Chapter

Wearable Supercapacitors, Performance, and Future Trends

Litty V. Thekkekara and Imtiaz Ahmed Khan

Abstract

The progress in portable technologies demands compactable energy harvesting and storage. In recent years, carbon-based lightweight and wearable supercapacitors are the new energy storage trends in the market. Moreover, the non-volatile nature, long durability, eco-friendliness, and electrostatic interaction mechanism of supercapacitors make it a better choice than traditional batteries. This chapter will focus on the progress of the wearable supercapacitor developments, the preferred material, design choices for energy storage, and their performance. We will be discussing the integrability of these supercapacitors with the next generation wearable technologies like sensors for health monitoring, biosensing and e-textiles. Besides, we will investigate the limitations and challenges involves in realizing those supercapacitor integrated technologies.

Keywords: carbon, energy storages, E-textiles, health monitoring, biosensing

1. Introduction

Wearable technologies can be defined as intelligent devices that can be worn or attached to the skin's surface where they can detect, analyze and transfer the data to relevant systems [1]. The best example of E-textiles in the current market is sensors integrated apparels incorporating technologies like antennas, energy harvesters, and sensors [2]. These can enable the development of next-generation self-reliant wearable applications for wireless communications [3, 4], health sensing and monitoring [5–7], and light-emitting devices [8–10], which can find applications in smart cities, remote areas, telecommunications, and biomedical industries [11].

In the current commercial market, we can find more than 1000 types of wearables. Some of them include products from famous brands like Apple smartwatches which includes healthcare monitoring, fitness trackers from Garmin, integrated sensors in apparels from Nike and Adidas [12]. In the modern days, the research is focused on developing textiles itself as a sensor to monitor the body functions [13]. The expected market size of wearables is around $57,653 million by 2022 [14].

In general, energy harvesters like piezo generators, which utilizes the energy delivered from the mechanical motions within the body functions, or solar cells which harvest energy from the Sun are utilized as a medium of energy harvesters, and traditional batteries are used as energy storage in wearable devices [15–18]. Further, wireless charging is a promising concept for the powering of wearables [19]. However, current wearable technologies are limited for continuous monitoring due to the power failures from the integrated coin-cells or pouch cell lithium-ion batteries [20]. Besides, batteries are volatile and suffer from heating issues [21].

Flexible supercapacitors are an alternative energy storage to be considered for wearable technologies due to the features like fast charging nature, long durability, integrability with the technologies, and eco-friendliness [22–24]. In the chapter, we will discuss how supercapacitors can be used as energy storage for supporting wearable technologies and the challenges involved in it.

2. Performance

Supercapacitors are generally divided into two types: *symmetric and asymmetric* based on their working mechanism. Symmetric supercapacitors can store electrical energy through ion adsorption–desorption (electrical double layer capacitive, EDLC) mechanism. In contrast, asymmetric supercapacitors work through the Faradaic reaction (pseudocapacitive) between the electrode and electrolyte [25]. Besides, there are two types of configuration for the supercapacitors: (1) those have a vertical structure comprising a separator sandwiched between two electrodes are known as sandwich supercapacitors and (2) a micro supercapacitor (MSC) is based on an interdigitated structures in the same plane as the current collectors, separated from each other by an insulating gap (typically in the range of 10–100 s of micrometers) [26]. Finally, an electrolyte is coated on top and between the electrodes and ensures ion transport along the basal plane of the electrodes [27].

In MSC, the insulating gap between the electrodes and electrode width decides the migrating distance of electrolyte ions, which generates the equivalent series resistance (ESR) [28]. With the reduction of the ESR, the performance of the MSCs can be improved, and the calculation can be. The electrode thickness is another factor deciding the storage capacity of the MSCs [29]. The ESR energy storage capacity of the supercapacitors is defined through the energy density (E_{den}), and the rate of the charge transfer process, power density (P_{den}) is analyzed using measurements like cyclic voltammetry (CV), galvanic charge–discharge (CC), and impedance measurements [27].

The formulas for calculating the ESR, E_{den} (Wh cm^{-2}) and Pden (W cm^{-2}), can be defined as follows;

$$R_{ESR} = V_{drop} / 2i \tag{1}$$

$$E_{den} = C_v \times (\Delta E)^2 \times (2 \times 3600) \tag{2}$$

$$P_{den} = (\Delta E)^2 / (4ESR \times V) \tag{3}$$

where R_{ESR} is the internal voltage drop at the beginning of the discharge, V_{drop}, at a constant current density, i calculated from the CC measurements, C_v is the volumetric capacitance, ΔE is the operating voltage window in Volts, V is the volume of the electrodes.

3. Materials and designs

Materials and designs are an essential factor that decides the energy storage performance like flexibility, lightweight, storage capacity, how fast electrolyte ions can move within the device, and electrochemical window of the device [27, 30].

For wearables, a particular type of supercapacitors needs to be designed to match the above specific requirements. In this session, we will discuss these aspects in detail.

3.1 Materials

3.1.1 Electrodes

The electrodes of supercapacitors require high surface area, long term stability, resistance to electrochemical oxidation or reduction, the capability of multiple cycling materials, optimum pore size distribution, minimized ohmic resistance with the contacts, sufficient electrode-electrolyte solution contact interface, mechanical integrity, and less self-discharge [25, 27, 31].

EDLCs mainly utilize carbon-based materials for the electrodes due to their high performance [32]. One of the first EDLC developed employs activated carbon as the electrode material, which exhibited capacity values of 2 F cm^{-2} in H_2S0_4 solutions [33]. However, carbon exhibits slow oxidation, besides having high ESR. The low performance of carbon is due to poor particle to particle contact of the agglomerates as well as the high ionic resistance from the electrolyte distributed in the microporous structure, resulting in the poor high-frequency characteristics of carbon-based capacitors. On the other hand, the carbon nanotubes do not produce satisfactory capacitance unless a conducting polymer [34] is used to form a pseudocapacitance.

Graphene is a form of carbon with a high surface area up to 2675 m^2 g^{-1} and intrinsic capacitance of 21 μF cm^{-2}, which set the upper limit of EDLC capacitance of all carbon-based materials [35]. Besides, both faces of graphene sheets are readily accessible by the electrolyte. However, in practical applications, the surface area of graphene will be much reduced due to agglomeration. Graphene-related materials like reduced graphene oxide are cost-effective and widely used electrode materials for EDLCs [36].

Pseudocapacitors which are asymmetric supercapacitors using different materials like RuO_2, Manganese oxide (MnO_2), and conductive polymers like polyaniline (PANI) with or without the symmetric electrode materials, becomes a direction of interest to achieve the high-performance supercapacitors [37]. For example, the hybrid of ultrathin supercapacitors made of MnO2 sheets and graphene sheets using the direct laser writing method offers an electrochemically active surface for fast absorption/desorption electrolyte ions (22). The contributions of additional interfaces at the hybridized interlayer areas to accelerate charge transport during the charge/discharge process resulting in an energy density and power density of 2.4 mWh cm^{-3} and 298 mW cm^{-3}, respectively. Flexible supercapacitors based on manganese hexacyanoferrate-manganese oxide and electrochemically reduced graphene oxide electrode materials (MnHCF-MnO_x/ErGO) exhibiting a remarkable areal capacitance of 16.8 mF cm^{-2} and considerable energy and power density of 0.5 mWh cm^{-2} and 0.0023 mW cm^{-2} [38].

Another approach is to use metals like the well-connected nanoporous gold film to fabricate interdigital electrode materials for supercapacitors with high mechanical flexibility [39]. These supercapacitors exhibit a capacitance of 127 F cm^{-3} and an energy density of 0.045 Wh cm^{-3}. The gold metal is known for its high electrical conductivity, and the concept adopted can be effectively used to integrate with devices in a lesser aerial footprint.

3.1.2 Electrolytes

The electrolyte of supercapacitors has a crucial role in deciding properties such as the energy density, power density, internal resistance, rate performance, operating temperature range, cycling lifetime, self-discharge, non-volatile nature, and toxicity of the energy storage. The electrochemical range of an electrolyte decides the cell voltage window of the energy storage like the batteries and supercapacitors [25] and is governed by the equation,

$$E = \frac{1}{2} CV^2 \quad (4)$$

where E = energy density, C = specific capacitance and V = cell voltage.

The electrolytes used in energy storage can be classified as liquid electrolytes and solid/quasi-solid state electrolytes [40]. Liquid electrolytes can be further classified as aqueous electrolytes with a voltage range of 1.0 to 1.3 V, organic electrolytes within the voltage range of 1 to 2 V, and ionic liquids (IL) with a voltage range of 3.5 to 4.0 V [41]. The solid or quasi-solid state electrolytes can be classified as organic and inorganic electrolytes with a voltage range of 2.5 to 2.7 V.

Among different electrolytes, aqueous-based electrolytes possess high conductivity and capacitance. However, they are limited by low cell voltage windows whereas organic, and IL electrolytes can operate at higher cell voltage windows. ILs are used in wearable energy storage owing to their interesting properties like non-flammability, low vapor pressure, and significant operating potential window. Solid-state electrolytes are devoid of leakage issues but are limited by the low conductivity [42].

3.1.3 Designs

It is highly recommended to have an optimized design for supercapacitor electrodes for high output performance. In the commercial supercapacitors, sandwich structures in which electrode-electrolyte-electrode configuration is utilized [26]. Nevertheless, these designs can result in bulky storages, which is less favorable for lightweight wearable technologies.

On the other hand, the printed supercapacitor, based on 2D planar interelectrode configuration, is utilized as the basic designs for the printed electrodes. However, the performance is limited in comparison to the sandwich counterpart [43]. This has lead to the consideration of other designs like a spiral, split rings, and onion petals which demonstrated an increase in the electrode-electrolyte interactions in the supercapacitor [44]. A considerable enhancement in the storage capacitance and power density was offered with the utilization of the fractals designs [18], which can offer an unlock towards the development of high capacity miniaturized [23, 45, 46] as well as large scale supercapacitors that can be integrated with the textiles and other wearables [47].

The other area of recent interest in the designs is the origami concepts to improve the performance of the printed supercapacitors [48]. The research used the active materials in suitable geometry to create self-folding structures to perform folding or unfolding functions without having kinetic movements due to external forces.

3.1.4 Encapsulation

The wearable energy storage will be exposed to conditions like water moisture conditions from sweating, washing, weather conditions, and atmospheric pollution. All these conditions can adversely affect the performance of these energy storage. Besides, the presence of corrosive and volatile electrolytes can be dangerous to the user's health. Effective encapsulation is an essential condition to sustain a safer storage performance while maintaining a flexible nature [49–51]. Ecoflex and polyvinyl alcohol (PVA) are the standard encapsulations used for the current wearable energy storage [47, 52].

4. Types of wearable supercapacitors

4.1 Coin/pouch supercapacitors

The most commonly used energy storages for portable devices like smartwatches are the coin and pouch cells. Due to the well-developed production line for the long-used methodology, there is high interest in the adaptability of the technique with the extension towards the supercapacitors for the emerging wearable technologies [53–55]. Pooachi et al. recently developed prototypes of coin cells and pouch cells from nitrogen-doped reduced graphene oxide electrodes with phenylenediamine-mediated organic electrolyte with a high specific capacitance of 563 and 340 F g^{-1} with high energy density 149.4 and 77.2 Wh·kg^{-1} at 1 A g^{-1} [56].

4.2 Printed supercapacitors

A less complex solution to the energy storage demands of wearables, printed technologies offer highly adaptive methodologies for producing adhesion between the electrodes and current collectors/substrates and eliminates the requirement of inert additives for active materials. In general, supercapacitor printing techniques can be classified into two categories, techniques which do not require a template (example-inkjet printing and 3D printing) and techniques utilizing a template (example-screen printing). All these techniques must be coordinated with the printable materials for improving electrochemical and mechanical performance in a less footprint [57].

Among them, laser-induced graphene based supercapacitors attained exceptional attention due to the cost-effectiveness and ability to integrate with wearable applications in specific scales [58, 59]. Recently, demonstrated textile integrated solar graphene energy storages of 100 cm^2 with a performance of an areal capacitance, 49 mF cm^{-2}, energy density, 6.73 mWh cm^{-2}, power density, 2.5 mW cm^{-2}, and stretchability up to 200%, which can effectively be utilized for the realization of functional textiles to support applications like sensors, and displays [47, 60].

Printing high-performance supercapacitors in lesser footprints can develop three-dimensional (3D) supercapacitors [61]. The concept of the layer by layer stacking of individual supercapacitors obtained from the laser-induced graphenes from PET sheets which result in an areal capacitance >9 mF cm^{-2} [62, 63]. This methodology is a promising direction towards the future of energy storages to be considered for the ultra-portable and flexible applications. Besides, there are reports of using multilayered structures made of rGO/Au particles [64]. The development of additional features like stretchability up to 50% in 1000 stretch cycles with the 3D supercapacitors will contribute towards the withstanding of the deformations and prevention against the performance degradation [65].

Nonimpact printing technology like inkjet printing is an additive-based approach that can create patterns either continuously or in steps by propelling droplets of liquid precursor materials onto various substrates without the aid of predesigned masks through the control of printer head and ink toner [66]. The formation of printed features depends on the capability of the inkjet printing apparatus, the viscosity, surface tension, dispersibility of the inks, and the wettability of the substrates to be printed on [67]. Yu and co-workers reported paper-based, all-solid, flexible, planar supercapacitors by inkjet printing PEDOT: PSS-CNT/silver nanoparticle as the electrode material [68]. The obtained microdevices were able to demonstrate rate capability up to 10 000 mV s^{-1}, fast frequency response (relaxation time constant of 8.5 ms), high volumetric specific capacitance (23.6 F cm^{-3}), and long cycle stability (92% capacitance retention after 10, 000 cycles).

Screen printing is another approach for printing and is conducted through squeegee by pressing the ink down with enough force to penetrate through prepatterned masks (screen or stencil) onto the desired substrate [69]. The process can be conducted on both rigid (silicon or glass) and flexible substrates (textiles or papers) and can reach a minimum resolution of 30–50 μm [70]. The quality of the resulting features depends on the stenciling techniques, the printability of the inks, and the affinity between the ink and substrate. Even though this method is capable of mass production, some issues like printable ink must have a high viscosity, and suitable shear-thinning property limits the potential. Using this methodology, Lu et al. prepared an all-solid MSC by screen-printing FeOOH/MnO_2 composites on different substrates like PET, paper, and textile. The fully printed supercapacitor exhibits a high area-specific capacitance of 5.7 mF cm^{-2} and an energy density of 0.0005 mWh cm^{-2} at a power density of 0.04 mW cm^{-2} [71].

Roll to roll printing of supercapacitors through the low-temperature laser annealing process of roll-to-roll (R2R) printed metal nanoparticle (NP) ink on a polymer substrate is an area of interest that can have the largescale commercial applications [72]. Another approach is to laser-print the toner on metal foils, followed by thermal annealing in a hydrogen environment, finally resulting in the patterned thin graphitic carbon or graphene electrodes for supercapacitors. The electrochemical cells are made of graphene–graphitic carbon electrodes, which can be roll-to-roll printed [73].

4.3 Yarn based supercapacitors

E-textiles are the new frontiers in the history of fabrics that incorporate the technologies like displays and sensing [60, 74, 75]. Textiles or fabrics are flexible materials, which use fibers originating from natural or synthetic as fundamental building blocks, with a considerable length to diameter ratio (~1000 to 1) [76]. The fabrics can be in the form of staples or filament.

Natural fibers such as cotton staple fiber have a limited length. Filament fiber tends to be continuous in length, whereas silk is an example of a natural filament An example of synthetic fibers are filament fibers. Both staple fibers and threads can be made into yarns and fabrics. A more recent form of textile is electrospun, where the fabrication is achieved by applying a high voltage to an aqueous polymeric solution. The polymer can be organic or inorganic, depending on the intended application. *Yarn* is a long strand constituting textile fibers, filaments, or similar material converted to a textile fabric through weaving, knitting, or other intertwining techniques [77]. The yarn can be formed from various manufacturing processes. The spinning process is used to convert fibers into yarns, usually by twisting together several fibers. Usually, in spinning, fibers are aligned in one axis and are axially twisted. The direction of twist is denoted by 'S' or 'Z' twist.

When looking for 2D fabric devices such as supercapacitor devices, the usual architecture found in the sandwich [78] and in-plane (planar) configurations [79]. The in-plane architecture is more flexible than its sandwich structure counterpart due to its lightweight and flexibility (structural design), making it a more suitable option when working with 2D active electrode materials [80]. In the case of 1D yarn supercapacitors, common existing device shapes include coaxial [81], core-spun [82], parallel [83], two-ply twisted [84], and helical structures [85].

5. Future trends—scalability and integration of wearable supercapacitors

The major hindrance of the current wearable energy storage to be commercialized is its limitation for large-scale fabrications to meet the power requirements of integrated technologies [86]. Besides, for textile-based wearable technologies, another challenge is developing a single textile unit incorporating energy storage and devices together. The achievement of cost-effective all-in-one wearable technologies without compensating the performance of the technologies is a great challenge in this area [87–96]. Some fo the research groups demonstrated the laboratory protoypes in this area and in **Figure 1**, we summarized these studies.

Only a few groups so far that reported about the possibilities of developing their energy storages can be developed into self-powered wearable technologies using the industrial machinery because of the low performance [97]. Besides, the cost-effectiveness of the process needs to be attractive in comparison to the existing battery technology. Nevertheless, the development of printing methodologies like screen printing [56], inkjet printing [61], and laser printing seems to be a solution to the stitching issues currently faced by the yarn-based energy storages. The successful generation of high-performance flexible, lightweight, miniaturized supercapacitors will enable a step closer to realizing eco-friendly, non-volatile portable and wearable devices.

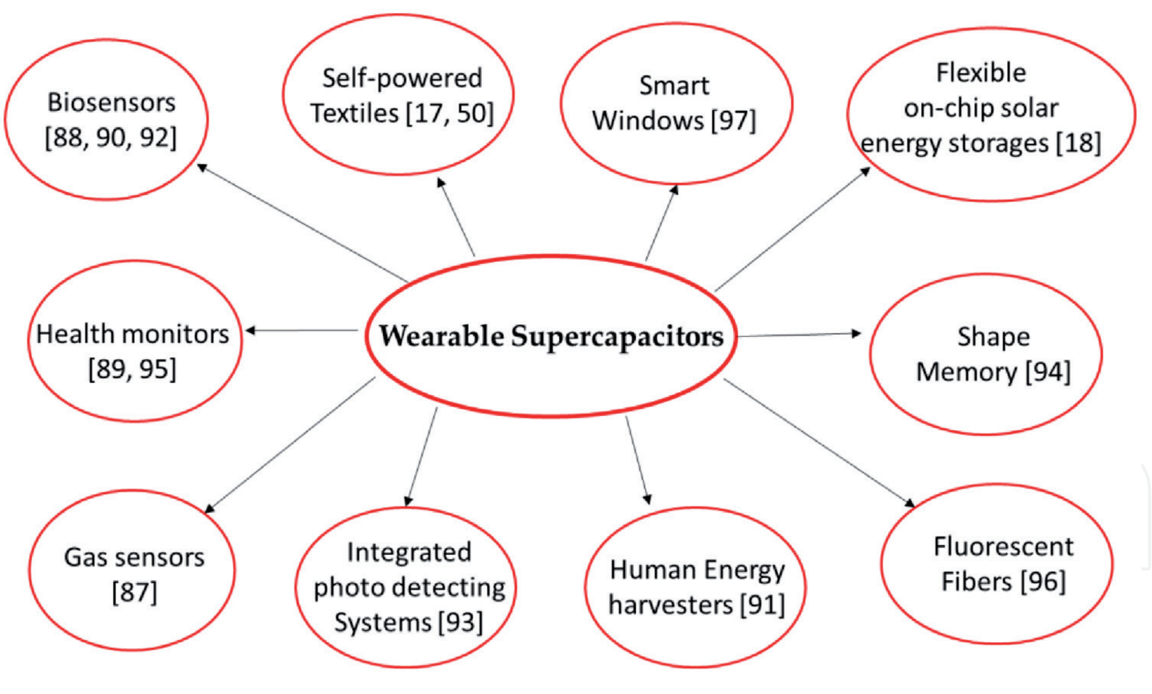

Figure 1.
Applications benefited from the wearable supercapacitors.

6. Conclusions

Supercapacitors which leaves the further possibilities of miniaturization without compromising the high energy storage capacity and transfer rate provides the scope of improvement to be adopted as an eco-friendly, non-voltaile energy storage source for the future wearable technologies.

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Conflict of interest

The authors declare no conflict-of-interest declaration.

Appendices and nomenclature

MSC	Microsupercapacitor
EDLC	Electrochemical double layer capacitance

Author details

Litty V. Thekkekara[1,2]* and Imtiaz Ahmed Khan[1]

1 Department of Manufacturing, Materials and Mechatronics, School of Engineering, RMIT University, Melbourne, Australia

2 Functional Materials and Microsystems, Department of Electronic and Telecommunications, School of Engineering, RMIT University, Melbourne, Australia

*Address all correspondence to: littyvarghese.thekkekara@rmit.edu.au

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