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Conducting Polymer-Based Flexible Supercapacitor Devices

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Abstract

Flexible supercapacitors are gaining considerable attention because of their wide range of applications in the area of flexible electronics. Significant opportunities exist and will continue to exist for the development of flexible energy storage devices through intensive research. The level of R&D activity in the general field of energy storage technology has been rising considerably all over the world during the last two decades, because of the growing recognition of the commercial potentialities of energy storage technology. This chapter focuses on the different types of conducting polymer-based supercapacitors, incorporating polymers such as polyaniline, polypyrrole, polythiophene, and the derivatives of polythiophene. Emphasis is given to the methods of fabricating flexible supercapacitor devices. The different electrolytes employed for the development of flexible supercapacitors are discussed. In the beginning, a brief account of the principles and classification of supercapacitors is described. The chapter concludes with a consideration of the prospects for flexible supercapacitor. To compile this chapter and to provide adequate information to the readers, we have explored all the possible materials available in the literature.

***Keywords*:** Conducting polymers, electrodes, electrolytes, supercapacitors, flexible devices

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20.1 Introduction

Supercapacitors are a type of energy storage devices, which can store and deliver energy at higher rates as compared to batteries [1]. If we compare supercapacitors with other portable energy storage devices, the advantages include longer life, higher power, wider thermal range (−40 to 70 °C), flexible packaging, lighter weight and lower maintenance [2]. Supercapacitors find major applications in sources of energy recapture, like electric vehicles, load cranes, power quality improvement, forklifts, etc. [3–5]. Supercapacitors can also act as temporary energy storage devices to store energy from braking when used with fuel cells or batteries [6, 7]. The performance of supercapacitor-electrode materials depends on various factors, such as electrical conductivity, surface area, the permeability of electrolyte solutions and wettability of electrode material [8, 9]. Batteries provide energy densities up to 150 Wh kg^{-1}, which is more than ten times that of electrochemical capacitors. However, in terms of power density, batteries barely reach 200 W kg^{-1}, which is 20 times lower performance than that of a capacitor. The batteries exhibit drawbacks such a reduction in performance due to rapid charging/discharging cycles or in a cold environment. Moreover, batteries are generally expensive to maintain and exhibit limited lifetimes [10].

The storage of energy is one of the significant challenges facing societies in this century. Therefore, we need to find alternative charge storage arrangements which are cheaper and eco-beneficial, because of the rising energy demand in the present society [11]. As a consequence of the full range of applications of supercapacitors, many researchers initiated research on composites for supercapacitor electrode materials based on metal oxides (MOx) and conducting polymers (CPs).

In this chapter, we have set out to compile a list of the CPs that has been used in flexible supercapacitor devices. We have focused on polymers, such as polyaniline, polypyrrole, polythiophene and derivatives of polythiophene. We start with the principles and classification of supercapacitors, and since the electrolyte is an integral part of a supercapacitor, we discuss the electrolytes employed for flexible supercapacitor devices. Future perspectives for flexible supercapacitors are summarized to stimulate future research on flexible supercapacitors.

20.2 Principles of Supercapacitor

Two-storage principles are involved in the electrode materials; firstly the double-layer capacitance and secondly the pseudocapacitance that contributes

to the total capacitance of supercapacitors. In double-layer capacitance, the electrical energy is stored by the separation of charge in a Helmholtz double layer. With pseudocapacitors, the electrochemical storage of the electrical power is achieved by Faradic redox reactions with charge-transfer.

20.3 Classification of Supercapacitors

The operation of supercapacitors is dependent on the distribution and storage of ions arising from electrolytes on the surface of the electrode. Depending on the charge storage principles, the supercapacitors are broadly categorized into two classes: Electrochemical double-layer capacitors (EDLCs) and Pseudocapacitors.

20.3.1 Electrochemical Double-Layer Capacitors

EDLC devices are fabricated using two electrodes generally on the basis of carbonaceous materials, a separator, and an electrolyte. EDLCs can store charge either electrostatically or through the process of non-Faradic. The energy storage process in EDLCs includes the formation of an electrochemical double layer. When a voltage is applied across EDLCs, a deposition of charge occurs on the surface of electrode owing to the potential differences as well as the attraction between the opposite charges. This leads to the migration of ions present in the electrolyte over the separator as well as into the pores of the oppositely charged electrode. A double layer of charge is formed to avoid the recombination of those ions at the electrodes. This double-layer provides the EDLC supercapacitors with a high energy density due to the increased specific surface area. The storage mechanism of the EDLC device allows a rapid charge uptake, transmission and improved power performance. Since EDLCs devices suffer from a low energy density, research is mainly emphasized on enhancing the energy and improving the temperature range. In the fabrication of EDLC type supercapacitors, carbon materials in their various forms are widely used as electrode materials due to their high surface area, ease of availability and low cost. The carbon materials, such as activated carbon (AC), carbon nanotubes (CNTs) and graphene, are used as electrode materials.

20.3.2 Pseudocapacitors

Pseudocapacitors involve the use of CPs and MOx. Pseudocapacitors can store charge electrostatically via a Faradic process, and this involves the

mobility of charge between the electrode and the electrolyte. The process of oxidation and reduction occurs on the electrode material when a voltage is applied on the pseudocapacitor, and this evolves the transition of charge over the double layer. The Faradic process involves the transition of current across the supercapacitor cells and results in higher electrochemical performance as compared to EDLCs. The most common pseudocapacitor electrode materials include MOx, such as manganese oxide, vanadium nitride, ruthenium oxide; and electrically CPs, such as polyaniline, polypyrrole, and other oxygen/nitrogen-containing surface functional groups [12].

Pseudocapacitance can arise because of different of electrochemical processes, mainly adsorption of ions from the electrolyte on the surface; redox reactions of the active material of CPs. The Faradic electrochemical methods which arise from the redox or doping/de-doping processes of CPs are similar to the process of charging and discharging as found in conventional batteries. However, the charge transfer process is dependent on the voltage. On the contrary to an EDLC the time response of the storage redox reactions is slower, typically 10^{-2} to 10^{-4}s due to reaction impedance. However, due to the Faradic nature of the reaction, pseudocapacitors can exhibit capacitance, which is 10–100 times more than that of double-layer capacitors.

20.3.2.1 Conducting Polymers

Conducting polymers have been studied as supercapacitor electrode materials because of their simple synthetic routes and economically feasible [13]. Such polymers exhibit comparatively better conductivity and capacitance in comparison with EDLC type materials. The n/p type configuration electrodes provide high energy densities. With CPs, the redox mechanism is utilized to store and release the charge. In the oxidation process, which is the context of CPs is usually referred as doping, the ions are driven to form an association with the polymer backbone, while in the reduction process (de-doping), ions are liberated within the electrolytes. These reactions may cause mechanical stress which in turn can hinder the performance of the electrode materials over a significant number of charge–discharge cycles [14].

20.3.2.1.1 Polyaniline

Polyaniline (PANI) is considered as a highly promising supercapacitor electrode material due to the fact that it exhibits a high conductivity with excellent energy storage capacity, easy synthesis, and low cost [15]. However,

repeated charge–discharge cycles cause swelling and shrinkage in the active material pattern, and as a result, the performance of PANI decays quite quickly. Some reports show that this limitation can be overcome through the use of carbon-based nanoparticles with PANI, which strengthens the stability of PANI and maximizes the capacitance values [16, 17].

20.3.2.1.2 Polypyrrole

Electrochemical processing produces polypyrrole (PPy) films with a higher degree of flexibility as compared to other CPs. Since PPy never be used as n-doped, it can only be employed as a cathode electrode.

20.3.2.1.3 Polythiophene and its Derivatives

Although very high capacitance values have been reported for polythiophene (PTh) films [18], only limited studies have considered applications in energy storage due to its instability. More promising results were obtained in an extensive study of one of the derivatives of PTh, namely poly(3,4-ethylene dioxythiophene), which is often referred to as PEDOT. PEDOT supercapacitor electrodes exhibit fast switching speed and excellent chemical stability [19], and specific capacitances of 210 F g^{-1}, energy densities of 1–4 Wh kg^{-1} with power densities of 35–2,500 W kg^{-1} have been reported for PEDOT based supercapacitors [20–22].

20.4 Conducting Polymer-Based Flexible Supercapacitors

Conducting polymers have been widely explored for supercapacitors applications in the last two decades due to their reversible redox nature, a low cost compared to MOx and their high charge density [23–25]. Generally, CPs and the mechanism for conductivity at the molecular level and its relationship to the molecular conformations remains a matter of debate, some experiments have proposed a hopping mechanism between localized charged states arising from a coupling of the geometry and the electronic configuration, but the experimental evidence is not strong due to the disordered structure of the polymers. Polymers such as PANI, PPy and PTh's derivatives are studied extensively as supercapacitor electrode materials because of their high pseudocapacitance, high electrical conductivity and low cost [26–31]. As a result, CPs are considered as promising electrode materials for the applications of flexible supercapacitors owing to their highly flexible nature and simple synthetic routes. The morphology

of CPs attributes a significant character in determining the electrochemical performance of supercapacitors. From the literature, CPs have been synthesized in various forms, including, thin films, bulk powder, nanosheets, nanowalls and nanorods. Nanostructured CPs exhibit a high surface area and a high porosity which provides unique conducting pathways, a high surface-to-volume contribution and hence a high surface area per unit mass and various surface interactions. A recent study demonstrated that nanowire arrays of CPs could develop one-dimensional nanostructures with a very high pseudocapacitance than that of its bulk counterpart [32].

20.4.1 Polyaniline-Based Flexible Supercapacitors

In the literature, a high specific pseudocapacitance value is reported for supercapacitors prepared with PANI electrode materials [33–37]. In this context, the protonated emeraldine form of PANI is reported to exhibit a lower conductivity, and it has been widely studied as it is possible to dope to a higher level and it exhibits good environmental stability [38, 39].

PANI was synthesized using methods of both chemical and electrochemical oxidation on different substrates, such as nickel, carbon, stainless steel, as well as flexible substrates and blended with various materials for supercapacitors applications. In the literature, several researchers reported the specific capacitance values from 30 to 3,000 F g^{-1} for PANI based supercapacitors. This wide range of values reflects the variation in structural morphology, the polymerization method used and the resultant dopant concentration, as well as the ionic diffusion path of the electroactive material. The main requirement for the improvement of the performance of PANI based pseudocapacitors involves achieving a high surface area through the use of nanoscale architectures. There are various reports in the literature on an increase in the supercapacitor performance of PANI based electrodes. PANI deposited on porous carbon exhibited the stable response of electrochemical over a wide range of cycles (~1,000) maintaining a high density of current of 19.8 A g^{-1} [40].

To overcome the stability issue of PANI, it is necessary to utilize a range of composite materials to build flexible PANI based supercapacitors. Dai *et al.* [41] have reported that the inclusion of carbon nonmaterial into PANI has several benefits on the overall supercapacitor performance. Han *et al.* [42] reported that a new approach to enhancing the electrochemical performance of reduced graphene oxide (RGO) aerogel supercapacitor using the electrodeposition of arrays of polyaniline on the aerogel. Q2 Figure 20.1 shows schematically the fabrication process for these novel hybrid composites, which have a significant advantage of being ultra-light.

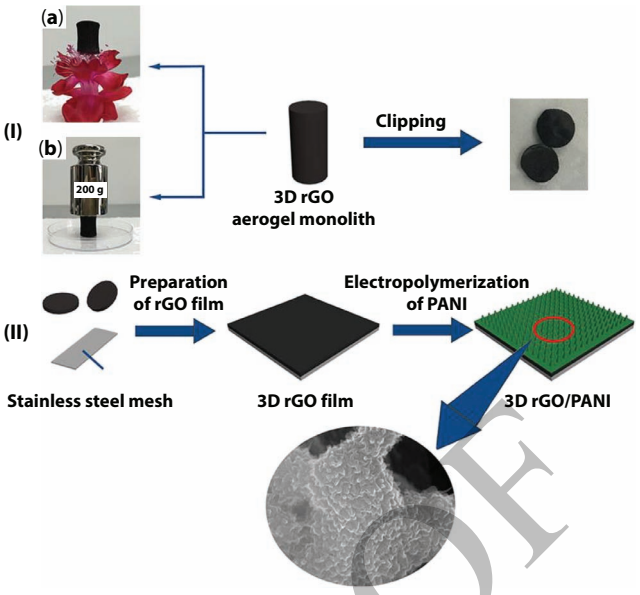

Figure 20.1 The schematic diagram of the fabrication process: 3D reduced graphene oxide aerogel slices from the monolith (I); and the composites developed by electrodeposition and mechanical pressing methods (II). (Adopted with the kind permission from Ref. [42] from ©Springer Nature.)

These hybrid composites exhibited a specific capacitance of 432 Fg^{-1} at 1 Ag^{-1} and retention of at least 85% of the capacitance after 10,000 charge–discharge cycles. We attribute this excellent performance is due to the growth of a rich open-pore structure, and the high capacitance contribution of PANI. Supercapacitors prepared using this approach have exhibited marked stability under different bending states demonstrating their suitability for use with portable electronic devices.

In a similar study, Wang *et al.* [43] described the fabrication of flexible supercapacitors based on PANI nanowires and carbon nanotubes using an *in-situ* electrochemical polymerization method. The scanning electron microscope images presented in Figure 20.2 shows the vertically aligned carbon nanotube arrays and the flexible epoxy/CNT porous membrane. The charging-discharging cycles of electrically CPs result in a considerable volumetric change, which can result in a decrease of the capacitance and lead to the degradation of electrodes. The authors described their new approach, in which they deposit polyaniline within the nanocavities of multiwalled carbon nanotubes using *in-situ* polymerisation. The carbon nanotubes serve to protect the polyaniline suppressing the structural changes in the polyaniline, which increases the valid lifetime of the device.

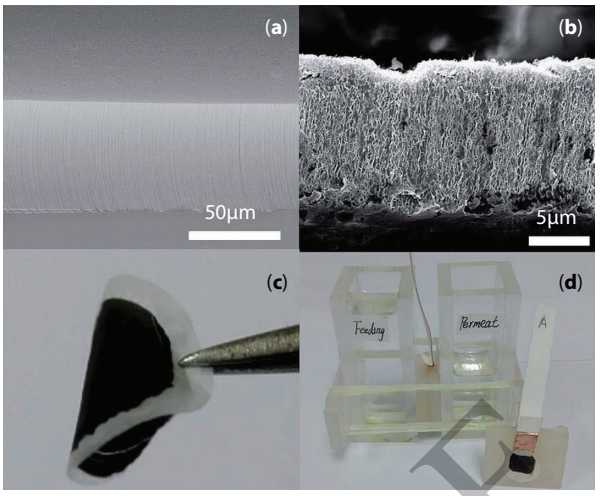

Figure 20.2 The SEM images of vertically aligned CNT arrays (a) and side-view of the epoxy/CNT porous membrane (b). The photographic images of the hybrid membrane (d) and the diffusion cell (d). (Adopted with the kind permission from Ref. [43] from © RSC.)

The carbon nanotubes are arranged in aligned arrays embedded in an epoxy membrane providing effective channels of charge transfer. The films developed in that work based on CPs encapsulated by MWCNTs exhibited a specific capacitance of 296 F g^{-1} with retention of 95% of the capacitance even after 2,000 cycles [43].

20.4.2 Polypyrrole-Based Flexible Supercapacitors

Polypyrrole (PPy), is a class of CPs, which has attracted considerable attention for supercapacitor applications [44, 45]. Polypyrrole demonstrates high specific capacitance with different electrolytes [46–48]. Similar to electrochemically deposited PANI, PPy works very well in a variety of electrolytes. One drawback for PPy is that it cannot be n-doped as with thiophene derivatives, which limits the application of PPy to use as a cathode material. However, on the positive side, PPy does exhibit an enhanced degree of flexibility than displayed by other CPs and can be easily adapted to different forms [49]. Several reports have shown the combination of PPy with graphene and carbon nanotubes leads to "wrinkled" nanocomposites with an enhanced charge storage capacity which could be attributed to the greater surface area and the ion diffusion rate [50–52]. These features make PPy a promising component of flexible, lightweight supercapacitors with excellent electrochemical performance to meet the requirements of portable and flexible electronic devices.

The electrochemical properties of PPy based supercapacitors also depend on the effective surface area of the active electrode and the method used to prepare the electrode. Accordingly, several researchers have developed PPy based flexible supercapacitor electrodes using different methods and achieved good electrochemical performances [53–59]. The electrochemical performance of composite electrodes varies with the preparation conditions such as polymerization time and methodology as well as the dopant concentration.

Very recently, our group has developed a flexible membrane electrode material successfully by *in-situ* polymerization of pyrrole in tetraethyl orthosilicate (TEOS) crosslinked poly(vinyl alcohol) (Figure 20.3) [58]. The membrane prepared using this approach demonstrated a specific

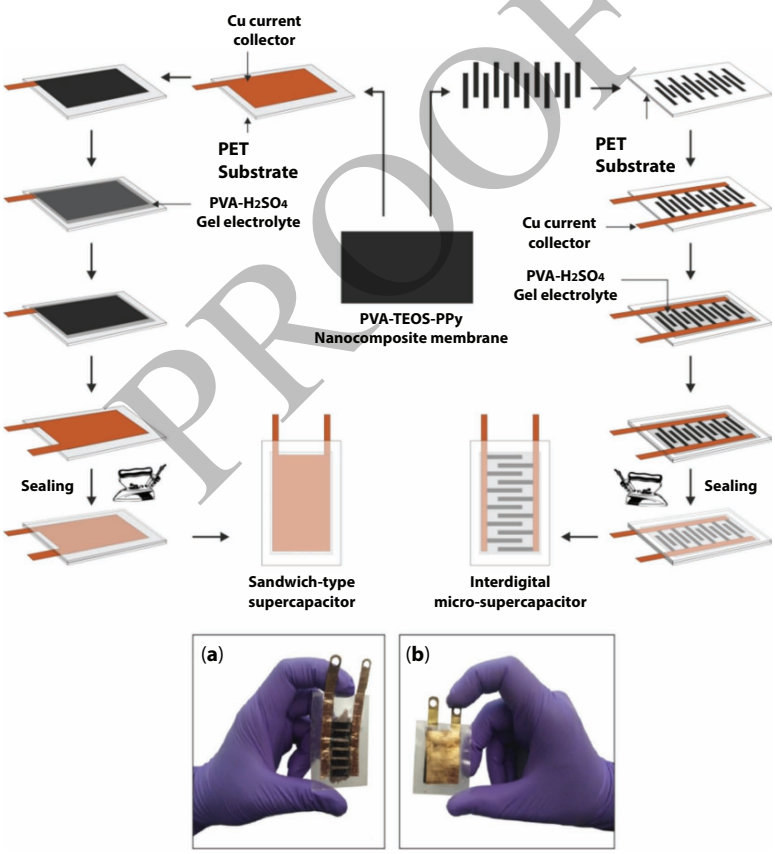

Figure 20.3 The schematic representation of supercapacitor devices: interdigital micro-supercapacitor (a) and sandwich-type supercapacitor (b). (Adopted with the kind permission from Ref. [58] from © Elsevier.)

capacitance of 484 F g^{-1} at a current density of 0.1 A g^{-1}. From this material, we have fabricated sandwich-type and interdigital micro-supercapacitors. The interdigital micro-supercapacitor exhibited a high energy density of 7.14 Wh kg^{-1} with a power density of 47.60 W kg^{-1}.

Sun *et al.* [60] developed polypyrrole/carbonized cotton fabric (PPy/CCF) hybrid electrodes by coating PPy on carbonized cotton fabric via *in-situ* electrodeposition method. The developed PPy/CCF (1:2) hybrid electrode exhibited a specific capacitance of 3,596 mF cm^{-2} with 96.5% retention of this capacitance even after 4,000 charging/discharging cycles. This flexible supercapacitor displayed a capacitance of 5.9 F cm^{-3}, with a volume energy density of 1.18 mWh cm^{-3} at a power density of 17 mW cm^{-3}, without loss of its performance over many bending situations. This device is a potential candidate for wearable electronics. Using the chemical interfacial polymerization and chemical vapor deposition methods, Ren *et al.* [61] have fabricated highly stretchable supercapacitor electrodes from the composite of graphene foam and polypyrrole. The supercapacitor device fabricated in this approach with graphene/polypyrrole electrodes exhibited 258 mF cm^{-2} specific capacitance, 22.9 μWh cm^{-2} energy density at 0.56 mW power density. In addition, this flexible supercapacitor exhibited good stretchability (50% strain) and excellent flexibility (180°).

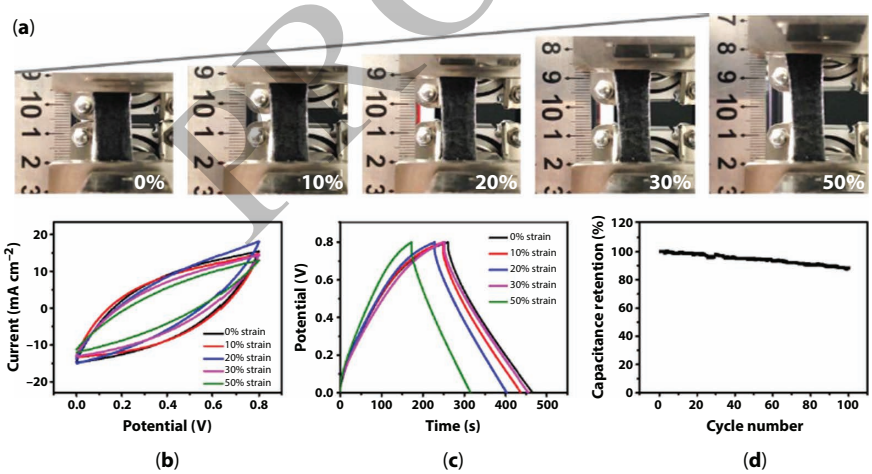

Figure 20.4 The photographs of solid-state supercapacitor devices assembled from graphene and PPy (stretched from 0 to 50% strain) (a). The cyclic voltammetry curves of the supercapacitors (b) shown in (a) at a scan rate of 100 mV s^{-1}. The galvanostatic charge and discharge curves of supercapacitors under different tensile strains at current density of 1 mA cm^{-2} (c). The stability of the normalized capacitance as a function of stretching cycle number for 100 cycles with a tensile strain of 30% (d). (Adopted with the kind permission from Ref. [58] from © Elsevier.)

Flexible electronic devices require supercapacitors with excellent deformability without any degradation of the electrochemical performance. Ren *et al.* [61] have measured the capacitive performance of stretchable supercapacitors deformed to different tensile strains, and the values obtained are presented in Figure 20.4a. The cyclic voltammetry curves (Figure 20.4b) and the galvanostatic charging and discharging curves (Figure 20.4c) did not reveal any significant changes over the strain range of 0 to 50%. The specific capacitance retentions were found to be 98, 92, 84, and 69% when the device was stretched from 0, 20, 30, and 50%. The cycle-life stability of a device measured at 30% tensile strain (Figure 20.4d) showed capacitance retention of more than 88% after 100 cycles of charge–discharge, suggesting excellent stability. Based on these results, the flexible supercapacitor assembled using the developed graphene/PPy composite electrode is a promising energy storage device for flexible and wearable electronics.

20.4.3 Polythiophene and its Derivatives-Based Flexible Supercapacitors

There are many reports of polythiophene and its derivatives being used in supercapacitor applications because of their easy structural modification and solution processability [62–70]. Unfortunately, n-doped polythiophene exhibits low stability to oxygen and water at very low potentials (below −2.0 V vs $Ag|Ag^{+}$). Polythiophene displays a high self-discharge and low cycle-life stability in devices as well as low conductivity as compared to the p-doped state [71]. To overcome these drawbacks, the preparation of polythiophene derivatives with a lower band-gap is important [72–77]. Thus, Arbizzani *et al.* have reported improved stability with regard to oxygen and water upon substitution of phenyl, ethyl, and alkoxy groups at 3-position of the thiophene ring [78]. Other polythiophene derivatives have been studied including poly(3,4-ethylene dioxythiophene) (PEDOT), poly(3-(3,4-difluorophenyl)thiophene) (MPFT), poly(3-(4-fluorophenyl) thiophene) (PFPT) and poly(1-cyano-2-(2-(3,4- ethylene dioxylthienyl))-1-(2-thienyl)vinylene) (ThCNVEDT) [79].

PEDOT has been employed as an active material for many numbers of applications both in the field of energy generation and its storage [80–82] due to interesting properties including a narrow band-gap, good optical transparency, good environmental and thermal stability, a wide potential window and low oxidation potential. The electrochemical charge storage mechanism for PEDOT is similar to the other CPs like PANI and PPy. There are several reports on the improvement of the capacitive performance

of PEDOT based supercapacitor electrodes by both chemical and electrochemical methods [83–85].

Amongst recent reports on novel PEDOT nanostructure-based supercapacitors with high electrochemical stability [86, 87], Bu *et al.* [87] have developed flexible thin nanofiber paper supercapacitor electrodes (~12 μm in thickness) combining the advantages of highly ordered PEDOT conductive polymer chains and the 3-dimensional porous nanostructure of bacterial cellulose. This flexible symmetric supercapacitor device with the bacterial cellulose-PEDOT paper electrodes demonstrated excellent electrochemical performance with a specific capacitance of 106.3 F cm^{-3}, which displayed outstanding cycle-life stability. The authors have investigated the GCD curves of the two devices connected in series and parallel, as shown in Figure 20.5a, and the results indicate the regularity of both series and parallel connections of capacitors. The practical application of the supercapacitor devices was confirmed by powering a LED, as shown in Figure 20.5b.

Ginting *et al.* [88] have reported an easy and cost-effective approach for the preparation of hybrid transparent conductive electrodes (TCEs). The hybrid TCEs exhibited a high capacitance of 443 F cm^{-3}, which exhibited transparency of 86%. To date, this is the best transparent supercapacitor that exhibited high performance by maintaining transparency and electrochemical performance. The micro-supercapacitor (MSC) fabricated by Lee *et al.* [89] using a patterned graphene flake (GF)/PEDOT composite electrode using pen lithography technique. The schematic representation of the fabricated Micro-supercapacitor based on graphene flake/PEDOT is shown in Figure 20.6. Three different gel electrolytes (H_3PO_4, PVA/H_2SO_4 and $LiClO_4$) were employed in the micro supercapacitor to achieve a high power density. The device with a GF/PEDOT electrode with a PVA/H_2SO_4

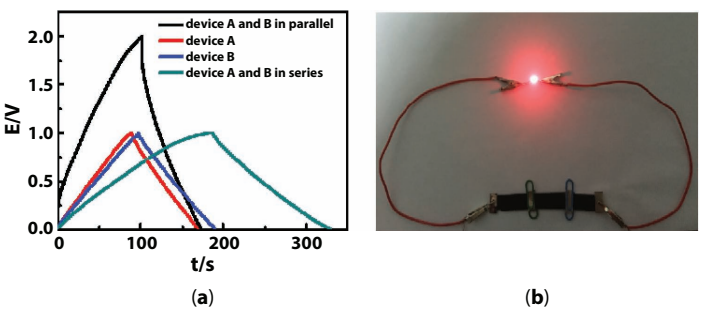

Figure 20.5 The galvanostatic charging and discharge curves of two individual supercapacitors in parallel and series at a fixed current of 2 mA (a). The photo image of LED powered by three flexible supercapacitor devices assembled in series (b). (Adopted with a kind permission from Ref. [87] from © Elsevier.)

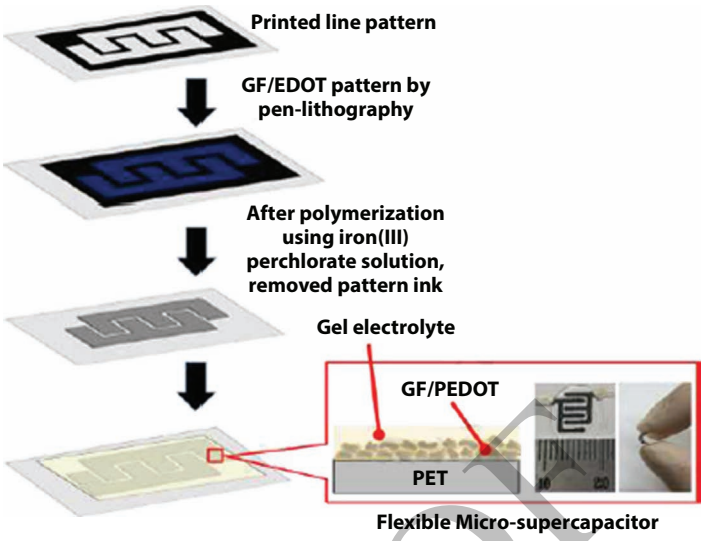

Figure 20.6 The schematic representation of the fabrication of micro-supercapacitor based on graphene flake/PEDOT composite deposited on a PET film through pen lithography. (Adopted with a kind permission from Ref. [89] from ©Elsevier.)

gel electrolyte exhibited a specific capacitance of 37.08 mF cm^{-2}, the energy density of 6.4 mWh cm^{-2} and high cycle-life stability with capacitance retention of 89% even after 2,500 cycles, suggesting that the developed MSC is a potential candidate for device applications.

Recently, flexible supercapacitors that retain an effective electrochemical performance under deformation have fascinated much attention with regards to flexible electronics applications. He *et al.* [90] developed flexible and compressible sponge self-supporting electrodes and fabricated all-solid-state symmetric supercapacitors. The starting point for the preparation of the supercapacitor is the formation of a sponge of multiwalled carbon nanotubes using chemical vapor deposition. After purification, the sponge was coated with PEDOT using cyclic voltammetry. Figure 20.7(a) shows the morphology of pure carbon nanotube sponge. Figure 20.7(b) clearly shows the coating of PEDOT on the surface of CNTs which exhibits a globular morphology owing to the aggregation of PEDOT particles, as shown in Figure 20.7(c). The supercapacitor was assembled with a PVA/H_2SO_4 gel electrolyte.

The particular characteristics of the MWCNT sponge allowed the electrode to be compressed up to 50% and to be bent freely, as shown in Figure 20.7d. The CNTs/PEDOT sponge electrode exhibited the highest mass-specific capacitance of 147 F g^{-1} and excellent cycle-life stability with capacitance retention of more than 95% even after 3,000 cycles. Besides, the

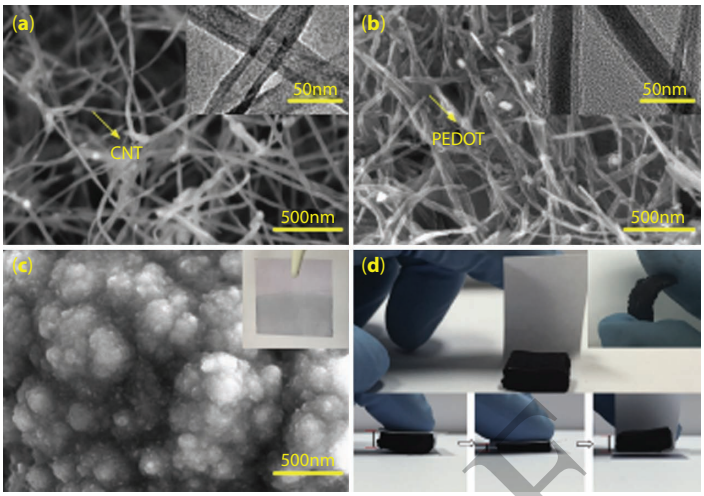

Figure 20.7 The morphology of electroactive sponges: SEM and TEM (inset) images of sponge prepared using MWCNTs (a); SEM and TEM (inset) images of sponges prepared using MWCNTs/ PEDOT sponge (b); SEM and optical (inset) images of PEDOT deposited on the ITO surface (c); and optical images of flexibility and compressibility of CNTs/PEDOT sponge electrode (d). (Adopted with kind permission from Ref. [90] from © Elsevier.)

fabricated symmetric supercapacitor device exhibited the highest power density of 10.2 kW kg^{-1} with the energy density of 8 Wh kg^{-1} and the highest energy density of 12.6 Wh kg^{-1} with the power density of 1 kW kg^{-1}.

20.5 Electrolytes for Flexible Supercapacitors

Apart from the electrodes, the electrolyte also plays a vital role in achieving the high performance of supercapacitor devices. The performance of a supercapacitor could be assessed by measuring the power density and the energy density; these are both greatly affected by the types of electrolytes used. Generally, the power density is affected by the resistance of the electrolyte, while the ion concentration of the electrolyte and the voltage window control the energy density. There are three main types of electrolytes that have been identified for use in supercapacitors. These are aqueous electrolytes, organic electrolytes and ionic liquid electrolytes. The requirements for an electrolyte used in a supercapacitor include high ionic concentration, high electrochemical stability, a wide voltage window, low solvated ionic radius, low viscosity, low volatility, low toxicity, low resistivity, low cost and high purity.

The electrolyte employed in flexible supercapacitors can be categorized into two types, such as liquid electrolytes and solid electrolytes (polymer electrolyte). Liquid electrolytes are organic or aqueous solutions. The aqueous electrolytes which are in use are either acid electrolytes (aqueous solutions of H_2SO_4 or H_3PO_4), alkaline electrolytes (aqueous solutions of LiOH, NaOH and KOH) or mild electrolytes (aqueous solutions of KCl, LiCl, Na_2SO_4, KNO_3, Li_2SO_4) [91–102]. Generally, organic electrolytes use a mixture of a salt dissolved in an organic solvent. The organic electrolytes which are widely used are: 1 M $LiPF_6$ in ethylene carbonate/diethylene carbonate (EC/DEC = 1:1) or ethylene carbonate/propylene carbonate/dimethyl carbonate (EC/PC/DMC) (1:1:1) and 1 M Et_4NBF_4/PC solutions [102–107].

Solid-state electrolytes are the key component in the design of flexible supercapacitors, and they significantly affect the electrochemical properties [103, 104]. In comparison to conventional liquid electrolytes, solid-state electrolytes offer many advantages such as simple fabrication steps, easy and inexpensive packaging and no possibility of the leakage of toxic electrolytes. The good mechanical stability of solid-state electrolytes is beneficial in the fabrication of different flexible and bendable supercapacitors. Electrolyte parameters such as high ionic conductivity, high chemical, electrochemical and thermal stabilities, dimensional stability, and good mechanical strength are the key factors in developing high-performance flexible supercapacitor devices. Currently, three major solid-state electrolytes are employed in supercapacitors. These are gel polymer electrolytes (GEs) [105], ceramic electrolytes (CEs) [106] and polyelectrolytes (PE). GEs are used widely because of their comparatively high ionic conductivity (10^{-4} to 10^{-3} S cm^{-1}) under ambient conditions. Gel electrolytes are a mixture of a gelling agent, a solute and a solvent and they are usually prepared using a sol-gel technique. Gel agents used include PVA [107], poly(ethylene oxide) PEO [108], poly(acrylonitrile) (PAN), poly(acrylate) (PAA) [109], poly(methyl methacrylate) (PMMA) [110], poly(amino ester) (PAE) [111], poly(ethylene glycol) blending poly(acrylonitrile) (PAN-b-PEG-b-PAN) [112], poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP). As an example, the method of preparation of an H_3PO_4/PVA solid-state electrolyte as follows PVA is dissolved in water. Then, H_3PO_4 is added to the resulting PVA solution to obtain the solid-state electrolyte. A solid electrolyte has an important role in transparent and flexible high-performance SCs, owing to its good ionic conductivity, safe operation, mechanical stability and non-toxic nature [113–117].

20.6 Conclusions and Future Perspectives

Among the energy storage devices, supercapacitors are considered as one of the most valuable inventions. Flexible, stretchable supercapacitors find their use in promising energy storage applications, ranging from flexible electronics to wearable displays. The synthesis of electrode materials with the appropriate electrical and mechanical properties and the fabrication of devices with required characteristics are the necessary pre-requisites for the device applications. CP-based electrode materials exhibit high electrochemical behavior because of the preparation methods providing an effective surface area. Conducting polymers are flexible, highly conducting and easily processable, and thus can serve as effective electrode material for flexible supercapacitors. CP-based supercapacitors demonstrate high specific capacitances and deliver energy at a relatively rapid rate. A large variety of flexible, stretchable, and even transparent supercapacitors have been developed. Conducting polymers can also be used as an essential component in supercapacitor electrolytes. The performance of supercapacitors depends on the optimisation of electrolytes, and gel electrolytes are highly promising. Recent developments in the field, as reviewed in this chapter, have indicated the adaptability of CPs in flexible supercapacitor applications. Flexible electronics is a rapidly developing research field and application area. However, further optimization is needed for the fabrication of competent flexible supercapacitors, and this could make flexible supercapacitors the most potential energy storage technologies.

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