioelectron. 78, 229–235.
Selvan, K.V., Mohamed Ali, M.S., 2016. Micro-scale energy harvesting devices: review of methodological performances in the last decade. Renew. Sustain. Energy Rev. 54, 1035–1047.
Shi, B., Zheng, Q., Jiang, W., Yan, L., Wang, X., Liu, H., Yao, Y., Li, Z., Wang, Z.L., 2016. A packaged self-powered system with universal connectors based on hybridized nanogenerators. Adv. Mater. 28 (5), 846–852.
Shin, D., Hwang, H., Yeo, T., Seo, B., Choi, W., 2016. Thermopower wave-driven hybrid supercapacitor charging system. ACS Appl. Mater. Interfaces 8 (45), 31042–31050.
Simon, P., Gogotsi, Y., 2008. Materials for electrochemical capacitors. Nat. Mater. 7 (11), 845–854.
Skunik-Nuckowska, M., Grzejszczyk, K., Stolarczyk, K., Bilewicz, R., Kulesza, P.J., 2014. Integration of supercapacitors with enzymatic biobatteries toward more effective pulse-powered use in small-scale energy harvesting devices. J. Appl. Electrochem. 44 (4), 497–507.
Snook, G.A., Kao, P., Best, A.S., 2011. Conducting-polymer-based supercapacitor devices and electrodes. J. Power Sources 196 (1), 1–12.
Soavi, F., Bettini, L.G., Piseri, P., Milani, P., Santoro, C., Atanassov, P., Arbizzani, C., 2016. Miniaturized supercapacitors: key materials and structures towards autonomous and sustainable devices and systems. J. Power Sources 326, 717–725.
Soh, P.J., Vandenbosch, G.A.E., Mercuri, M., Schreurs, D.M.M.P., 2015. Wearable wireless health monitoring: current developments, challenges, and future trends. IEEE Microw. Mag. 16 (4), 55–70.
Song, R., Jin, H., Li, X., Fei, L., Zhao, Y., Huang, H., Lai-Wa Chan, H., Wang, Y., Chai, Y., 2015. A rectification-free piezo-supercapacitor with a polyvinylidene fluoride separator and functionalized carbon cloth electrodes. J. Mater. Chem. A 3 (29), 14963–14970.
Strik, D.P.B.T.B., Timmers, R.A., Helder, M., Steinbusch, K.J.J., Hamelers, H.V.M., Buisman, C.J.N., 2011. Microbial solar cells: applying photosynthetic and electrochemically active organisms. Trends Biotechnol. 29 (1), 41–49.
Sun, H., You, X., Deng, J., Chen, X., Yang, Z., Chen, P., Fang, X., Peng, H., 2014. A twisted wire-shaped dual-function energy device for photoelectric conversion and electrochemical storage. Angew. Chem. Int. Ed. 53 (26), 6664–6668.
Sun, K., Zhang, S., Li, P., Xia, Y., Zhang, X., Du, D., Isikgor, F.H., Ouyang, J., 2015. Review on application of PEDOTs and PEDOT:PSS in energy conversion and storage devices. J. Mater. Sci.: Mater. Electron. 26 (7), 4438–4462.
Takei, K., Honda, W., Harada, S., Arie, T., Akita, S., 2015. Toward flexible and wearable human-interactive health-monitoring devices. Adv. Healthc. Materials 4 (4), 487–500.
Takshi, A., Yaghoubi, H., Tevi, T., Bakhshi, S., 2015. Photoactive supercapacitors for solar energy harvesting and storage. J. Power Sources 275, 621–626.
Wan, C., Tian, R., Azizi, A.B., Huang, Y., Wei, Q., Sasai, R., Wasusate, S., Ishida, T., Koumoto, K., 2016. Flexible thermoelectric foil for wearable energy harvesting. Nano Energy 30, 840–845.
Wang, D.-W., Li, F., Chen, Z.-G., Lu, G.Q., Cheng, H.-M., 2008. Synthesis and eectrochemical property of boron-doped mesoporous carbon in supercapacitor. Chem. Mater. 20 (22), 7195–7200.
Wang, G., Zhang, L., Zhang, J., 2012. A review of electrode materials for electrochemical supercapacitors. Chem. Soc. Rev. 41 (2), 797–828.
Wang, H., Lin, J., Shen, Z.X., 2016a. Polyaniline (PANi) based electrode materials for energy storage and conversion. J. Sci.: Adv. Mater. Devices 1 (3), 225–255.
Wang, H., Park, J.-D., Ren, Z.J., 2015a. Practical energy harvesting for microbial fuel cells: a review. Environ. Sci. Technol. 49 (6), 3267–3277.
Wang, J., Feng, S.-P., Yang, Y., Hau, N.Y., Munro, M., Ferreira-Yang, E., Chen, G., 2015b. "Thermal charging" phenomenon in electrical double layer capacitors. Nano Lett. 15 (9), 5784–5790.
Wang, Y., Song, Y., Xia, Y., 2016b. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. Chem. Soc. Rev. 45 (21), 5925–5950.
Wang, Z., 2017. Modeling and simulation of piezoelectrically driven self-charging lithium ion batteries. ACS Appl. Mater. Interfaces 9 (18), 15893–15897.
Wang, Z.L., 2014. Triboelectric nanogenerators as new energy technology and self-powered sensors – principles, problems and perspectives. Faraday Discuss. 176 (0), 447–458.
Wang, Z.L., Song, J., 2006. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. Science 312 (5771), 242.
Wang, Z.L., Wu, W., 2012. Nanotechnology-enabled energy harvesting for self-powered micro-/nanosystems. Angew. Chem. Int. Ed. 51 (47), 11700–11721.
Wei, X., Lee, H., Choi, S., 2016. Biopower generation in a microfluidic bio-solar panel. Sens. Actuators B: Chem. 228, 151–155.
Wen, Z., Yeh, M.-H., Guo, H., Wang, J., Zi, Y., Xu, W., Deng, J., Zhu, L., Wang, X., Hu, C., Zhu, L., Sun, X., Wang, Z.L., 2016. Self-powered textile for wearable electronics by hybridizing fiber-shaped nanogenerators, solar cells, and supercapacitors. Sci. Adv. 2, 10.
Xiao, X., Conghaile, P.Ó., Leech, D., Ludwig, R., Magner, E., 2017a. An oxygen-independent and membrane-less glucose biobattery/supercapacitor hybrid device. Biosens. Bioelectron. 98, 421–427.
Xiao, X., Conghaile, P.Ó., Leech, D., Ludwig, R., Magner, E., 2017b. A symmetric supercapacitor/biofuel cell hybrid device based on enzyme-modified nanoporous gold: an autonomous pulse generator. Biosens. Bioelectron. 90, 96–102.
Xing, L., Nie, Y., Xue, X., Zhang, Y., 2014. PVDF mesoporous nanostructures as the piezo-separator for a self-charging power cell. Nano Energy 10, 44–52.
Xu, J., Chen, Y., Dai, L., 2015a. Efficiently photo-charging lithium-ion battery by perovskite solar cell. Nat. Commun. 6, 8103.
Xu, J., Ku, Z., Zhang, Y., Chao, D., Fan, H.J., 2016. Integrated photo-supercapacitor based on PEDOT modified printable perovskite solar cell. Adv. Mater. Technol. 1 (5), 1600074 (n/a).
Xu, J., Wu, H., Lu, L., Leung, S.-F., Chen, D., Chen, X., Fan, Z., Shen, G., Li, D., 2014. Integrated photo-supercapacitor based on Bi-polar TiO_2 nanotube arrays with selective one-side plasma-assisted hydrogenation. Adv. Funct. Mater. 24 (13), 1840–1846.
Xu, X., Li, S., Zhang, H., Shen, Y., Zakeeruddin, S.M., Graetzel, M., Cheng, Y.-B., Wang, M., 2015b. A power pack based on organometallic perovskite solar cell and supercapacitor. ACS Nano 9 (2), 1782–1787.
Xue, X., Deng, P., He, B., Nie, Y., Xing, L., Zhang, Y., Wang, Z.L., 2014. Flexible self-charging power cell for one-step energy conversion and storage. Adv. Energy Mater. 4 (5), 1301329 (n/a).

Xue, X., Wang, S., Guo, W., Zhang, Y., Wang, Z.L., 2012. Hybridizing energy conversion and storage in a mechanical-to-electrochemical process for self-charging power cell. Nano Lett. 12 (9), 5048–5054.
Yamamoto, Y., Harada, S., Yamamoto, D., Honda, W., Arie, T., Akita, S., Takei, K., 2016. Printed multifunctional flexible device with an integrated motion sensor for health care monitoring. Sci. Adv. 2, 11.
Yang, P., Qu, X., Liu, K., Duan, J., Li, J., Chen, Q., Xue, G., Xie, W., Xu, Z., Zhou, J., 2018. Electrokinetic supercapacitor for simultaneous harvesting and storage of mechanical energy. ACS Appl. Mater. Interfaces 10 (9), 8010–8015.
Yang, Y., Guo, W., Pradel, K.C., Zhu, G., Zhou, Y., Zhang, Y., Hu, Y., Lin, L., Wang, Z.L., 2012. Pyroelectric nanogenerators for harvesting thermoelectric energy. Nano Lett. 12 (6), 2833–2838.
Yang, Y., Zhang, H., Zhu, G., Lee, S., Lin, Z.-H., Wang, Z.L., 2013. Flexible hybrid energy cell for simultaneously harvesting thermal, mechanical, and solar energies. ACS Nano 7 (1), 785–790.
Yu, H., Wu, J., Fan, L., Lin, Y., Xu, K., Tang, Z., Cheng, C., Tang, S., Lin, J., Huang, M., Lan, Z., 2012. A novel redox-mediated gel polymer electrolyte for high-performance supercapacitor. J. Power Sources 198, 402–407.
Yu, M., Ren, X., Ma, L., Wu, Y., 2014. Integrating a redox-coupled dye-sensitized photoelectrode into a lithium–oxygen battery for photoassisted charging. Nat. Commun. 5.
Yu, Z., Tetard, L., Zhai, L., Thomas, J., 2015. Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions. Energy Environ. Sci. 8 (3), 702–730.
Zhang, Y.-Z., Wang, Y., Cheng, T., Lai, W.-Y., Pang, H., Huang, W., 2015. Flexible supercapacitors based on paper substrates: a new paradigm for low-cost energy storage. Chem. Soc. Rev. 44 (15), 5181–5199.
Zhao, D., Wang, H., Khan, Z.U., Chen, J.C., Gabrielsson, R., Jonsson, M.P., Berggren, M., Crispin, X., 2016. Ionic thermoelectric supercapacitors. Energy Environ. Sci. 9 (4), 1450–1457.
Zheng, Q., Shi, B., Li, Z., Wang Zhong, L., 2017. Recent progress on piezoelectric and triboelectric energy harvesters in biomedical systems. Adv. Sci. 4 (7), 1700029.
Zhi, M., Xiang, C., Li, J., Li, M., Wu, N., 2013. Nanostructured carbon-metal oxide composite electrodes for supercapacitors: a review. Nanoscale 5 (1), 72–88.
Zhong, C., Deng, Y., Hu, W., Qiao, J., Zhang, L., Zhang, J., 2015. A review of electrolyte materials and compositions for electrochemical supercapacitors. Chem. Soc. Rev. 44 (21), 7484–7539.
Zhong, J., Yang, Z., Mukherjee, R., Varghese Thomas, A., Zhu, K., Sun, P., Lian, J., Zhu, H., Koratkar, N., 2013. Carbon nanotube sponges as conductive networks for supercapacitor devices. Nano Energy 2 (5), 1025–1030.
Zhong, J., Zhang, Y., Zhong, Q., Hu, Q., Hu, B., Wang, Z.L., Zhou, J., 2014. Fiber-based generator for wearable electronics and mobile medication. ACS Nano 8 (6), 6273–6280.
Zhong, Y., Xia, X., Mai, W., Tu, J., Fan Hong, J., 2017. Integration of energy harvesting and electrochemical storage devices. Adv. Mater. Technol. 2 (12), 1700182.
Zhou, F., Ren, Z., Zhao, Y., Shen, X., Wang, A., Li, Y.Y., Surya, C., Chai, Y., 2016. Perovskite photovoltachromic supercapacitor with all-transparent electrodes. ACS Nano 10 (6), 5900–5908.
Zhu, Z., Kin Tam, T., Sun, F., You, C., Percival Zhang, Y.H., 2014. A high-energy-density sugar biobattery based on a synthetic enzymatic pathway. Nat. Commun. 5, 3026.
Zi, Y., Wang, J., Wang, S., Li, S., Wen, Z., Guo, H., Wang, Z.L., 2016. Effective energy storage from a triboelectric nanogenerator. Nat. Commun. 7, 10987.