Batteries & Supercaps
Minireviews
doi.org/10.1002/batt.202000333
Chemistry Europe
European Chemical Societies Publishing

Special Collection

Recent Progress and Application Challenges of Wearable Supercapacitors

Ming Ren,[b] Jiangtao Di,[b] and Wei Chen*[a, c]

The rapid development of wearable electronics has accelerated the development of wearable energy storage devices. Wearable supercapacitors have aroused widely interest due to their large power density. However, there are still many challenges in the practical application of wearable supercapacitors. This paper summarizes the structure, working mechanism, materials and key parameters of wearable supercapacitors. And we reviewed the challenges of wearable supercapacitors in practical applications, namely safety, mechanical adaptability, self-charging capability, environmental tolerance, and multifunction. Finally, these challenges are summarized and prospected. We hope to inspire some work to solve the practical application challenges of wearable supercapacitors.

1. Introduction

Recently, portable devices, wearable electronic devices, flexible displays, the Internet of Things, sensors and microchips are developing rapidly.[1] The use of these wearable devices cannot be separated from the continuous supply of energy. Therefore, energy storage devices are a very critical component in wearable electronic devices.[2] Among energy storage devices, electrochemical energy storage has attracted wide attention as an efficient, clean, stable, and safe energy storage method. According to different energy storage mechanisms, electrochemical energy storage can be divided into battery energy storage and supercapacitor energy storage. Compared with battery energy storage, supercapacitors have great advantages in terms of power density and cycle stability, which has caused extensive research.[3,4] The rapid development of wearable electronic devices also puts forward many requirements for supercapacitors. However, the traditional supercapacitors are large and hard, which cannot meet the requirements of application in the field of wearable electronic devices. Therefore, high-performance portable wearable supercapacitors have been developed. Such wearable supercapacitors have the characteristics of good volumetric energy density, lightness and flexible, which are very important for wearable electronic devices.[5]

In 2003, Baughman et al. reported on supercapacitors based on carbon nanotube fibers, which could already be woven into fabrics.[6] This is the first time that the concept of flexible supercapacitor was proposed, more than ten years ago. Flexible supercapacitors have made great progress. In terms of structure, 1D fibrous and 2D planar flexible supercapacitors have been developed.[7] Electrode materials have also evolved from nano-carbon materials or conductive polymers to composite electrode materials.[8] And the hydrogel electrolytes,[9] organic gel electrolytes,[10] and ionic liquid gel electrolytes[11] have been developed. A large number of review papers on wearable supercapacitors have been reported. Cheng et al. discussed the electrode materials of stretchable supercapacitors, and detailed the stretchability and electrochemical properties of 1D, 2D, and 3D supercapacitors. In addition, they also introduced multifunctional supercapacitors and the integration of stretchable supercapacitors with other energy conversion devices.[12] Li et al. introduced in detail the development of flexible solid-state supercapacitors in materials (electrodes and electrolyte), structure (symmetrical and asymmetrical), and potential applications, and made a prospect for the development of flexible supercapacitors.[3] However, in current practical applications, flexible supercapacitors still face many challenges in wearable electronics, making them unsuitable for industrial production and application. It mainly includes the challenges of safety, environmental tolerance, mechanical adaptability, and self-charging capability of flexible supercapacitors. At present, a detailed overview of the key issues of wearable supercapacitors in practical applications has not been reported.

In this paper, we reviewed the basic situation of flexible supercapacitors, including the structure, working principle, and key parameters of performance evaluation; We focused on the progress and challenges of wearable supercapacitors in practical applications, including: safety, environmental tolerance, mechanical adaptability, Self-charging capability, and multifunction; Finally, we look forward to the future development of wearable supercapacitors.

[a] Prof. W. Chen
Research Centre for Smart Wearable Techanology,
Institute of Textiles and Clothing
The Hong Kong Polytechnic University
Hung Hom, Kowloon, Hong Kong 999077, P. R. China
E-mail: weii.chen@polyu.edu.hk
[b] M. Ren, Prof. J. Di
Key Laboratory of Multifunctional Nanomaterials and Smart Systems,
Advanced Materials Division
Suzhou Institute of Nano-Tech and Nano-Bionics,
Chinese Academy of Sciences
Suzhou 215123, P. R. China
[c] Prof. W. Chen
The Hong Kong Polytechnic University Shenzhen Research Institute
Shenzhen 518057, P. R. China

Special Collection An invited contribution to a Special Collection dedicated to Metal-Ion Hybrid Supercapacitors

2. Structures and Materials of Wearable Supercapacitors

2.1. Structure

Structurally, wearable supercapacitors include current collectors, electrodes, electrolytes, and separators.[8] At present, composite materials are widely used in wearable supercapacitors. These composite materials have good electrical conductivity and can act as electrode active materials and current collectors at the same time.[13] The electrolyte of wearable supercapacitors is mostly a gel electrolyte layer with good mechanical and shape stability,[7] which could separate electrode materials and avoid short-circuiting of the electrodes. According to different structures of wearable supercapacitors, it can be mainly divided into two-dimensional planar wearable supercapacitors and one-dimensional fiber wearable supercapacitors,[7] as shown in Figures 1 a and b. The planar wearable supercapacitor has a sandwich structure, which is formed by sandwiching an electrolyte layer between two electrodes. And it has a simple structure and is easy to prepare. Fiber wearable supercapacitors are mainly divided into: (1) a coaxial structure containing inner and outer electrodes (Figure 1b top) and (2) a structure with two electrodes placed in parallel and coated with an electrolyte layer (Figure 1b). The fiber wearable supercapacitors are easily integrated into fabrics through weaving or knitting.[7,14] With the development of printed electronics technology, microsupercapacitors have also been widely studied.[15] Generally, Microsupercapacitors include flexible substrates, interdigitated electrodes, and electrolyte layers (Figure 1c).

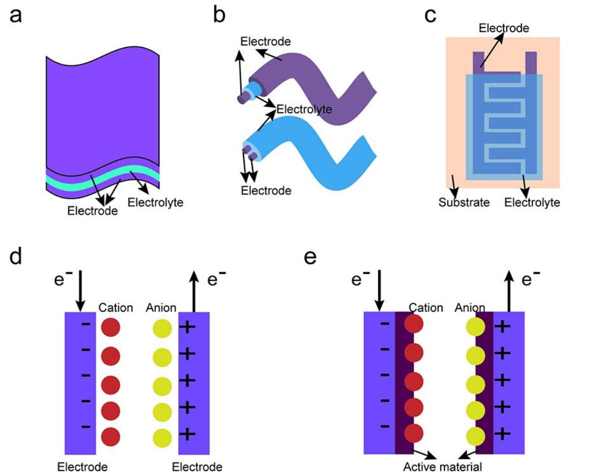
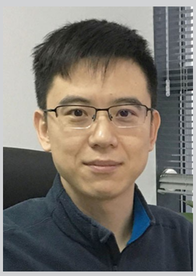


Figure 1. The schematic illustration of the structure and the charge storage mechanism of the wearable supercapacitors. a) Planar supercapacitor. b) Fiber supercapacitors. c) Microsupercapacitors d) Electrochemical double-layer capacitors. e) Pseudocapacitors.

2.2. Charge Storage Mechanism

According to the mechanism of charge storage, the wearable supercapacitors can be divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors.[8,16] The ions in the EDLCs are stored in the electrolyte near the interface between the electrode and the electrolyte (Figure 1d). This process mainly relies on the migration of ions in the electrolyte, so the wearable supercapacitors have a high power density and a good stability of cyclic charge and discharge. However, its energy density is low. Pseudocapacitors are mainly based on the active materials. The active material undergoes a reversible redox reaction, and ions are stored on the electrode surface (Figure 1e). Therefore, the pseudocapacitor has a high specific capacitance. However, since the speed of oxidation-reduction reaction is slow than that of the ion migration speed relatively,

Ming Ren obtained his B.S. degree from Hefei University of Technology in 2017. He currently performs PhD studies in School of Nano-Technology and Nano-Bionics, University of Science and Technology of China. His current research focus on wearable electronic device, including wearable supercapacitors and wearable actuators.



Prof. Jiangtao Di received his PhD degree from Chinese Academy of Sciences in 2013. From 2013 to 2016, he joined in the University of Texas at Dallas as a research assistant. In 2016, he joined in Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences as a professor. His current research focus on nano-carbon materials, including artificial muscle yarn, supercapacitors, and electrocatalysis.

Prof. Wei Chen obtained his Ph.D. from Chinese Academy of Sciences in 2001. From 2001 to 2006, he had a postdoctoral position at University of Science and Technology of China and Hong Kong Polytechnic University. From 2006 to 2018, he was a professor of Materials Science at Suzhou Institute of Nano-tech and Nano-bionics, CAS. He now is a full professor at Hong Kong Polytechnic University. He is internationally recognized for his leading research work in nanotechnology-based smart materials, including artificial muscle actuators, sensors, supercapacitors, generators, and functional systems for wearable applications.

the power density is low. Since the insertion and extraction of ions will change the volume of the electrode, the stability of cyclic charge and discharge is poor, and the conductivity of the electrode material is poor also.[17]

2.3. Materials for Wearable Supercapacitors

Research on materials for wearable supercapacitors mainly focuses on electrode materials and electrolyte materials. According to the different working mechanisms of wearable supercapacitors, electrode materials can also be divided into two categories: electrode materials based on the mechanism of EDLCs and pseudocapacitors. The electrode materials of EDLCs supercapacitors mainly include nano-carbon materials (carbon nanotubes,[18] graphene,[19,20] MXene,[21,22] activated carbon).[23] The electrode materials of pseudocapacitors mainly include transition metal oxides/sulfides (Mn_3O_4,[10] MnO_2,[24] NiO, CoS_2),[25] conductive polymers (PANI,[26] PPy,[27] PEDOT:PSS)[28] and composite nanomaterials.[9,13,29] The capacitive and mechanical properties of electrode materials are critical to the performance of wearable supercapacitors.

Gel electrolyte with good flexibility and ionic conductivity has a great influence on the safety, temperature tolerance, and fast charge-discharge performance of wearable supercapacitors. At present, gel electrolytes can be divided into three types: hydrogel electrolytes, organic solvent gel electrolytes and ionic liquid quasi-gel electrolytes. Hydrogel electrolytes usually include polyvinyl alcohol (PVA)- acid/alkali/salt systems (such as PVA/H_3PO_4,[6] PVA/H_2SO_4,[19] PVA/KOH,[25] or PVA/LiCl[29]), cellulose/KOH,[23] or Vinyl silica nanoparticles-polyacrylic acid/H_3PO_4.[9] Hydrogel electrolyte has high safety, but the operating voltage window is low, which limits the energy density of wearable supercapacitors. Organic solvent gel electrolytes (such as PMMA-PC-$LiClO_4$)[10] have a large operating voltage window, but organic solvents are easy to volatilize, and devices based on organic solvent gel electrolytes may explode at high temperatures. Ionic liquid gel electrolyte (for example: PVDF-HFP/$EMIBF_4$,[24] polyoxymethylene/nitrile butadiene rubber/$EMIBF_4$)[13] has a low vapor pressure and a wide electrochemical window. However, ionic liquid gel electrolytes generally have a higher price, and the ionic conductivity of ionic liquids is relatively low. We have summarized the materials and performance parameters of wearable supercapacitors, as shown in Table 1.

2.4. Key Parameters of Performance Evaluation

The specific capacitance, the energy density, the power density, the cycle life, and the charge and discharge rate. are the key parameters for evaluating the performance of the wearable supercapacitors.[3,17] These parameters are usually tested by the methods of cyclic voltammetry (CV), Galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation. The specific capacitance (C) of the wearable supercapacitor can be calculated according to CV curve using the following formula:[5]

$$C = S/2\,m\Delta V$$

Where S is the integral area of the CV curve, m is the mass of active materials of electrodes, and ΔV is the change of the working potential.

The specific capacitance can also be calculated according to the GCD curve using the following formula:[16]

$$C = I\Delta t/m\Delta V$$

Where I is the discharge current, Δt is the discharge time, m is the mass of active materials of electrodes, and ΔV is the change of the working potential.

The energy density (E) and power density (P) can be calculated by following formula:[5]

$$E = C\Delta V/2$$

$$P = E/\Delta t$$

Where C is the specific capacitance, ΔV is the change of the working potential, and Δt is the discharge time.

3. Application Challenges of Wearable Supercapacitors

3.1. Safety

Used in the wearable field, so the safety of supercapacitors is the primary consideration. At present, researchers have done gratifying work in the selection of biocompatible materials, packaging technology, and temperature analysis under high currents. However, there are still many challenges to face in the development of flexible capacitors Since it is used close to the skin, biocompatible materials are one of the best choices for constructing supercapacitors. Cellulose is a biodegradable material with good biocompatibility, environmental friendliness, and low price. It is very important in flexible supercapacitors. Shen et al. prepared a high-performance composite electrode using natural bacterial cellulose. In this electrode, cellulose is used as a flexible substrate, multi-walled carbon nanotubes are used as the conductive layer, and electrodeposited polyaniline is used as the active material (Figure 2a). It shows a good specific capacitance, which is 656 $F\,g^{-1}$ at a discharge current density of 1 $A\,g^{-1}$. After 1000 cycles of charging/discharging at a discharge current of 10 $A\,g^{-1}$, the capacitance attenuation is less than 0.5 %.[30] In order to reduce the proportion of inactive materials, while ensuring the porosity of the electrode material. Wang et al. reported a cellulose fabric-based electrode. Cellulose fabric was used as the substrate, through in-situ polymerization, a layer of dopamine is deposited on the surface of the fabric as a binder, and

Table 1. Typical results of wearable supercapacitors.

Function type	Electrodes	Electrolytes	Specific capacitance	Energy density	Cycling stability	Ref.
Flexible	CNT fiber	PVA/H_3PO_4	5 F g^{-1}	0.6 W h kg^{-1} at 1 V	1,200 charge-discharge cycles	[6]
Bending	Graphene/CNT core-sheath fibres	PVA/H_3PO_4	177 mF cm^{-2}	3.84 mWh cm^{-2} @ 0.1 mA cm^{-2}	1000 cycles with bending angles of 180°	[20]
Flexible	MWNT/Mn_3O_4	PMMA–PC/$LiClO_4$	8.9 F cm^{-3} @ 0.1 A cm^{-3}	1.0 mWh cm^{-3}	1000 cycles of CV measurements in water for 3 h	[10]
Bending	Graphene fiber/ 3D graphene	PVA/H_2SO_4	1.7 mF cm^{-2}	1.7×10^{-7} Wh cm^{-2}	500 straight-bending cycles	[19]
Bending and twisting	Black phosphorous/carbon nanotubes	PVDF-HFP/$EMIBF_4$	308.7 F cm^{-3}	96.5 mWh cm^{-3}	1000 cyclic under bending at 180° angles	[11]
Bending	Continuous CNTs wired ZIF-8	Polyoxyethylene/ nitrile butadiene rubber/ $EMIBF_4$	190 F g^{-1} @ 1 A g^{-1}	59.40 Wh kg^{-1} @ 1 A g^{-1}	500 bending cycles	[13]
Biodegradable	Carbonized rGO/PDA/ cellulose textile	PVA/LiCl	1208.4 mF cm^{-2} (10.1 F cm^{-3})@ 1 mA cm^{-2}	–	4000 cycles at a high current density of 10 mA cm^{-2}	[29]
Biodegradable	Activated carbon	Mesoporous cellulose/KOH	191.66 F cm^{-3} at 10 mV s^{-1}	6.655 mWh cm^{-3}	1000 cycles at a scan rate of 200 mV s^{-1}	[23]
Biodegradable	PEDOT:PSS	polyester cellulose cloth/real human sweat	8.94 F g^{-1} (10 mF cm^{-2})@ at 1 mV s^{-1}	0.25 W h kg^{-1}	4000 cycles	[28]
Stretchable	CNT sheets wrapped elastic fiber	PVA/H_3PO_4	20 F g^{-1}	0.515 Wh kg^{-1} @ 0.05 A g^{-1}	1000 charge-discharge cycles under a strain of 75 %	[37]
Stretchable	$NiCo_2S_4$/CoS_2/ stainless-steel mesh	PVA/KOH	169.4 F g^{-1}	75.3 mAh g^{-1} @ 1 A g^{-1}	30 % strain for 1000 stretching cycles	[25]
Self-healing and stretchable	PPy@CNT paper	Vinyl silica nanoparticles-polyacrylic acid/ H_3PO_4	–	–	20 cycles of breaking/healing	[9]
Self-healing	PPy-gold nanoparticle/ CNT/poly (acrylamide) hydrogel	Gold nanoparticle /poly(acrylamide)	885 mF cm^{-2}	123 μWh cm–2	ten healing cycles	[44]
Self-charging	Carbon fiber felt-SWCNT-cellulose	Polarized PVDF/ $EMIBF_4$	8.8 mF g^{-1} @ 0.04 mA cm^{-2}	16.32 mWh kg^{-1}	80 charging and discharging cycles	[50]
Temperature resistant	Graphene	Montmorillonite/ PVA/ H_2SO_4	~80 F g^{-1} @ 50 °C and ~140 F g^{-1} @ 90 °C	–	–	[51]
Sensing	Gradually Crosslinking Carbon Nanotube Array	PVA/H_3PO_4	93.2 mF cm^{-2}	–	1900 compressive cycles	[57]
Shape-memory	TiNi alloy flake as the negative electrode and MnO_2/Ni film as the positive electrode	PVDF-HFP/$EMIBF_4$	25.9 F g^{-1}	22.4 Wh kg^{-1}	18 cycles of CV scanning during a whole dynamical shape memory process	[24]

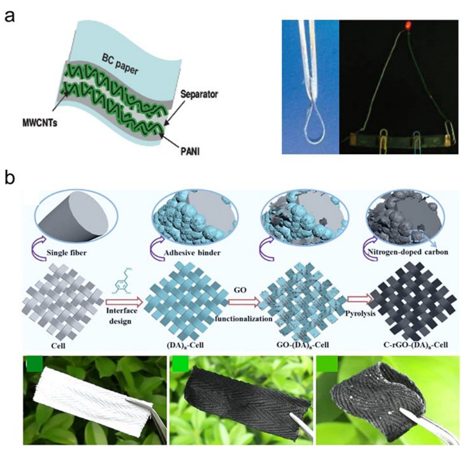


Figure 2. Supercapacitor based on biocompatible electrode materials. a) A schematic structure and the optical images of flexible supercapacitor device based on cellulose-MWCNTs-PANI. Reproduced with from Ref. [30] with permission. Copyright 2014, Wiley–VCH. b) Schematic illustration of the interface designed cellulose textile electrode. Reproduced from Ref. [29] with permission. Copyright 2020, Elsevier.

graphene oxide is used as the active material (Figure 2b). The specific surface area of this electrode reaches 347.6 $m^2 g^{-1}$. The specific area capacitance of the electrode reaches 3100 mF cm^{-2}. When assembled into a solid supercapacitor, the area specific capacitance still has 1208.4 mF cm^{-2}.[29] In addition to its application in composite electrodes, cellulose has also been used in polymer electrolyte membranes. Yu et al. reported a cellulose mesoporous electrolyte membrane. They first prepared a cellulose mesoporous membrane by phase inversion, which has good porosity and electrolyte carrying capacity (Figure 3a). The flexible all-solid-state supercapacitor assembled with the electrolyte membrane and active carbon electrode shows good stability, and the capacitance still retains 84.7 % after 10,000 long cycles.[23] Zhao et al. reported a chitosan/ sodium alginate polymer electrolyte with an ionic conductivity of 0.051 S cm^{-1} and a tensile strength of 0.29 MPa (Figure 3b). By forming an all-solid supercapacitor with polyaniline nanowires, it has a specific capacitance of 234.6 F g^{-1} at a scan rate of 5 mV s^{-1}, and the specific capacitance can still maintain 95.3 % after 1000 cycles.[31] Jiang et al. reported a very interesting work. They prepared an edible supercapacitor. In

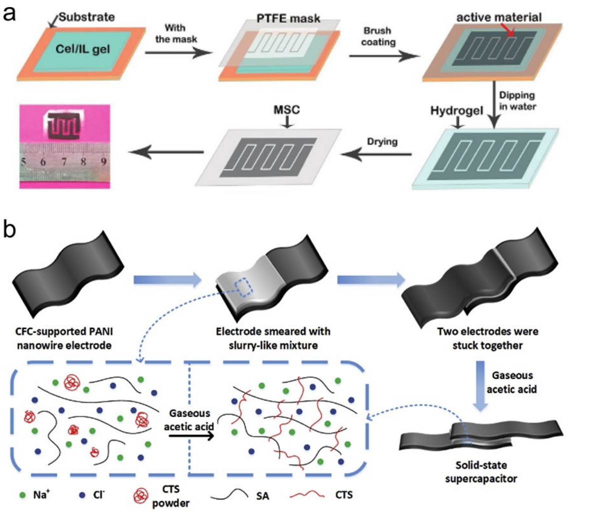


Figure 3. Supercapacitor based on biocompatible electrolyte materials. a) Schematic diagram of the preparation of the cellulose-membrane-based supercapacitor. Reproduced from Ref. [23] with permission. Copyright 2017, Wiley-VCH. b) Schematic diagram of the fabrication process of the solid-state supercapacitor with a polyelectrolyte complex hydrogels electrolyte and the sol-gel transition process of the polyelectrolyte complex hydrogels. Reproduced from Ref. [31] with permission. Copyright 2018, Elsevier.

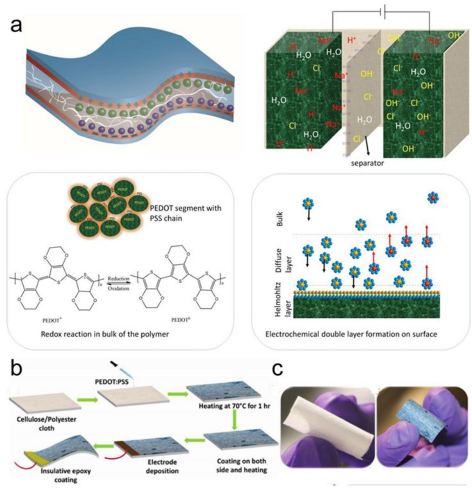


Figure 4. The wearable supercapacitor based on PEDOT:PSS-coated cloth and a sweat electrolyte. a) Schematic representation and mechanism of the sweat as an electrolyte for wearable supercapacitors. b) Scheme for the fabrication of PEDOT:PSS-based electrodes on cloth. c) Photographs of the cloth before (left) and after (right) PEDOT:PSS coating. Reproduced from Ref. [28] with permission. Copyright 2020, The Authors.

this work, gelatin is used as encapsulation, edible gold leaf is used as current collector, functional drink is used as electrolyte, seaweed is used as separator, and cheese is used as segregation layer, and egg white is used as binder. Finally, a specific capacitance of 78.8 $F\,g^{-1}$ was achieved. When glutamate was added to the electrolyte, the capacitance was optimized to 129 $F\,g^{-1}$. At a discharge current density of 1 $A\,g^{-1}$, the maximum power density is about 9.5 $Wh\,kg^{-1}$.[32]

As a part of supercapacitors, electrolyte is also the object of research by researchers. Organic electrolyte is flammable and corrosive, and its use in wearable devices can cause huge safety hazards to the human body. The other type of inorganic aqueous electrolyte has better safety. Sweat contains a lot of positive and negative ions, which is a natural non-toxic electrolyte. Dahiya et al. recently reported a supercapacitor based on sweat (Figure 4). In this capacitor, sweat is used as the electrolyte, polyester cellulose fabric is used as the base and diaphragm material, and PEDOT:PSS is used as the active electrode. Polyester cellulose fabric has good sweat absorption capacity, and PEDOT:PSS has good biocompatibility and other characteristics. This electrode has a specific capacitance of 8.94 $F\,g^{-1}$ (10 $mF\,cm^{-2}$) at a scan rate of 1 $mV\,s^{-1}$. When artificial sweat is used, at 1.31 V, the energy density and power density of the supercapacitor are 1.36 $Wh\,kg^{-1}$ and 329.7 $W\,kg^{-1}$, respectively. When using real human sweat, the power density and energy density attenuate to 0.25 $Wh\,kg^{-1}$ and 30.62 $W\,kg^{-1}$, respectively.[28] The low voltage window of the inorganic electrolyte severely limits the energy density of water-based supercapacitors, which is still a problem to be solved.

In addition to using materials with good biocompatibility, packaging of capacitors is also a very important method to improve the safety of the device. Good packaging can avoid electrolyte leakage, avoid direct contact between the human body and electrodes or electrolyte, improve its safety, and at the same time extend the service life of the device and improve its environmental tolerance.[7,33]

When the supercapacitor is quickly charged and discharged under high current, the temperature inside the device will increase.[34] A large amount of heat will cause oxidation-reduction reaction on the surface of the electrode material or decomposition of the electrolyte, which will accelerate the aging failure of the device and even cause an explosion.[35,36] therefore, high-current rapid charge and discharge has a greater impact on the safety of supercapacitors.

3.2. Mechanical Adaptability

During the wearing process, the device will inevitably be bent, twisted and stretched. Therefore, the device needs to have good mechanical adaptability and maintain stable performance during the deformation process.

Bendable and twistable: Chen et al. designed a continuous phase MOF porous carbon material electrode. A layer of MOF structure is grown in situ on the surface of carbon nanotubes. This electrode has a high specific surface area given by MOF and flexibility given by carbon nanotubes. After being assembled with the electrolyte layer to form a flexible supercapacitor, it shows good mechanical flexibility. Whether it is twisted or 10% tensile deformation, the performance can be maintained stably, especially when it is bent in the range of 0–180°, CV curve almost coincide (Figure 5a).[13] Wu et al. reported a black phosphorus composite fiber non-woven fabric electrode prepared based on microfluid spinning technology. Due to the existence of the non-woven fabric electrode structure, the flexible supercapacitor assembled by this electrode material has a higher energy density (96.5 $mWh\,cm^{-3}$) and stable

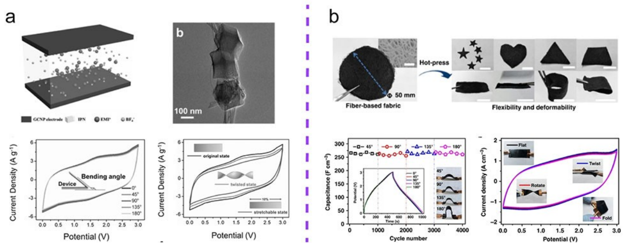


Figure 5. a) Electrochemical properties and flexibility performance of the supercapacitor based on continuous phase MOF porous carbon material electrode. Reproduced from Ref. [13] with permission. Copyright 2017, Wiley–VCH. b) Flexibility, stability and application of supercapacitors based on black phosphorus composite fiber non-woven fabric electrode. Reproduced from Ref. [11] under the terms of the Creative Commons License. Copyright 2018, The Authors.

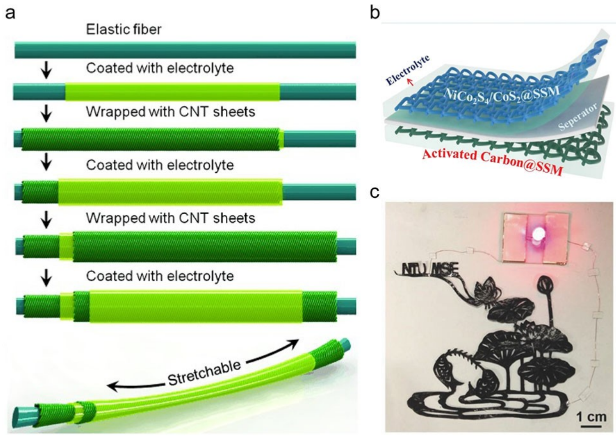


Figure 6. The stretchable supercapacitors. a) The fabrication of the stretchable fibrous supercapacitor. Reproduced from Ref. [37] with permission. Copyright 2013, Wiley-VCH. b) The stretchable supercapacitor device based on the woven two-dimensional network electrode structure. Reproduced from Ref. [25] with permission. Copyright 2020, Wiley-VCH. c) The stretchable supercapacitor tailored into more complicated and delicate paper-cutting. Reproduced from Ref. [41] with permission. Copyright 2017, Wiley-VCH.

deformation energy supply capacity. After 1000 cycles of 180° bending, the capacitance can still maintain 97.4% (Figure 5b).[11]

Stretchable: There are two main methods for preparing stretchable supercapacitors: (1) Supercapacitors made of intrinsic elastic materials. (2) Supercapacitor with stretchable structure.

Peng et al. first reported a stretchable fibrous supercapacitor. They sequentially covered elastic fibers with PVA gel electrolyte and CNT sheet electrode layers (Figure 6a). After 100 cycles of 75% stretching, this supercapacitor has a capacitance of 18 $F\,g^{-1}$.[37] Chen et al. reported a supramolecular gel electrolyte, and formed an integrated stretchable supercapacitor by in-situ polymerization of high concentration aniline on the surface of the gel electrolyte, which has good stretchability.[38] Chen et al. used 2-acrylamide-2-methylpropane sulfonic acid (AMPS) and N,N-dimethylacrylamide (DMAEMA) as monomers, and lithium algae earth (Laponite) and graphene oxide (GO) as double cross-linking agent, and synthesized a double cross-linked poly-(AMPS-co-DMAEMA)/Laponite/GO polymer composite hydrogel through a simple free radical copolymerization reaction. The hydrogel electrolyte is assembled with carbon nanotubes or its composite film electrode materials to form a stretchable supercapacitor. When stretched to 1000%, the capacity retention rate of the device is 97%.[39] The main defect of this preparation method is that due to the different moduli of the electrode and the electrolyte, the interface layer between the electrolysis and the electrolyte is easily broken during the stretching process.

Shao et al. reported a stretchable supercapacitor with a woven two-dimensional network electrode structure. They chose a stainless steel wire with a diameter of 50 μm to be woven into a two-dimensional network structure. This network structure is composed of stainless steel fiber coils nested together, which has excellent stretchability and stretch recovery. The active material is grown on the surface of the stainless steel network structure by hydrothermal method as the electrode material, and the electrode is assembled into a supercapacitor (Figure 6b). Under the current density of 8 $A\,g^{-1}$, the capacitance decreased by 6.8%, 12.5%, and 23.6% after 1000 cycles at 10%, 20%, and 30% tensile strain, respectively.[25] Niu et al. designed a wrinkled electrode based on SWCNT film and assembled a highly stretchable supercapacitor based on this electrode. When stretched by 200% and cyclically stretched, the device can still maintain excellent performance.[40] Chen et al. reported a honeycomb-shaped supercapacitor structure. They first prepared the MnO_2/CNT composite electrode, and then assembled it with PVA gel electrolyte to form a supercapacitor, and then the supercapacitor was shear-patterned (Figure 6c), and the specific capacitance reached 227.2 $mF\,cm^{-2}$. And it can be stretched 500% without reducing electrochemical performance.[41] The disadvantage of this method is that the tensile recovery of the prepared stretchable supercapacitor is low.

3.3. Self-Healing Capability

External physical damage (such as scratching, piercing, cutting) will cause great damage to the safety and reliability of energy storage devices. The self-healing capability of the device can solve this problem well. Self-healing means that when the device receives physical damage from the outside, it restores its energy storage properties without external stimulation. Gao et al. prepared an intrinsically stretchable and rGO-based fiber spring. The fiber was used as a stretchable electrode, and a self-healing polyurethane hydrogel was used as an electrolyte layer. The assembled supercapacitor had both stretchability and self-healing. The results shown that when stretched by 100%, the capacitance is preserved by 82.4%, and after 3 times of self-repair, the capacitance is preserved by 54.2%.[42] Pan et al. reported a supercapacitor with an integrated structure. They use common polyvinyl alcohol as raw materials, and through quaternary ammonium salt graft modification to alleviate the problem of salting out of polyvinyl alcohol. Then they integrated activated carbon, acetylene black and potas-

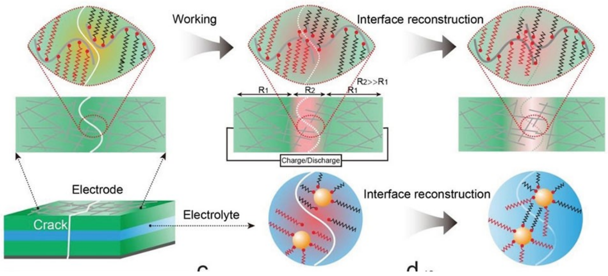


Figure 7. The real-time healing mechanism of the GCP@PPy based device during the charge-discharge process. Reproduced from Ref. [44] with permission. Copyright 2019, Wiley-VCH.

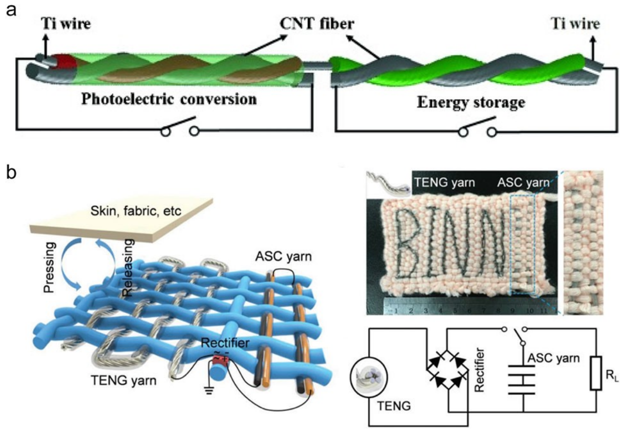


Figure 8. a) The photoelectric conversion and energy storage integrated fibrous devices. Reproduced from Ref. [46] with permission. Copyright 2012, Wiley-VCH. b) Schematic diagram of self-charging fabric and the equivalent circuit of the self-charging system uses the energy harvesting fabric. Reproduced from Ref. [49] with permission. Copyright 2019, Wiley–VCH.

sium chloride into the polyvinyl alcohol supramolecular framework to form a capacitor with an electrode/electrolyte/electrode integrated structure. After the supercapacitor is cut off, the electrode, electrolyte, and electrode/electrolyte interface can be repaired in all directions within 3 minutes by simple contact. The self-healing process can be repeated for at least 15 cycles.[43] Yu et al. reported a highly tough, highly conductive gold nanoparticle/carbon nanotube/polyacrylamide/polypyrrole nanocomposite hydrogel (GCP@PPy) and assembled it into a stretchable, self-healing flexible Supercapacitor. The hydrogel is chemically cross-linked by gold nanoparticles and has excellent tensile properties. Based on the dynamic interaction of gold-sulfur coordination bonds, it can reorganize polymer chains under the stimulation of near-infrared light and electric current to achieve self-healing (Figure 7). The assembled device shows high capacitance stability, and the capacitance retention rate is still 89.5% at 800% tensile strain. And under the condition of near-infrared light, it still maintains excellent capacitance performance after 10 healing cycles. At the same time, it has self-healing ability during charge and discharge.[44] The problem for reported self-healing supercapacitors is that after healing, the capacitance retention rate is low, and the healing cycle is less.

3.4. Self-Charging Capability

The durability of energy storage severely limits the application of wearable electronic devices, and repeated charging has seriously affected the user's willingness to use. Self-charging can solve this problem well. At present, it is mainly realized by integrating supercapacitors with energy harvesting devices such as solar cells, biofuel cell or triboelectric nanogenerators (TENG), or introducing piezoelectric layers in supercapacitors to realize integrated self-charging devices.[45]

Peng et al. proposed and developed fibrous photoelectric conversion and energy storage integrated devices.[46] In a typical fibrous integrated device, the photoelectric conversion and energy storage unit share a titanium wire electrode. One end of the titanium wire electrode is coated with a photoelectric conversion active material, and the other end is coated with an electrochemical energy storage material. Then, the CNT fiber is used as another electrode (Figure 8a). Through a simple and low-cost method, photoelectric conversion and energy storage can be realized on one fiber at the same time. The overall photoelectric conversion and storage efficiency of this novel wire device is 1.5%. This integrated device fiber can be easily integrated into electronic textiles and used as a self-powered system for portable microelectronic devices and equipment.

Wang et al. prepared an integrated system of energy harvesting and storage by integrating supercapacitors with biofuel cells. The device mainly includes supercapacitors and biofuel cell module printed on both sides of the flexible fabric. The biofuel cell module is close to the wearer's skin, which can collect biochemical energy from the wearer's sweat. The supercapacitor module is based on MnO_2/CNT composite electrode material and LiCl/PVA gel electrolyte, which store the energy collected by biofuel cells. The composite system can provide a high power density of 252 mW cm^{-2}.[47]

Hu et al. reported a self-charging fabric integrated with yarn-based energy harvesting TENG and supercapacitors based on energy storage yarn. The nickel-plated polyester yarn is used as the conductive substrate, and rGO is used as the active material of the two electrodes. TENG can collect mechanical energy during movement, and supercapacitors can store the collected energy. The device has high specific capacitance (72.1 mF cm^{-2}), stable cycle performance (96% capacitance retention rate in 10,000 cycles), high areal energy density (1.60 μWh cm^{-2}).[48] Compared with symmetrical supercapacitors, asymmetrical supercapacitors using different active materials on the two electrodes can have a larger potential window, thereby significantly increasing the energy density. Hu et al. reported a self-charging fabric made of yarn-based energy harvesting TENGs and energy storage yarn-type asymmetric supercapacitors, (Y-ASC). The ordinary polyester yarn with nickel/copper coating was used as the one-dimensional current collector of Y-ASCs and the electrode of TENGs (Figure 8b). The solid Y-ASC has high areal energy density (78.1 Wh cm^{-2}), high power density (14 mW cm^{-2}), stable cycle performance (82.7%

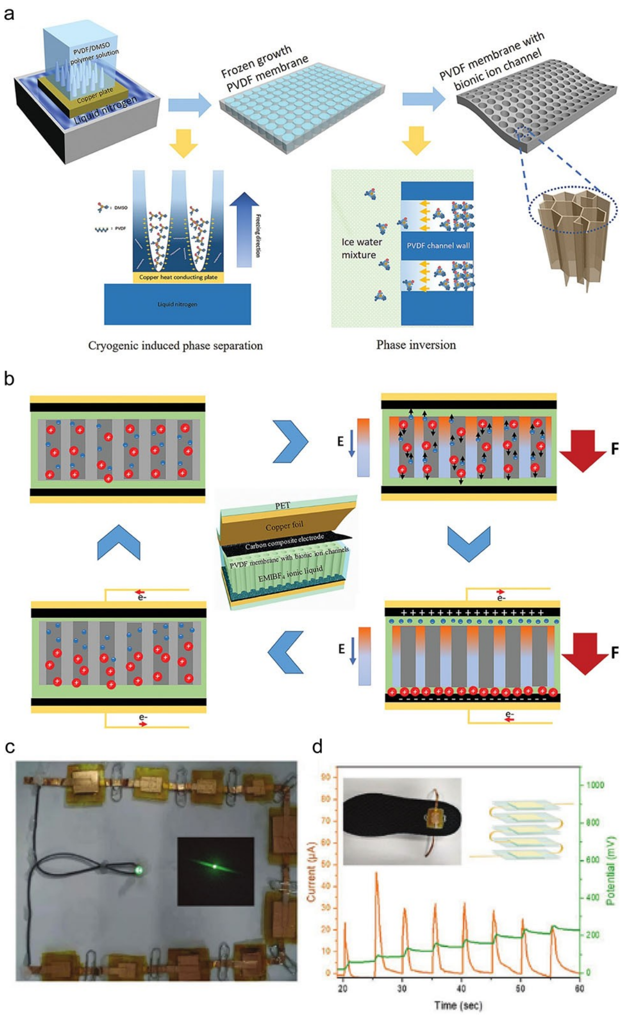


Figure 9. The self-charging supercapacitor based on piezoelectric electrochemistry. a) Formation of internal bionic ion channels. b) Principle of power generation of ion piezoelectric generator. c) A green LED is powered by successively pressing the series of supercapacitors. d) Performance of folded series supercapacitors placed in the insole at low frequency pressure (Frequency = 0.2 Hz, force = 150 N). Reproduced from Ref. [50] with permission. Copyright 2020, Wiley-VCH.

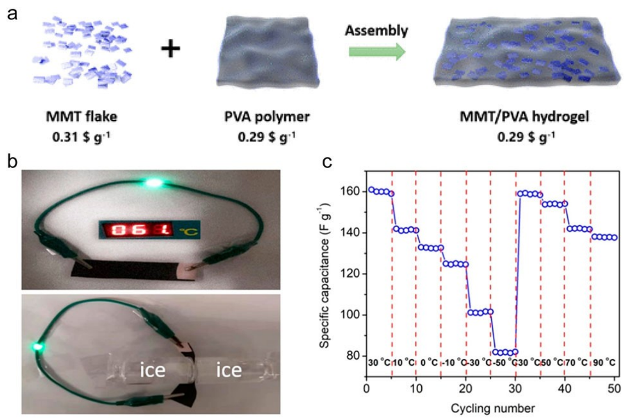


Figure 10. a) The fabrication of MMT/PVA hydrogel. b–c) The supercapacitors work at a wide range of temperatures. Reproduced from Ref. [51] with permission. Copyright 2020, American Chemical Society

capacity retention rate under 5000 cycles) and good flexibility (bending 1000 times at 180 degrees). In addition, TENG yarns can be woven into ordinary fabrics, which can collect mechanical energy from the daily movement of the human body to obtain high output (60 V open circuit voltage and 3 μA short circuit current). The integrated self-charging power textile can drive the electronic watch to work without the need for other power sources to charge.[49]

Chen et al. constructed a self-charging supercapacitor based on piezoelectric electrochemistry. They first prepared a PVDF membrane with up and down through micropores by the ice crystal growth method (Figure 9a), then polarized the PVDF membrane, soaked the polarized PVDF membrane in ionic liquid. The PVDF membrane and carbon composite electrodes were assembled into a device. When pressure was applied to the device, the polarized PVDF will generate a piezoelectric field. Anions and cations are subjected to electric field forces from different directions, and thus move in different directions. As a result, a difference in the concentrations of anions and cations occurs near the electrodes. In this process, the potential difference between the two electrodes increases. After the pressure is removed, the ions are desorbed from the composite carbon electrode under the action of the difference in ion concentration near the composite carbon electrode and the electrostatic force. During this process, the potential difference between the electrodes at both ends continues to decrease (Figure 9b). Quickly charge at low frequency pressure (20 N, 1 Hz), an open circuit voltage of 150 mV was obtained within 80 s. And the performance can be improved through series connection (Figure 9c–d).[50]

3.5. Environmental Tolerance

Wearable supercapacitors can be integrated with fabrics, and then power electronic devices. However, in practical applications, wearer's activity environment changes, so the device needs to have a large environmental tolerance. Wearable supercapacitors need to be able to work stably in a large temperature range. The integrated electronic devices are easily affected by human sweat, rain, washing and other environments, so they need to have good waterproof performance.

Lu et al. reported a flexible supercapacitor in the all-temperature range. The supercapacitor is based on a montmorillonite/polyvinyl alcohol (MMT/PVA) hydrogel electrolyte that is both freeze-resistant and thermally stable (Figure 10a). The layered montmorillonite improves the thermal stability of the PVA hydrogel and at the same time promotes the ionic conductivity of the hydrogel. The ionic conductivity of the gel electrolyte at −50 °C is still 0.17×10^{-4} S cm^{-1}. The supercapacitor assembled with this electrolyte shows high capacity in a wide temperature range of −50 to 90 °C (Figure 10b), and exhibits excellent cycle stability in 10,000 cycles.[51] Pan et al. prepared a new type of Mn_3O_4 functionalized 3D N/P co-doped carbon foam and assembled it with PVA/KOH gel electrolyte to form a supercapacitor, which has excellent temperature stability. The CV curve was measured at three temperatures of −20, 25 and 80 °C at a scan rate of $100\ mV\,s^{-1}$, and specific capacitances of 142, 174 and $193\ F\,g^{-1}$ could be achieved, respectively. They attributed this phenomenon to the three-dimensional structure of the electrode material, large specific surface area and excellent electrical conductivity of Mn_3O_4.[52] Kang et al. prepared graphene/carbon nanotube/manganese oxide flexible composite film with an area of up to $550\ cm^{-2}$. It is assembled with an ionic gel electrolyte containing 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfony) imide ([EMIM][TFSI]) into a supercapacitor. This flexible supercapacitor can maintain good electrochemical performance and flexibility in the temperature range of −20–200 °C.[53]

Package is a common method to avoid direct contact of supercapacitors with the environment, and it is also an effective method to improve the water resistance of supercapacitors. Zheng et al. designed a high-capacity flexible electrode. The electrode and PVA gel electrolyte are assembled into a flexible supercapacitor, and then the supercapacitor is packaged with TPU. After 48 hours of operation in a 20 cm deep water tank, the capacitance retention rate of the device is about 96 %. The excellent waterproof performance not only improves the resistance of the supercapacitor in environments such as sweating and rain, but also ensures a lower risk of leakage. The device can work normally even at high temperatures. A flame is applied to the supercapacitor for more than 30 seconds. Even if the surface temperature of the equipment exceeds 250 °C, no combustion or explosion is observed. The capacitance only slowly decays as the burning time increases, which is mainly due to the evaporation of water in the gel electrolyte. The device can be easily edited into the desired shape and then integrated into the garment (Figure 11a).[54] Ha et al. reported a flexible supercapacitor based on Ecoflex film packaging. They sprayed carbon nanotubes on the polyethylene terephthalate film as electrodes, which will be assembled with ionic gel electrolyte to form a supercapacitor, and then packaged with Ecoflex film. By integrating five supercapacitors in parallel, a micro light-emitting diode (μ-LED) can be lit. After being kept underwater for 4 days, its capacitance still maintained 82 % of its initial value. When bent and stretched underwater, the brightness of the μ-LED is not significantly reduced when it is lit (Figure 11b).[55] In addition to packaging the device, the good bonding ability between the components of the device can also play a role in water resistance. Gao et al. reported a supercapacitor with good washability. They used glutaraldehyde to crosslink the graphene oxide layer and the PVA gel electrolyte to the PET fabric. The obtained supercapacitor has good flexibility, and the specific capacitance does not decrease after being exposed to water for 30 minutes.[56]

3.6. Multifunction

In addition, in addition to the key issues mentioned above, the versatility of wearable supercapacitors is also a direction of its development.

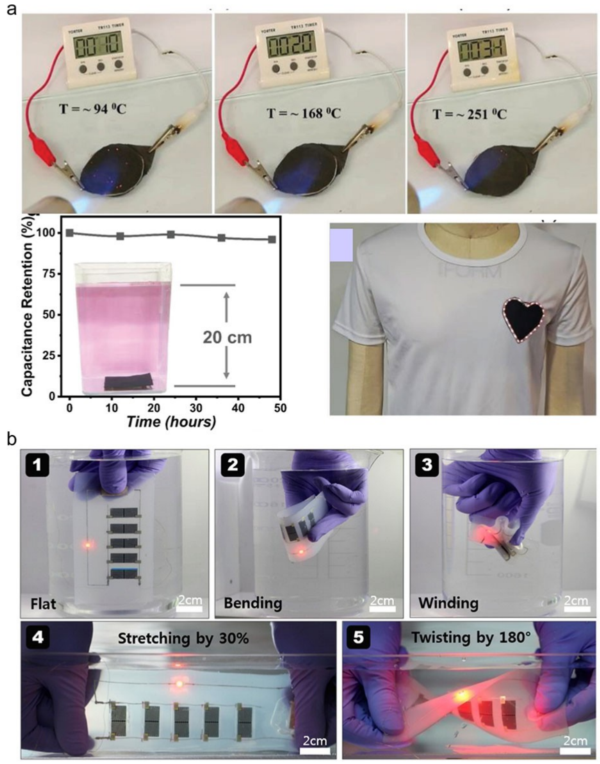


Figure 11. a) Demonstrations of heat resistance, water resistance and wearability of supercapacitors. Reproduced from Ref. [54] with permission. Copyright 2019, Wiley-VCH. b) Optical images of the encapsulated supercapacitors array integrated with a μ-LED, under various deformations in water: without deformation. Reproduced from Ref. [55] with permission. Copyright 2016, American Chemical Society.

Supercapacitors with sensing function: During the use of flexible supercapacitors, tensile or compressive deformation will occur, which will cause certain changes in its capacitance. Therefore, by constructing the relationship between the capacitance change and the deformation of the capacitor, the supercapacitor can be given the ability to sense deformation and play the role of a strain sensor. Peng et al. designed and prepared a compressible carbon nanotube (CNT) array with a gradient cross-linked structure by imitating the gradient cross-linked structure of the squid's mouth. In the vertical direction from top to bottom, the CNT array material has a gradual structure from oriented arrangement to highly cross-linked (Figure 12a). The CNT array can withstand different degrees of compressive strain, has a reversible compression performance of up to 100,000 times and a high conductivity of $105\ S\,m^{-1}$. By using the CNT array as an electrode material, a compression sensing supercapacitor with excellent energy storage and sensing functions was fabricated. The supercapacitor shows a high capacitance of $93.2\ mF\,cm^{-2}$, which can maintain 94 % even after 3000 consecutive compression cycles with 60 % strain, and has excellent sensing capability and stability up to 1900 compression cycles.[57]

Supercapacitors with electrochromic function: Some electrode materials undergo oxidation-reduction reactions during charging and discharging, and the electrode materials exhibit different color states under different oxidation or reduction

Minireviews
doi.org/10.1002/batt.202000333

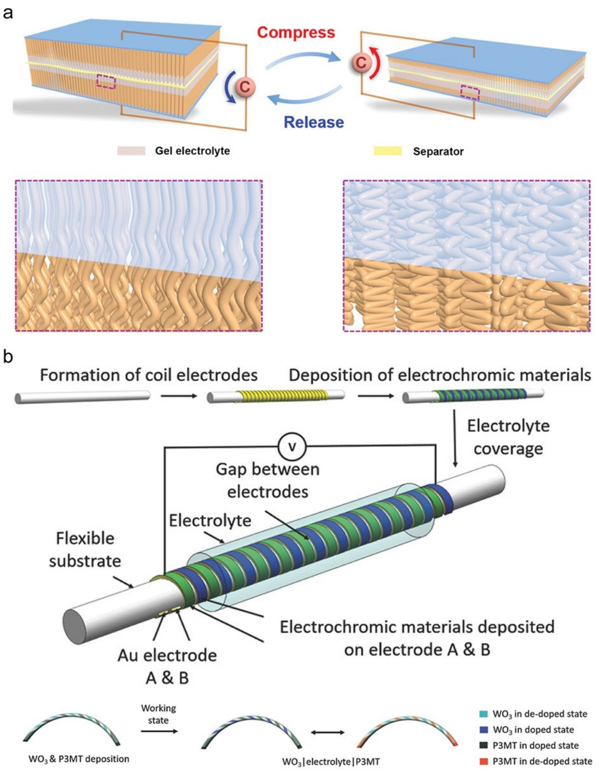


Figure 12. a) The compression-sensing supercapacitor function as a strain sensor before and after compressing. Reproduced from Ref. [57] with permission. Copyright 2019, Wiley-VCH. b) The preparation process and working state of the supercapacitor with electrochromic function. Reproduced from Ref. [59] with permission. Copyright 2018, Wiley-VCH.

states. Feng et al. reported a supercapacitor with reversible electrochromic function. They used the synergistic effect of one-dimensional V_2O_5 nanowires and two-dimensional expanded graphene (EG) nanosheets to prepare an EG/V_2O_5 electrode. In polyvinyl alcohol (PVA)/LiCl gel electrolyte at a scan rate of 10 mV s^{-1}, the specific capacity of this electrode can reach 130.7 F cm^{-3}, and the energy density can reach 20 mWh cm^{-3}. After solidifying the PVA/LiCl gel and methyl viologen together, the resulting supercapacitor exhibited a significant reversible electrochromic effect during 0–1 V charge and discharge. The state of the electrodes of the supercapacitor during the charge.[58] Lin et al. designed an electrochromic supercapacitor with a parallel spiral electrode structure. Fiber devices can be prepared by forming double helix metal electrodes on a plastic fiber substrate, and then depositing tungsten oxide and poly(3-methylthiophene) on the two electrodes, respectively. Reversible electrochromism is driven by a voltage between −1.5 and +1.5 V. It shows high coloring efficiency (77.82 $cm^2 C^{-1}$ for WO_3 and 54.41 $cm^2 C^{-1}$ for poly(3-methylthiophene)) and fast response (up to 5 s). The electrochromic fiber can be change the color between deep red, green and gold (Figure 12b).[59]

Supercapacitors with shape-memory function: When subjected to external stimuli, the shape of the shape memory material will change. When it is used in a supercapacitor, the supercapacitor is also given a shape memory function. Titanium-nickel alloy is a shape memory alloy (SMA) that deforms at a relatively low temperature and can be heated to a phase transition temperature (15 °C) or higher to restore the shape before deformation. Yan et al. developed a wristband supercapacitor with shape-memory effect.[24] A titanium nickel alloy (TNA) sheet deposited with reduced graphene oxide (rGO) is used as the negative electrode of the supercapacitor, an ultra-thin nickel foil (MNF) deposited with MnO_2 is used as the positive electrode of the supercapacitor, and a gel electrolyte is used as a separator. The supercapacitor completed 18 cycles in the entire dynamic shape memory process at a sweep speed of 100 mV s^{-1}. Peng et al. prepared a shape memory supercapacitor fiber. They first wound a carbon nanotube sheet on a thermoplastic polyurethane fiber, then coated a PVA gel electrolyte, and then wound a layer of carbon nanotube sheet as another electrode. After the assembled supercapacitor repeated the deformation-recovery cycle 20 times, no detectable drop in specific capacitance was found. In addition, it has good stability under stretching-recovery deformation.[60]

4. Summary and Outlook

In summary, firstly safety is the application challenge of wearable supercapacitors. The electrode and electrolyte materials of the device must be biocompatible. The package stability and stability under thermal effects of the device need to be guaranteed. At present, the main problem in safety is that the capacitance of the reported biocompatible devices is relatively low. There is relatively little research work on the influence of temperature field on device performance. The wearable supercapacitors need to have good mechanical adaptability (bending, twisting, stretching and self-healing). Wearable supercapacitors with bending, twisting and stretching properties have good mechanical properties. And the interface bonding between the components of the device should be stable. The recoverability of stretchable supercapacitors is low. Self-healing supercapacitors mainly face a long healing time, a significant decrease in capacitance, and fewer self-healing cycles. To reduce the complexity of charging, it is better for wearable supercapacitors to have the ability to be self-powered. Self-powered supercapacitors are mainly prepared based on integration with solar cells or TNEG. However, the preparation method of the integrated devices is more complicated and the energy conversion efficiency of the integrated system is low. The self-powered supercapacitor based on the piezoelectric electrochemical process has the function of integrating energy collection and storage, however the energy density and power density of this wearable supercapacitors are relatively low. Improving the environmental resistance of wearable supercapacitors is one way to expand its application range. The current method of improving temperature resistance is mainly to improve the freezing resistance and thermal stability of the electrolyte, or to package the device. However, the devices prepared by the strategies that have been reported so far can only work for a short time at extreme temperatures. Packaging the device can also improve the humidity tolerance of the device, but the flexibility and the air permeability of the packaged device will be reduced. At the same time, some smart materials or structures are applied to wearable supercapacitors, which can give supercapacitors versatility, such as sensing function, electrochromic function and shape memory function. When some smart materials or structures are applied to wearable supercapacitors, the supercapacitors can be endowed with multifunction, such as sensing function, electrochromic function and shape memory function.

Compared with traditional supercapacitors, wearable supercapacitors are normally light, thin and flexible to fit the practical application such as easy integration, wearing comfort, stretchability and so on. Mass normalization and volumes normalization which are usually used to evaluate the performance (such as capacitance) of traditional supercapacitors, are not suitable for evaluating wearable supercapacitors. For wearable supercapacitors, mechanical compliance and biocompatibility would be primary evaluation criteria, instead of energy density and power density. It is practical to report the capacitance values by normalizing area by specify the device thickness in skin-like supercapacitors.[61,62] Regarding wearable supercapacitors in configurations of fiber or yarn, capacitance values by normalizing length by specify the device diameter would be an alternative parameter for comparison.[37,63] In near future, we expect a standard methodology for evaluating the performance of unconventional wearable supercapacitors will be established.

The practical application of wearable supercapacitors is inseparable from a large scale of production. At present, the preparation of wearable supercapacitors is carried out in small batches in the laboratory. This method of preparation is inefficient, and there are differences between individual devices. This also hinders the practical application of wearable supercapacitors. Therefore, it is necessary to build a process technology that can mass-produce wearable supercapacitors. Recently, the rapid development of printed electronics technology can provide certain reference value.

In addition to some of the key issues mentioned above, improving the performance of the device is also a key issue. The stability and energy density of current wearable supercapacitors still need to be improved. Compared with traditional supercapacitors, wearable supercapacitors will inevitably undergo certain deformations. In the continuous random deformation process, the interface structure of the supercapacitors will be destroyed, and the capacitance of the supercapacitors will drop. Therefore, it is necessary to improve the stability of supercapacitors from the perspective of structure or materials. As we all know, the power density of supercapacitors is high, however the energy density is low. Increasing the specific capacitance of electrode materials is an effective way to increase the energy density, which often affects the flexibility of supercapacitors due to the increase in the content of pseudocapacitance materials. Additionally, the energy density can be improved by introducing an electrode material of battery into the supercapacitor to form a hybrid supercapacitor. However, the current hybrid supercapacitors have not yet reached the ideal energy density, and their cycle stability is poor. Therefore, the development of wearable supercapacitors with high energy density is also a future development direction.

Acknowledgements

The authors would like to thank the project 21975214 supported by National Natural Science Foundation of China, the project 2018YFC2000900 supported by National Key R&D Program of China, and the project BE1H supported by Start-up Fund of The Hong Kong Polytechnic University.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: wearable supercapacitors · safety · mechanical adaptability · self-charging · multifunction

[1] J. Shi, S. Liu, L. Zhang, B. Yang, L. Shu, Y. Yang, M. Ren, Y. Wang, J. Chen, W. Chen, Y. Chai, X. Tao, *Adv. Mater.* **2019**, *32*, 1901958.
[2] W. Liu, M. S. Song, B. Kong, Y. Cui, *Adv. Mater.* **2017**, *29*, 34.
[3] X. Lu, M. Yu, G. Wang, Y. Tong, Y. Li, *Energy Environ. Sci.* **2014**, *7*, 2160.
[4] D. P. Dubal, N. R. Chodankar, D. H. Kim, P. Gomez-Romero, *Chem. Soc. Rev.* **2018**, *47*, 2065.
[5] W. Raza, F. Z. Ali, N. Raza, Y. W. Luo, K. H. Kim, J. H. Yang, S. Kumar, A. Mehmood, E. E. Kwon, *Nano Energy* **2018**, *52*, 441.
[6] A. B. Dalton, S. Collins, E. Muñoz, J. M. Razal, V. H. Ebron, J. P. Ferraris, J. N. Coleman, B. G. Kim, R. H. Baughman, *Nature* **2003**, *423*, 703.
[7] L. Li, Z. Lou, D. Chen, K. Jiang, W. Han, G. Z. Shen, *Small* **2018**, *14*, 1702829.
[8] L. B. Dong, C. J. Xu, Y. Li, Z. H. Huang, F. Y. Kang, Q. H. Yang, X. Zhao, *J. Mater. Chem. A* **2016**, *4*, 4659.
[9] Y. Huang, M. Zhong, Y. Huang, M. Zhu, Z. Pei, Z. Wang, Q. Xue, X. Xie, C. Zhi, *Nat. Commun.* **2015**, *6*, 10310.
[10] G. Lee, D. Kim, D. Kim, S. Oh, J. Yun, J. Kim, S.-S. Lee, J. S. Ha, *Energy Environ. Sci.* **2015**, *8*, 1764.
[11] X. J. Wu, Y. J. Xu, Y. Hu, G. Wu, H. Y. Cheng, Q. Yu, K. Zhang, W. Chen, S. Chen, *Nat. Commun.* **2018**, *9*, 11.
[12] T. An, W. Cheng, *J. Mater. Chem. A* **2018**, *6*, 15478.
[13] C. Lu, D. Wang, J. Zhao, S. Han, W. Chen, *Adv. Funct. Mater.* **2017**, *27*, 1606219.
[14] G. Wu, P. Tan, X. Wu, L. Peng, H. Cheng, C.-F. Wang, W. Chen, Z. Yu, S. Chen, *Adv. Funct. Mater.* **2017**, *27*, 1702493.
[15] X. Pu, M. Liu, L. Li, S. Han, X. Li, C. Jiang, C. Du, J. Luo, W. Hu, Z. L. Wang, *Adv. Energy Mater.* **2016**, *6*, 1601254.
[16] Q. F. Meng, K. F. Cai, Y. X. Chen, L. D. Chen, *Nano Energy* **2017**, *36*, 268.
[17] Y. G. Wang, Y. F. Song, Y. Y. Xia, *Chem. Soc. Rev.* **2016**, *45*, 5925.
[18] L. Hu, M. Pasta, F. La Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, Y. Cui, *Nano Lett.* **2010**, *10*, 708.
[19] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, *Adv. Mater.* **2013**, *25*, 2326.
[20] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, *Nat. Commun.* **2014**, *5*.
[21] Z. Ling, C. E. Ren, M. Q. Zhao, J. Yang, J. M. Giammarco, J. S. Qiu, M. W. Barsoum, Y. Gogotsi, *Proc. Nat. Acad. Sci.* USA **2014**, *111*, 16676.
[22] C. F. Zhang, B. Anasori, A. Seral-Ascaso, S. H. Park, N. McEvoy, A. Shmeliov, G. S. Duesberg, J. N. Coleman, Y. Gogotsi, V. Nicolosi, *Adv. Mater.* **2017**, *29*, 1702678.
[23] D. W. Zhao, C. J. Chen, Q. Zhang, W. S. Chen, S. X. Liu, Q. W. Wang, Y. X. Liu, J. Li, H. P. Yu, *Adv. Energy Mater.* **2017**, *7*, 1700739.
[24] L. Liu, B. Shen, D. Jiang, R. Guo, L. Kong, X. Yan, *Adv. Energy Mater.* **2016**, *6*, 1600763.
[25] G. Shao, R. Yu, X. Zhang, X. Chen, F. He, X. Zhao, N. Chen, M. Ye, X. Y. Liu, *Adv. Funct. Mater.* **2020**, *30*, 2003153.

[26] C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, *Nano Lett.* **2010**, *10*, 4025.
[27] J.-H. Sung, S.-J. Kim, S.-H. Jeong, E.-H. Kim, K.-H. Lee, *J. Power Sources* **2006**, *162*, 1467.
[28] L. Manjakkal, A. Pullanchiyodan, N. Yogeswaran, E. S. Hosseini, R. Dahiya, *Adv. Mater.* **2020**, *32*, 1907254.
[29] R. Chen, Y. Yang, Q. Huang, H. Ling, X. Li, J. Ren, K. Zhang, R. Sun, X. Wang, *Energy Storage Mater.* **2020**, *32*, 208.
[30] S. Li, D. Huang, B. Zhang, X. Xu, M. Wang, G. Yang, Y. Shen, *Adv. Energy Mater.* **2014**, *4*, 1301655.
[31] J. Zhao, Y. Chen, Y. Yao, Z.-R. Tong, P.-W. Li, Z.-M. Yang, S.-H. Jin, *J. Power Sources* **2018**, *378*, 603.
[32] X. Wang, W. Xu, P. Chatterjee, C. Lv, J. Popovich, Z. Song, L. Dai, M. Y. S. Kalani, S. E. Haydel, H. Jiang, *Adv. Mater.* **2016**, *1*, 1600059.
[33] K.-H. Choi, J. Yoo, C. K. Lee, S.-Y. Lee, *Energy Environ. Sci.* **2016**, *9*, 2812.
[34] K. Wang, L. Zhang, B. Ji, J. Yuan, *Energy* **2013**, *59*, 440.
[35] H. Gualous, R. Gallay, G. Alcicek, B. Tala-Ighil, A. Oukaour, B. Boudart, P. Makany, *Microelectron. Reliab.* **2010**, *50*, 1783.
[36] H. Gualous, H. Louahlia, R. Gallay, *IEEE Trans. Power Electron.* **2011**, *26*, 3402.
[37] Z. Yang, J. Deng, X. Chen, J. Ren, H. Peng, *Angew. Chem. Int. Ed.* **2013**, *52*, 13453.
[38] J. Yang, X. Q. Yu, X. Sun, Q. Kang, L. Zhu, G. Qin, A. G. Zhou, G. Z. Sun, Q. Chen, *ACS Appl. Mater. Interfaces* **2020**, *12*, 9736.
[39] H. Li, T. Lv, H. Sun, G. Qian, N. Li, Y. Yao, T. Chen, *Nat. Commun.* **2019**, *10*, 536.
[40] C. Chen, J. Cao, X. Y. Wang, Q. Q. Lu, M. M. Han, Q. R. Wang, H. T. Dai, Z. Q. Niu, J. Chen, S. S. Xie, *Nano Energy* **2017**, *42*, 187.
[41] Z. Lv, Y. Luo, Y. Tang, J. Wei, Z. Zhu, X. Zhou, W. Li, Y. Zeng, W. Zhang, Y. Zhang, D. Qi, S. Pan, X. J. Loh, X. Chen, *Adv. Mater.* **2018**, *30*, 1704531.
[42] S. Wang, N. Liu, J. Su, L. Li, F. Long, Z. Zou, X. Jiang, Y. Gao, *ACS Nano* **2017**, *11*, 2066.
[43] Z. Wang, Q. Pan, *Adv. Funct. Mater.* **2017**, *27*, 1700690.
[44] C.-R. Chen, H. Qin, H.-P. Cong, S.-H. Yu, *Adv. Mater.* **2019**, *31*, 1900573.
[45] K. Krishnamoorthy, P. Pazhamalai, V. K. Mariappan, S. S. Nardekar, S. Sahoo, S.-J. Kim, *Nat. Commun.* **2020**, *11*, 2351.
[46] T. Chen, L. Qiu, Z. Yang, Z. Cai, J. Ren, H. Li, H. Lin, X. Sun, H. Peng, *Angew. Chem. Int. Ed.* **2012**, *51*, 11977.
[47] J. Lv, I. Jeerapan, F. Tehrani, L. Yin, C. A. Silva-Lopez, J.-H. Jang, D. Joshuia, R. Shah, Y. Liang, L. Xie, F. Soto, C. Chen, E. Karshalev, C. Kong, Z. Yang, J. Wang, *Energy Environ. Sci.* **2018**, *11*, 3431.
[48] X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, Z. L. Wang, *Adv. Mater.* **2016**, *28*, 98.
[49] M. Liu, Z. Cong, X. Pu, W. Guo, T. Liu, M. Li, Y. Zhang, W. Hu, Z. L. Wang, *Adv. Funct. Mater.* **2019**, *29*, 1806298.
[50] C. Li, Y. Yang, Y. Wu, X. Tao, W. Chen, *Adv. Mater.* **2020**, *5*, 2000050.
[51] C. Lu, X. Chen, *Nano Lett.* **2020**, *20*, 1907.
[52] L. Sun, Q. Fu, C. Pan, *J. Alloys Compd.* **2020**, *849*, 156666.
[53] X. B. Zang, Y. Hou, T. Wang, R. J. Zhang, F. Y. Kang, H. W. Zhu, *Sci. China Mater.* **2019**, *62*, 947.
[54] J. Shang, Q. Huang, L. Wang, Y. Yang, P. Li, Z. Zheng, *Adv. Mater.* **2020**, *32*, 1907088.
[55] H. Kim, J. Yoon, G. Lee, S.-h. Paik, G. Choi, D. Kim, B.-M. Kim, G. Zi, J. S. Ha, *ACS Appl. Mater. Interfaces* **2016**, *8*, 16016.
[56] G. Wang, V. Babaahmadi, N. He, Y. Liu, Q. Pan, M. Montazer, W. Gao, *J. Power Sources* **2017**, 367, 34.
[57] Y. Zhao, J. Cao, Y. Zhang, H. Peng, *Adv. Funct. Mater.* **2020**, *30*, 1902971.
[58] P. P. Zhang, F. Zhu, F. X. Wang, J. H. Wang, R. H. Dong, X. D. Zhuang, O. G. Schmidt, X. L. Feng, *Adv. Mater.* **2017**, *29*, 7.
[59] Y. Zhou, J. Fang, H. X. Wang, H. Zhou, G. L. Yan, Y. Zhao, L. M. Dai, T. Lin, *Adv. Electron. Mater.* **2018**, *4*, 1800104.
[60] J. Deng, Y. Zhang, Y. Zhao, P. Chen, X. Cheng, H. Peng, *Angew. Chem. Int. Ed.* **2015**, *54*, 15419.
[61] S. Gong, W. Cheng, *Adv. Energy Mater.* **2017**, *7*, 1700648.
[62] T. An, Y. Ling, S. Gong, B. Zhu, Y. Zhao, D. Dong, L. W. Yap, Y. Wang, W. Cheng, *Adv. Mater.* **2019**, *4*, 1800473.
[63] T. Khudiyev, J. T. Lee, J. R. Cox, E. Argentieri, G. Loke, R. Yuan, G. H. Noel, R. Tatara, Y. Yu, F. Logan, J. Joannopoulos, Y. Shao-Horn, Y. Fink, *Adv. Mater.* **2020**, *32*, 2004971.

Manuscript received: December 29, 2020
Revised manuscript received: February 22, 2021
Accepted manuscript online: February 28, 2021
Version of record online: March 18, 2021

