Chapter

Supercapacitors: Fabrication Challenges and Trends

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Abstract

Supercapacitors have shown great potential as important complements to batteries. We first describe the principle of supercapacitors, including the categories and the main components of supercapacitors. In the second part, we compare the advantages of supercapacitors with other energy storage devices, and then the power densities of active materials are compared with each other. In the third part, we show how various technologies are used to fabricate electrodes and supercapacitors. In the last part, several applications are presented, showing the high value of supercapacitors, including hybrid vehicles, solar cells, and wearable and portable devices.

Keywords: supercapacitors, energy storage, portable devices, wearable devices

1. Introduction

The urgent need for renewable energy sources has resulted in concerted research efforts into electrochemical energy storage. Capacitors can maintain power for a long time, according to the following equation:

$$E = \frac{1}{2} CV^2 \tag{1}$$

where C is the capacitance and V is the applied voltage [1]. However, even though capacitors have been known to scientists for many centuries, conventional capacitors still have values at pF and uF/cm^2, which are far from energy storage requirements. When applying capacitors to energy storage, the capacity of capacitors must be increased, which are known as supercapacitors. Following developments over the past decade, supercapacitors have shown great promise for next-generation energy storage devices [2]. Supercapacitors feature a high power density [3], fast charge and discharge capacity, environmental friendliness [4], safety, and a long life cycle [5], allowing them to be used as important complements to batteries [6]. To promote the application field of supercapacitors for researchers, in this chapter, we introduce the main characteristics of supercapacitors, including categories, components, advantages, fabrication, and applications. Moreover, we discuss future application trends.

In the first section, we introduce the types and main components of supercapacitors, which can be separated into three categories: (1) double-layer capacitors [7], (2) pseudo-capacitors, and (3) hybrid supercapacitors [8], which consist of active materials, collectors, separators, and electrolytes. Conductive metal-organic frameworks operate as collectors, while the active materials are the main components that determine the power density of supercapacitors. Separators are composed of fibers and polymers, while ions are the main components of the electrolytes. Moreover, we illustrate the structure of supercapacitors and compare the power densities in different active materials. **Table 1** shows the various supercapacitors and their power densities. The MnO_2 and NiO are the most popular oxide metals with the high energy density, and they usually worked with the graphene and carbon nanotubes (CNTs) to fabricate the hybrid supercapacitors. As can be seen, both the flexibility and stretch ability are common parameters in advanced supercapacitors; however, the high energy density hardly achieved in the supercapacitors compared to the Li-batteries.

Comparing with other energy storages, this chapter exhibits many advantages, including the long-term cycling stability, high safety, and power density, which make them promising candidates for energy storage in many applications.

No	Active materials	Parameters	Capacitance	Applied voltage	Reference
1	AU/MnO_2	Transparency, flexibility	524 F/g	2 V	[9]
2	AU/MnO_2	Transparency, flexibility	1370 F/g	1.5 V	[10]
3	CNTs/PANI	Flexibility	243 F/g	0.8 V	[11]
4	AU/MnO_2	Transparency, flexibility	3.68 mF/cm^2	1 V	[12]
5	Ni-Co oxide/ MnO_2	Stretchability	0.77 F/cm^2	1 V	[13]
6	NiO/carbon	N/A	317 F/g	0.5 V	[14]
7	rGO-PPY	Flexibility	232 mF/cm^2	0.8 V	[15]
8	Nitrogen-doped graphene	Stretchability	806 F/cm^3	1 V	[16]
9	GO@PPY	Flexibility	419 mF/cm^2	1 V	[17]
10	Self-doped lignin-based biocarbon	Flexibility	140 F/g	1 V	[18]
11	Multi-walled CNTs	N/A	671 F/g	0.7 V	[19]
12	PPY@rGO	N/A	882.2 F/g	1 V	[20]
13	GO@carbon aerogel@MnO_2	Micro	8.7 mF/cm^2	1 V	[21]
14	PEDOT: PSS	Flexibility, deformability	232 mF/cm^2	1 V	[22]
15	Multi-walled CNTs	Flexibility, stretchability, and self-charging	167 mF/cm^2	0.9 V	[23]
16	PPY	Stretchability and micro-characteristics	221.2 mF/cm^2	0.6 V	[24]
17	PPY	Flexibility	203 mF/cm^2	0.8 V	[25]

No	Active materials	Parameters	Capacitance	Applied voltage	Reference
18	GO@-MnO_2	Micro	1100 F/cm^3	1 V	[26]
19	CNTs	Flexibility/ stretchability	0.6 mF cm^{-2}	2.5 V	[7]
20	PPY@graphene	Flexibility	89.6 mF/cm^2	1.4 V	[27]
20	PPY	Transparency	5.6 mF/cm^2	0.6 V	[28]
21	Ag/NixFeyOz@ rGO	Transparency	282.1 uF/cm^2	4 V	[8]
22	Carbon fiber	Flexibility	246.1 F/g	1.8 V	[29]
23	PPY	Micro	128 mF/cm^2	1 V	[30]
24	GO/CNTs	Flexibility	269 mF/cm^2	2.5 V	[31]
25	GO	Environmentally friendly	173.8 F/g	1 V	[4]
26	ZIF-L (Zn)@ $Ti_3C_2T_x$	Flexibility	854 F/cm^3	1 V	[32]
27	MnO_2@TiN NWs@CNTs	Flexibility	61.2 mW h cm^{-3}	3.5 V	[3]
28	NiO@graphene	Micro-characteristics	605.9 mF/cm^2	0.8 V	[33]
29	PANI/N-CNTs@ CNTs	Flexibility	323.8 F/g	0.8 V	[34]

Table 1.
Parameters of various main supercapacitors.

In this chapter, we present the advanced achievements of supercapacitors over the past 5 years, and we overview the technologies used for fabricating supercapacitors, including lithography, laser writing, inkjet printing, template sacrifice, and physical and chemical vapor deposition.

We also present an overview of applications where supercapacitors have been widely used such as in vehicles and other storage buffers. We describe the stretchable and flexible supercapacitors in wearable devices. We also present wirelessly rechargeable flexible supercapacitors used in soft and smart lenses. The later have shown potential applications for implantable and wearable medical devices. Moreover, we present supercapacitors that may be completely biodegradable and bioabsorbable, which has never been achieved in other power storage devices. As complementary storage for batteries, supercapacitors are becoming increasingly important in several applications.

PANI, polyaniline; GO, graphene Oxide; PPY, polypyrrole; CNTs, carbon nanotubes; PEDOT, poly(3,4-ethylenedioxythiophene); PSS, polystyrene sulfonate.

2. The categories of supercapacitors and main components of supercapacitors

There are three types of categories (**Figure 1**), depending on the charge storage mechanism. (1) The first one is double-layer capacitors [35], which form capacitance using double large electrodes, consisting of a physical process. The sandwich structure forms capacitance, according to the following equation:

$$C = \varepsilon s / d, \quad (2)$$

where C is the capacitance and is determined by ε, s, and d, where s is the area of the two electrodes, d is the thickness between them, and ε is the permittivity of the electrolyte. The capacitance will also be different between capacitors and supercapacitors. The active materials consist of CNT, graphene, and a conductive polymer with a large area that is stable during the charge and discharge process. (2) For pseudo-capacitors [36], the energy storage in pseudo-capacitive comes from the surface redox reaction [2] between the metal oxide and conductive polymers, as they generally have many oxidation states that can absorb and emit electrons such as Ni oxide, Co oxide, Mn oxide, and Co oxide. (3) Hybrid supercapacitors, which mix double-layer capacitors and pseudo-capacitors, have more advantages than each individual type. They exhibit a high charge ability and an increase in the capacitance compared with double-layer capacitors, resulting in good performance with high cycle and charge abilities, with the same high capacitance as pseudocapacitors. Based on the discussion mentioned earlier, the hybrid supercapacitors are future trend to overcome the limitation of power density and applications. The supercapacitors can be divided into different categories, and they all have the same components, including collectors, separators, electrolytes, and active materials, with designed pore space for active materials.

2.1 Collectors

Conductive metal-organic frameworks operate as collectors and can be regarded as the supporting components for capacitors. To fabricate metal-organic frameworks, various approaches can be used, which can be divided into bare metal foam, sacrificial templates, micro/neon network structures with in situ deposition, and free-standing fiber films through electrospinning. Cellulose and self-doped multi-porous lignin-based biocarbon with a three-dimensional network structure are frameworks that can be used as the substrate of a solid-state flexible supercapacitor. The shape design of anodic aluminum oxide (AAO) and nanomesh template [37] have shown excellent nanostructures and mechanical properties, making them suitable for the fabrication of supercapacitors with many properties, exhibiting easy fabrication, versatility, and a high surface area. Sacrificial polystyrene colloidal particles [19] and cube sugar were shown to increase the power intensity with a large specific surface area per mass volume for the electrodes. The metal coating on the pre-electrospinning fiber film resulted in the formation of metal-framework networks, with a process to fabricate a larger area collector with auto-fabrication. Other approaches have also

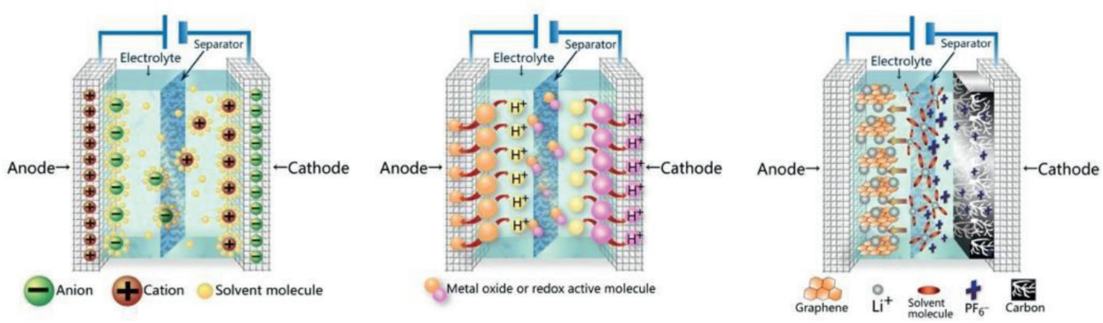

Figure 1.
Three categories of supercapacitors and they consist of collectors, active materials, separators and electrolytes.

been used, such as wrinkled graphene on polydimethylsiloxane [7], as well as crackle and leaf templates, which have been used to fabricate metal frameworks with deposited conductive metals. The shape design of collectors is more suitable used in various fabrications and applications due to its higher energy density.

2.2 Separators and electrolyte

Separators are filters through which ions migrate in and out, and they can reject connections between two electrodes. Resistance and stability are the key parameters for separators. Many types of commercial separators are available, which consist of fiber separators, high polymer separators, electrospinning separators, and biological separators. The poly(vinyl alcohol) (PVA), which is a high polymer separator, has shown high conductivity, biodegradability, and high alkaline stability. PVA-based gels in aqueous electrolytes have been researched for solid-state supercapacitor applications and fuel cells. However, PVA-based gels have some limitations in aqueous solutions, i.e. the voltage window should be under or equal to 1 V. Researchers have now focused on finding inorganic ceramic solid-state electrolytes. Polyacrylonitrile (PAN) is a type of electrospinning separator that has shown great shrinkage and porosity, with many applications. In addition, studies have been conducted on biological separators, such as egg shell membranes [38], fish bubbles [39], and other biological separators. Furthermore, separators should be stretchable, stable, and in a staining state in flexible and stretchable supercapacitors, which has shown to be a challenging property in separators. Electrolytes consist of a conductive liquid mixture containing an aqueous or organic solvent, based on active materials and ions that include OH^-, H^+, Li^+, Na^+, K^+, SO_4^{2-}, and Cl^- [40]. The concentration of ions and the PH value have shown the impact of power intensity in supercapacitors, and the less volume ions performed better in the transfers with less impedance.

2.3 Active materials

Depending on the charging mechanism, active materials can usually be divided into four categories. (1) Carbonaceous materials include CNTs, graphene, and its allotrope, where graphene is mainly based on double-layer capacitance, which utilizes only the surface of the electrode material; however, the capacitance of bare carbonaceous will be relatively small, limiting the applications of supercapacitors. (2) Metal oxides, especially Ni oxide, Co oxide, Mn oxide, and Co oxide, include MnO_2 [12], NiO, Co_3O_4, and $Co(OH)_2$ [13], and these metals have many energy levels [41], which can easily absorb and emit some electrons. Furthermore, the power density of these metal oxides is the largest among all active materials; however, they have shown poor high cycle and charge abilities, as well as environmental pollution. (3) Conductive polymers include polypyrrole (PPY) [24], polyaniline (PANI) [11], polythiophenes (PYH), polyphenylenevinylene (PPA), and polyacetylene (PA). These conductive polymers have shown good mechanical properties, easy fabrication, power density, and environmental friendliness. (4) Composites of the aforementioned active materials have shown better performance in all of these parameters, especially a higher power density, better mechanical properties, and charge and cycle abilities. These materials include graphene@ MnO_2, PPY@NiO, Graphene@PPY film, C@TiN [3], and ZIF-Li(Zn)@TisC2Tx [32]. Comparing the performances of the single active materials, the association of the different active materials shows the promising candidates in power storages.

2.4 Designed pore space for active materials

The power density relies both on the active materials and pore space of the active materials. The optimization of the structure of active materials and dynamics of ions at

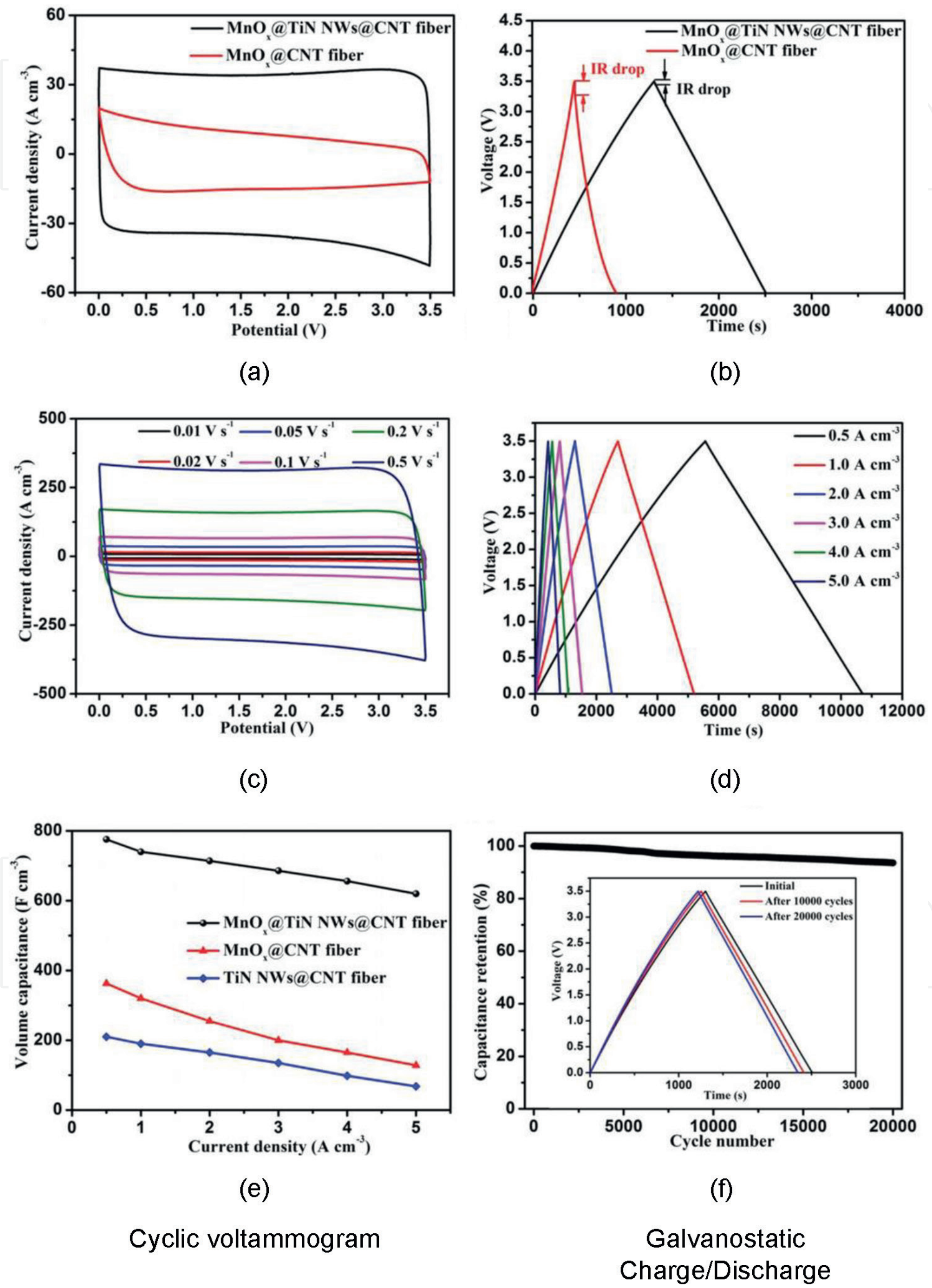

Figure 2.
(a) and (b) CV curves and GCD curves of two different fiber electrodes, (c) CV curves under different scan rates, (d) GCD curves at different current densities of the MnOx@TiN NWs@CNT fiber electrode, (e) comparison of volumetric capacitances versus different current densities for three different fiber electrodes, and (f) cycling stability of the MnOx@TiN NWs@CNT fiber electrodes as a function of cycle number under a current density of 2.0 A cm^{-3} [3].

the electrode-electrolyte interface are the two promising routes for enhancing the electrochemical performance of supercapacitors [2]. The immobilized ions diffuse into the electrolyte, which not only is the key parameter for the supercapacitors, but also affect the impedance of the supercapacitors. For controlling the diffusing rate, researchers have designed and fabricated various superior architectures, including fabricating 3D structures [27], which include MXenes structures, core-sheath fibers, asymmetric fiber structures [3], and hierarchical nanoarrays. The synthetic strategy of hierarchical nanoarrays [33] can be used as a template for the epitaxial growth of secondary structures by controlling the reaction condition using a one-pot strategy to fabricate the hierarchical structure. Studies have shown that three-dimensional structures will increase the surface area considerably, especially in shape design structures. The asymmetric fiber structure has shown high potential applications because of multidimensional stacking and winding, resulting in unbelievable capacitance and power density values. **Figure 2** shows the different parameters of the supercapacitors, and **Figure 2a** and **c** shows the stability performance in the cyclic voltammetry curves at different scan rates. The charge and discharge curves of the different supercapacitors at different current densities are shown in **Figure 2b** and **d**, where the volumetric capacitances were calculated from the charge and discharge rates as a function of the current density in different capacitances (**Figure 2e**). **Figure 2f** shows the stability of supercapacitors, indicating the performance of the supercapacitors under different current and voltage values, which can be used to design the pore space and select the suitable active material.

3. Supercapacitors offer many advantages compared with other energy storage devices

Traditionally, batteries are the main energy storage centers in devices, with a hard shell and the toxicity of the electrolyte in coin cells. Compared with lithium-ion batteries, the cell configurations of supercapacitors will be much simpler and safer due to the use of water or polymer gel electrolytes instead of flammable and moisture-sensitive organic electrolytes. Furthermore, the fast and highly reversible double-layer capacitive and/or pseudocapacitive energy storage mechanism of supercapacitors will enable a significantly better high-power capability and cycling stability compared with lithium-ion batteries. Even if the lower energy density of supercapacitors restricts the wide application of supercapacitors, due to their superior high-power performance, long-term cycling stability, and high safety, supercapacitors have been regarded as promising candidates for energy storage in some applications, as introduced in the following section.

3.1 High safety

Compared with ion batteries, which use toxic electrolytes with a hard shell, many biocompatible electrodes can be used in supercapacitors, with a more moderate electrolyte. Some supercapacitors can exhibit self-degradation, biodegradation, and bioabsorption [42] with no effects on the body, making them extremely suitable for some implantable devices.

3.2 Long-term cycling stability

The lifetime of Li-ion micro-batteries is typically less than 1000 cycles, with charges retention higher than 98% after 1000 charge-discharge cycles in supercapacitors. Generally, these materials have lifetimes of over 100,000 cycles with excellent recharge rate capabilities.

3.3 Power performance

The power density is different in various active materials. For PPY, the capacity can reach 230 mF/cm^2, while for MnO_2, the capacity can reach as high as 570 F/g, and asymmetric micro-SC has a maximum volumetric energy density. The supercapacitors shown high-power density with many other advantages, the low-energy density limits their applications. The future trend of supercapacitors is still to overcome this drawback and find the active materials with more energy density. For energy transform devices, the unstable voltage supplied by energy harvesting limits their applications; thus, we will not compare their performance.

4. Technologies for fabricating supercapacitors

Various structures can be observed supercapacitors, including sandwich structures, interdigitated structures, MXene fiber structures, and core-shell structures. Sandwich structures generally consist of one, composed of two electrodes surrounding a separator at its center, with numerous technologies available to build electrodes, which can be further packaged into sandwich structures. Some supercapacitors, especially micro-supercapacitors, may not require separators, as the electrodes can be fixed without a connection between them. In this section, we list some methods for designing and fabricating electrodes and decorating active materials in sandwich and interdigitated structures.

4.1 Lithography

Lithography has been used to design and fabricate interdigitated circuit chips with an ultra-nanoscale size, making it extremely easy to fabricate micro-supercapacitors. Using lithography, the supercapacitor can integrate a circuit chip on the silicon wafer. These types of supercapacitors do not require separators, as they do not contain a short circuit with a fixed and hard substrate. Porous silicon and an interdigitated shape are generally used, as they exhibit a large area. Researchers have also designed and fabricated various flexible and transparent supercapacitors on special templates using lithography.

4.2 Electrospinning

Electrospinning can be used to fabricate a designed nanoscale space pose, making it suitable for the electrodes of supercapacitors. Long nanofibers have been produced into a thin film through electrospinning, and then metals were coated or deposited onto the surfaces of these pre-electrospinning films, where the diameter and thickness of these films could be controlled by the diameters of the nanofibers.

4.3 Inkjet printing

Dedicated inks consisted of metal nanoparticles, CNTs, and graphene, and after mixing with the gel, these inks could be injected and printed onto the template surface, forming an active material. They can usually be fabricated in the shapes of interdigitated electrodes to increase the active area.

4.4 Laser scribing

Various micro- and nanofabrications can be used to build supercapacitors. Direct laser writing also offers the potential to realize a lower cost and largely scalable fabrication [43]. For the preparation of active materials films, which are composed of CNT, metal oxides, and graphene, lasers have generally been used to fabricate interdigitated electrodes, with large capacitors.

4.5 Electrophoretic deposition, electrolytic deposition, physical/chemical vapor deposition, and spurting

Many methods are available to attach electrodes with active materials, such as electrophoretic deposition, electrolytic deposition, physical/chemical vapor deposition [44], and spurting. The substrate and collectors can be deposited by atmospheric application, where the active materials will be deposited on the conductive metal-organic frameworks. The same method has also shown to be suitable for use in conductive polymers, which are also one of the main active materials with high quality and stability.

4.6 Sacrificial template

In terms of geometries, key design considerations can be used to increase the surface areas of electrodes, where a sacrificial template is used to increase the area of the electrode. These sacrificial templates include AAO film, polystyrene colloidal particles film, and cube sugar. Template films can be built with sacrificed nanoparticles, which can be dissolved with the target reagent. Pre-curve PDMS has usually been used as the supporting film, while the AAO template has also shown to be a fantastic sacrifice film with a controllable shape, on the nanoscale [30].

4.7 Transfer printing technologies and screen printing

Transfer printing and screen printing are mature technologies that transfer the shape from the donor wafer to the receiving substrate. After printing, the inks will be released from the stamp to form the desired functional layouts on the receiver substrate. The inks for transfer printing include various organic materials and carbon materials, which can be used to fabricate the flexible and stretchable circuits and supercapacitors [45].

Over the discussion mentioned earlier, many technologies have already been used to design and fabricate the supercapacitors; however, the main works is still focusing on increasing the energy density of the active materials and shape designing for active materials. These new fabrications technologies are hopefully to increase the density of the supercapacitors with suitable active materials.

5. Applications of supercapacitors

As a power storage technology, there are still many challenges for the practical applications of supercapacitors, and the major drawback of supercapacitors is their low energy density. Significant efforts have been made to improve their performance. Unlike work on main power storage systems, supercapacitors have shown to be more important as battery complements, especially due to the many advantages of supercapacitors compared with lithium-ion batteries, such as a highly charge ability, long-term stability, and power density, as well as flexibility, transparency, microscale, and stretchability. Furthermore, the ions and electrolyte are both the key considerations at the electrode-electrolyte interface for various applications. The biocompatible electrolytes and ions are more suitable for solid-state and stretch ability supercapacitors using in wearable applications, while the highly diffusing rate of ions can be used in hybrid electric vehicles and solar cells with low impedance. The dynamic of the ion at the electrode-electrolyte interface endows electrochemical energy storage apparatuses. Finally, there are many applications, and we list some important samples, including portable electronics [43], solar cells, hybrid electric vehicles [46], and wearable devices [5, 47].

5.1 Vehicles

Vehicles are common devices, as fossil fuels are no longer sustainable and result in significant pollution. To achieve efficient energy management systems [6], combination of batteries and supercapacitors has been proposed, as the supercapacitor can absorb energy from braking and provide energy when powered on, and these electrochemical energy storage apparatuses are based on the highly diffusing rate at the electrode-electrolyte interface with high energy or power density, long lifetime, and high safety insurance. This energy management system has been used in many electronic buses, and the same saving power technology has been used in elevators and trains.

5.2 Integration of solar cells and supercapacitors

Solar energy [48] is the main energy source for all plants and humans, with a major utilization of solar energy relying on photovoltaic technology; however, this process is unstable because solar radiation is intermittent and unstable [49], which can destroy the lifetime of solar cells and devices. Advanced approaches have been proposed using electric energy storage systems, where the integration of supercapacitors and solar cells [50] consisted of three parts, namely, dye-sensitized solar cells, perovskite solar cells, and organic solar cells. Overall, supercapacitors have shown the potential to be next-generation power sources [51], especially for providing power supply over a short amount of time and working as an energy buffer and integrating with other power storage systems.

5.3 Supercapacitors for wearable devices

Wearable systems offer a considerable amount of health information, such as heart rate, electrocardiogram, and activity data, and these devices have rapidly gained market approval. Driven by the rapid growth of portable and wearable electronics, significant research attention has been focused on the development of energy storage devices. Traditionally, energy is stored in Li-ion micro-batteries; however, their lifetime usually imposes the need for costly and impracticable maintenance, and the integrated devices and immune reactions restrict periodic part replacements. Furthermore, the hard shell and toxicity of the electrolyte in coin cells will be harmful

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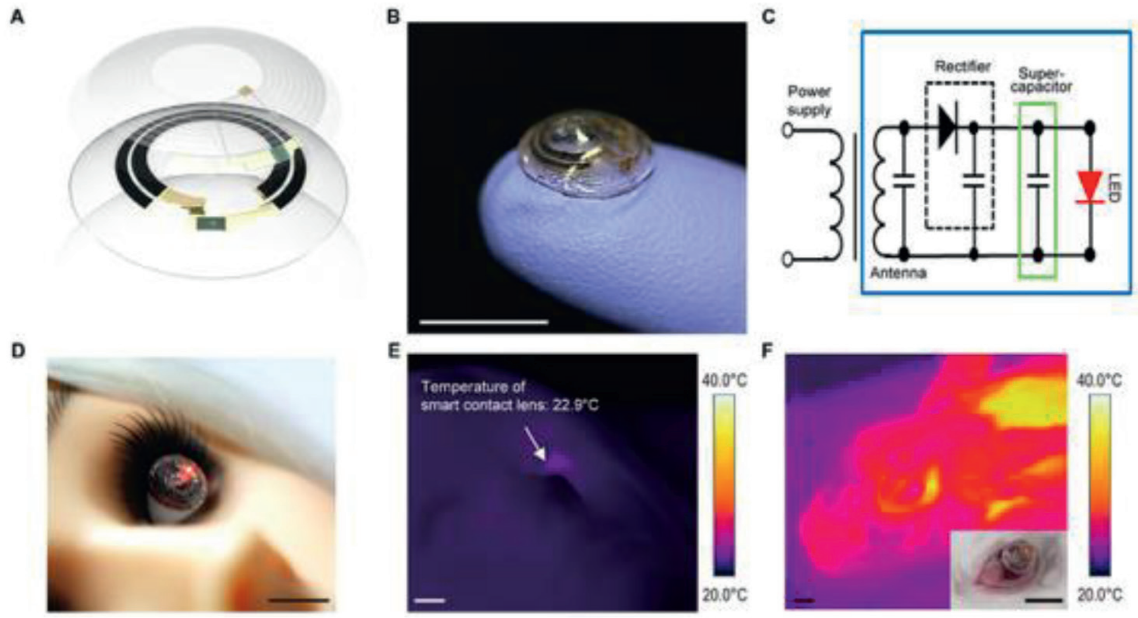

Figure 3.
Smart soft contact lens with wireless charge supercapacitor: (a) illustration of integrated contact lens, (b) photograph of the fully integrated device, scale bar 1 cm, (c) circuit diagram of supercapacitor recharge, (d) photograph of contact lens on an eye of a mannequin, scale bar 1 cm, (e) infrared radiation image of this contact lens on an eye of a mannequin, scale bar 1 cm, and (f) infrared radiation image and photograph (inset) during the discharging state on the eye of a live rabbit eye, scale bar 1 cm [52].

to organisms. The need for power for wearable electronics has motivated the development of suitable replacements. Supercapacitors are promising candidates for portable and wearable devices [37], as they should be light in weight, compact in size, and high in energy density and have a lifetime of over 100,000 cycles with excellent recharge rate capabilities. Furthermore, the biocompatible electrolyte and mild reactions at the electrodes-electrolyte interface shows highly potential being the batteries complements and new generation power storages, including remote sensors [23], implantable biosensors [52], and nanorobots. As can be seen, **Figure 3** is a sample supercapacitor application with integrated soft, smart contact lens with wireless charge supercapacitors. In this system, the supercapacitor worked as a complementary storage system for the lens, and it could charge with an antenna from the power supply. Moreover, supercapacitors may be completely biodegradable and bioabsorbable, which have never been achieved in other power storage systems [42].

6. Conclusions

Supercapacitors are devices for energy storage systems, which shown great potential as important complements to batteries. These devices consist of collectors, electrodes, active materials, separators, and electrolytes. We introduced the principle and components of supercapacitors, and then we compared the advantages of supercapacitors with other energy storage systems. In the third part, the approaches for supercapacitor fabrication were described. Finally, as complementary storage for batteries, supercapacitors are becoming increasingly important in certain applications. The applications of supercapacitors for electronic devices were described, indicating that supercapacitors may be more suitable for use in wearable and portable devices.

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Conflict of interest

The authors declare no conflict of interest.

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