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Abstract

Supercapacitors (SCs) as portable systems and electric vehicles have aroused great interest due to their high power in short term. The composite materials of carbon nanotubes and conducting polymers have been considered for SC electrodes. Carbon nanotubes (CNTs), due to their outstanding electric properties and nanoscale texture, such as large specific area, low cost, and cycle stability, exhibit a large and stable double layer capacitance. However, the pure CNTs have low specific capacitance and relatively poor energy density, which limit the commercial application for SCs. On the other hand, conducting polymers have been intensively investigated as the electrode material in SCs. Higher electrical conductivity, larger pseudo-capacitance, and faster doping/dedoping rate during charge/discharge process are their main advantages. The possible application of conducting polymers in SCs is dictated by their significant capacitance values and huge faradaic capacitance. They undergo a redox reaction to store charge in the bulk of the material and thereby increase the energy stored and reduce self-discharge. But they are not ideal materials used alone as advanced capacitors materials, because of their low mechanical strength, poor electrical conductivity and low porosity.

This chapter looks at the major conducting polymer materials, namely, polyaniline, polypyrrole, and ethylene-vinyl acetate copolymer, as well as composites of these materials with CNTs. These composites of the CNTs with these electroactive species propose a facile solution to the capacitance limitation of the CNTs and the structural defects of these electroactive species. In order to achieve low contact resistance and high surface area, surface activation through dispersion or ordered assembling of CNTs have been investigated.

Keywords: Supercapacitors, conducting polymer, electrode, electrodeposition, carbon nanotubes
1. Introduction

In recent years, much great attention has been paid to the development of flexible supercapacitors (SCs) and batteries. SCs have not only high power density, high cyclic stability and high discharge rate, comparable to dielectric capacitors, but also high energy density comparable to that of the batteries [1–4].

According to the electrode material and the operational mechanism of SCs, there are three major types of SCs. Electrochemical double-layer capacitor (EDLC) is the first type. In this system, the capacitance can be stored as a build up of charge in the electrical double-layer in the solution interface close to the surface of the carbon to balance the charge in the carbon material [5]. In charging and discharging process, carbon based electrodes undergo faradaic processes. They can provide a reversible adsorption for the ions on the high surface area [6]. Recently, many kinds of carbon materials and their composites have also been used in SCs with high energy density (155 Wh kg\(^{-1}\)) [7–11].

The second type SCs are transition metal oxides based electrochemical capacitors, which are developed based on the fast and reversible redox reactions at the surface of active materials (such as MnO\(_2\) and RuO\(_2\)) [12–27]. A high specific capacitance can be obtained in this type of SCs, but the defect is the poor power performance due to its relatively high electrical resistance.

Conducting polymer–based SC is the third type [28–35]. The conductive polymers offer a high specific capacitance and low production cost, though the conductive polymer–based SCs usually have poor stability during cycling because of the destabilization of the polymeric backbone structure. The composite materials of carbon nanotubes and conducting polymers have been considered for SC electrodes. Carbon nanotubes, due to their outstanding electric properties and nanoscale texture, such as large specific area, low cost, and cycle stability, exhibit a large and stable double layer capacitance. However, the pure CNTs have low specific capacitance and relatively poor energy density, which limit the commercial application for SCs. On the other hand, conducting polymers have been intensively investigated as the electrode material in SCs. Higher electrical conductivity, larger pseudo-capacitance, and faster doping/dedoping rate during charge/discharge process are their main advantages [36]. The possible application of conducting polymers in SCs is dictated by their significant capacitance values and huge faradaic capacitance. They undergo a redox reaction to store charge in the bulk of the material and thereby increase the energy stored and reduce self-discharge. But they are not ideal materials used alone as advanced capacitors materials, because of their low mechanical strength, poor electrical conductivity and low porosity.

This chapter focuses on the major conducting polymer materials, namely, polyaniline (PANI), polypyrrole (PPy), and ethylene-vinyl acetate copolymer (EVA), as well as composites of these materials with carbon nanotubes. These composites of the CNTs with the electroactive species propose a facile solution to the capacitance limitation of the CNTs and the structural defects of these electroactive species. In order to achieve low contact resistance and high surface area, surface activation through dispersion or ordered assembling of CNTs have been investigated [37].
2. CNTs–PANI

2.1. Electrodeposition of CNTs–PANI

Over the past few years, various CNTs–PANI electrodes have been synthesized by many methods [38–53]. Among them, electrochemical preparation is a promising method because of its simplicity, ease of scale-up, low cost, and environmental friendliness.

In 2014, our group prepared nano PANI via cyclic voltammetry technique in acidic condition [51]. The prepared PANI has a large area with rough surface. The symmetric SCs based on the composites of PANI, CNT and poly dimethylsiloxane (PDMS) show a high capacitance and

![Figure 1](image-url). (a) SEM image of CNT/PANI hydrogel film; (b) SEM image of CNT/PANI film; (c) TEM image of CNT/PANI hydrogel film; (d) TEM image of CNT/PANI; (e) scheme of forming process. (Reproduced with permission from Zeng et al. [52]. The Royal Society of Chemistry). © 2015.
stretchability. Zeng et al. [52] also obtained the nano PANI on the untreated CNT hydrogel film by the similar method, as shown in Figure 1.

Cai et al. also prepared CNT–PANI composites by electrochemical polymerization [53]. Bare MWCNT fibers were first dipped into the electrolyte containing 1 M H₂SO₄ and 0.1 M aniline for 5 h, so the aniline monomer can be effectively infiltrated into them. Electrodiposition of aniline was mainly performed from 50 to 2000 s at a potential of 0.75 V. After polymerization, the as prepared multi-wall carbon nanotubes (MWCNTs) –PANI composite fibers were washed with deionized water and dried at room temperature for over 2 h.

Zhang et al. fabricated the MWCNTs/PANI composite films for SC electrode by an in-situ electrochemical polymerization onto stainless-steel sheet from an aniline solution containing a small content of MWCNT, and the whole process with no sonication [54]. The electrochemical polymerization was carried by the CV technique at 100 mV·s⁻¹ between -0.2 and -1.2 V for 100 cycles in a solution of 0.5 M H₂SO₄ + 0.325 M aniline dissolved MWCNT in different mixture ratios. Three different electro-polymerization methods (potentiodynamic, potentiostatic and galvanostatic) of PANI have been studied by Tran et al. [55]. Potentiodynamic is carried out with a condition of sweeping voltage between -0.1 and 1 V at 20 mV·s⁻¹; potentiostatic is applying a constant potential of 0.8 V; and galvanostatic is applying a constant current of 9 mA. After deposition, samples were thoroughly washed with deionized water to remove any adsorbed electrolyte and dried at 60°C for at least 2 h.

2.2. Structure and electrochemical performance of CNTs–PANI composite electrodes

Our group reported that MWCNT-based stretchable film can be formed via water surface assisted method [51]. In the research, combined with the PDMS, the composite electrodes have a uniform surface, excellent conductivity, and high stretchability. The conductivity of the MWCNT/PDMS film is 0.55 S·cm⁻¹ with 3 wt% MWCNTs, which will increase to 4.19 S·cm⁻¹ with 10 wt% [51]. This variation of the conductivity is due to the formation of 3D-like net structure. The 10wt% MWCNT/PDMS film also has a good stretchability, which can reach to 50% without damaging its conductivity and structure. When the content of MWCNTs is over 10%, the film is hard to be continuous. The 10wt% MWCNT/PDMS film substrate combined with PANI nanofibers show an excellent SC performance at a scan rate of 5 mV·s⁻¹ (specific capacitance: 1023 F·g⁻¹, areal capacitance: 481 mF·cm⁻²) In this work, a solid-state symmetric SC device was assembled with PANI/10wt% MWCNT/PDMS, which shows excellent stretchability and capacitance. An elastomeric polyurethane textile separator and PVA/H₂SO₄ gel electrolyte was shown in Figure 2. This device was able to deliver the highest volumetric capacitance of 2.1 F·cm⁻³ and the highest specific capacitance of 159 F·g⁻¹ at 5 mV·s⁻¹. Additionally, its maximum volumetric energy density is about 0.15 mW·h·cm⁻³. After 500 cycles under the condition of stretching and releasing, the as-assembled devices can keep more than 95% capacitance. These results indicate that this device possesses good and stable electrochemical behavior.
PANI coated onto individual CNTs and CNT bundles in the activated CNT film can be formed into CNT/PANI hydrogel film [52]. This nanostructure largely benefits the uniform dispersion of PANI among the CNT network scaffold, thus its PANI utilization efficiency is relatively high. In their experiment, the diffusion of electrolyte towards the electrodes was blocked. This is due to the formation of a PANI layer, which can cover the open channels of the scaffold in the film. The optimized deposition condition of PANI is 400 cycles in their study. Along with the increasing cycles, the rate performance will become poor, which may be caused by the decreasing of utilization efficiency and surface area of PANI. The capacitance of the CNT/PANI hydrogel film at 1 mA·cm\(^{-2}\) is 0.68 F·cm\(^{-2}\), which is much higher than many flexible electrodes such as carbon films, conductive polymers and even metallic oxides. The excellent electrochemical performance may be due to the porous microstructure. This structure maintains the facile electrolyte penetration, fast proton exchange, and metallic conductivity, thus ensuring the high electrochemical performance of the flexible film electrodes. The all-solid state flexible SC is assembled by two identical CNT/PANI hydrogel film electrodes and a layer of H\(_2\)SO\(_4\)/PVA gel electrolyte, which has the sandwich structure. Specific capacitance (Csp) of the capacitor at 1 mA·cm\(^{-2}\) is 184.6 mF·cm\(^{-2}\). Even at a current density of up to 5 mA·cm\(^{-2}\), the Csp of this device can retain a high value of 120 mF·cm\(^{-2}\), which indicates that the good rate performance of this SC device. The rolled-up SC is similar to that under pristine condition at 5 mA·cm\(^{-2}\) and the Csp values are almost the same. The cyclic performance of the flexible SC of the flexible SC remained almost the same after 500 cycles of charge–discharge. The electrochemical performances are shown in Figure 3.
MWCNTs–PANI composite fiber remained almost unchanged in diameter. The resulting MWCNTs–PANI composite fibers were flexible and can be easily bent [53]. No obvious damage to the structure was observed, and both tensile strength and electrical conductivity remained almost unchanged after bending for over a hundred cycles, as shown in Figure 4. PANI could be stably attached on the aligned MWCNTs possibly due to the interaction between them in the composite fiber. The aligned MWCNTs–PANI composite fibers were then coated with a layer of H₃PO₄–poly(vinyl alcohol) gel electrolyte on the surface. Two modified composite fibers were finally twisted to fabricate the SC wire. Cyclic voltammograms of MWCNTs–PANI (weight percentage of 24%) composite fiber at a scan rate of 10 mV·s⁻¹ show a typical rectangular shape, which is corresponding to a double layer capacitor obtained for the bare MWCNT fiber, that can been seen in Figure 5. While redox peaks at 0.3–0.4 V that indicates a pseudo-capacitance derived from different oxidation states of PANI are observed for the MWCNTs–PANI composite fiber. The specific capacitances increase to the maximum
value (274 F·g⁻¹) with the increasing PANI weight percentage from 0 to 40%. Interestingly, further increase of PANI has decreased the specific capacitance, e.g., 245 F·g⁻¹ at 70 wt%.

Zhang et al. [54] also considered that three-dimensional network structure is conducive to increase the contacting chance between the PANI and the electrolyte, and more active sites of the composite films for faradic reaction and larger SCs than pure PANI film. The highest SCs of 500 F·g⁻¹ was obtained for MWCNTs/PANI-stainless-steel sheet composite films when the content of MWCNT is only 0.8 wt%. This kind of composite electrode shows a higher specific capacitance, better power characteristic, better cyclic stability, and more promising for applications in SCs than a pure PANI film electrode.
3. CNTs–PPy

3.1. Electrodeposition of CNTs–PPy

PPy, one of the most interesting conducting polymers, have been studied in SCs due to due to its low cost, high specific capacitance, excellent flexibility and ductility [55]. Over the past few years, various CNT–PANI electrodes have been synthesized by many methods, such as \textit{in situ} chemical polymerization, chemical oxidative polymerization and electrochemical polymerization [57–62].

Electrodeposition or electrochemical polymerizations of CNTs-PPy composites has been extensively reported [63–64]. Electropolymerization of PPy films is an attractive method that can dissolve the pyrrole monomer in a solvent, and form a film at the electrode surface by the applied anodic potential. Carbon nanotubes are suitable for electrode materials because of their good electronic and mechanical properties and high stability [65–67]. Composites of PPy and carbon nanotubes have been prepared by chemical or electrochemical oxidation and the capacitance [26, 68–70] of these composites have also been studied.

Chen et al. carried out electropolymerization of PPy in a three electrode configuration with CNT film as the working electrode, Ag/AgCl electrode as the reference electrode and a graphite rod as the counter electrode [56]. The electrolyte contains 0.1 M pyrrole and 0.05 M Na$_2$SO$_4$, and the electrodeposition was conducted at a constant current density of 1 mA·cm$^{-2}$ for different time lengths. The fabrication process of CNT/PPy films is illustrated in Figure 6. PPy can be electroplated at a constant current density in pyrrole and dodecylbenzenesulfonate (NaDBS) solution in acetonitrile [71].

![Figure 6. Schematic procedure of the paper-like CNT film and the CNT/PPy film. (Reproduced with permission from Chen et al. [56]). © 2015, Elsevier.](image-url)
Pulsed potentioamperometric method was also applied by Fang et al. [72]. The MWCNTs membrane with a stainless steel (SS) ring as the current collector was used for the working electrodes. The counter electrode and reference electrode are Pt coil and a Ag/AgCl (saturated KCl) electrode, respectively. Pulsed potentioamperometric deposition of PPy was carried out in aqueous solutions containing pyrrole and 1.0 M KCl. The electrode potential was programmed with a waveform consisting of a potential step to 1.05 V (vs. Ag/AgCl).

The solution of 0.1 M pyrrole and NaClO4 was also used as electrolyte for PPy deposition. In order to deposit the PPy on the CNTs evenly, the CNT films were supported by two stainless steel wire meshes [73–74]. Pretreatment of CNT is very important to improve the electrode capacitance. Generally, CNT should be immersed in 30 wt% H2O2 solution for 2 days and in 37 wt% HCl solution for 1 day to remove the amorphous carbon and catalyst particles.

3.2. Structure and electrochemical performance of CNTs-PPy composite electrodes

The detailed structure of the electrodeposited CNTs/PPy film analyzed by transmission electron microscopy show that a layer of amorphous PPy is well coated on the outer surface of the crystalline CNT, which is beneficial to the fast diffusion and migration of ions in the polymer, thereby improving the performance of the CNTs/PPy film [56]. The electrodes show an ultimate tensile strength of 16MPa for this film. The actual capacitance of the robust CNTs/PPy electrode is calculated to be 0.28 F·cm⁻² at a current density of 1.4 mA·cm⁻², which is 5.6 times larger than that of the pure CNTs electrode (0.05 F·cm⁻²). All-solid-state SCs assembled with the robust CNT/PPy electrodes sandwiching by PVA/H2SO4 solid-state electrolyte exhibit

Figure 7. Electrochemical properties of SC device. (a) Ragone plots; (b) Cycle performance at 0.1 A·cm⁻²; (c) CV curves at 100 mV·s⁻¹ under different conditions; (d) Digital photos. (Reproduced with permission from Chen et al. [56]). © 2015, Elsevier.
high electrochemical performance (device volumetric capacitance of 4.9 F·cm\(^{-3}\) at 0.05 A·cm\(^{-3}\))
and a favorable rate performance (device volumetric capacitance of 3 F·cm\(^{-3}\) at 0.5 A·cm\(^{-3}\)). The
values are higher than those of other solid-state SCs reported previously based on transition
metal oxides and CNT [75–82]. The power density of the device achieved 0.15 W·cm\(^{-3}\) while the
energy density was 0.26 mWh·cm\(^{-3}\). Its cycling stability is excellent that the capacitance
retention is larger than 95\% after 10,000 cycles. The results are shown in Figure 7.

Xu et al. fabricated core–shell structured composite of PPy and CNTs (PPy@CNTs) by
electrodeposition, which indicates the PPy is distributed evenly in the CNT fiber [73]. When
the content of PPy is 51 wt%, this composite shows a maximum value of 350 F·g\(^{-1}\) and has high
electrochemical stability under bending and twisting.

Vertically aligned carbon nanotubes (VACNT)-PPy nanocomposites prepared by electro
polymerization shows a specific capacitance of 5 mF·cm\(^{-2}\), which is 500\% higher than that of
as-grown VACNT or pure PPy film [71]. Different from the PANI, the deposition time and the
thickness of PPy have no effect on the surface phenomenon. Fast redox reaction on PPy can
enhance the energy density in the VACNT-PPy nanocomposite. The VACNT-PPy nanocomposite
with 1 min electroplating time also has the lowest leakage current (about 5\% of the
device current at 0.5 V) compared to uncoated VACNTs and the 4 min electroplated VACNT-
PPy nanocomposite. Life cycle testing indicates that the 4 min electrode reached its maximum
capacitance after 1000 cycles. After 3000 cycles, the 4 min electroplated VACNT-PPy nano-
composite retained 92\% of its maximum capacitance (capacitance at 1000 cycles). But the
electrochemical capacitance maintained only 65\% for the 1 min electrode over 3000 cycles.

Figure 8. (a) Schematic of MWCNT film (top) and the pulsed electrodeposition condition (bottom); (b) and (c) Schematic of the PPy/MWCNTs under pulse deposition; (d) and (e) TEM image of the MWCNTs and PPy/MWCNTs; (f) SEM image of the PPy/MWCNT membrane (Reproduced with permission from Fang et al. [72]). © 2010, Elsevier.
Pulse deposition of PPy on MWCNT can improve the SCs value about 30 times [72]. In general, short deposition time allows monomers to diffuse from the bulk solution into the space between carbon nanotubes inside the membrane and thus produces more uniform PPy coating. The clogging of the space between carbon nanotubes at the membrane exterior is found to lower the SC value, as shown in Figure 8. PPy deposition with short pulses allows the polymer backbone to rearrange to form more ordered structure. Both the structural uniformity and high conductivity of PPy coating help to provide higher pseudo-capacitance in this application.

4. EVA-CNT

EVA is very attractive as a very promising membrane material due to its excellent mechanical property such as good softness, high flexibility and good processability. Additionally, conductive EVA-based membranes are easily obtained by combining EVA with conductive additives (CNT). In previous reports, some materials were often used for the substrates, such as carbon cloth, nickel foam, titanium foil, and et al. However, Lens wiping paper has been paid much more attention for the preparation of the conductive substrates, due to its low cost, lightweight and flexibility [83]. The EVA/40 wt% CNT paper exhibits a high conductivity of 12.1 S·cm\(^{-1}\) with good flexibility, lightweight and durability. MnO\(_2\) was electrodeposited on the as-prepared EVA/CNTs paper via potentiostatic technique. The CV curves of 45 s-
MnO₂/EVA/40 wt% CNT electrodes collected at various scan rates exhibit quasi-rectangular shapes and do not significantly change when the scan rate increases from 10 to 200 mV·s⁻¹, revealing the good capacitive behavior and high-rate capability, which demonstrates that MnO₂ is a good pseudo-capacitive electrode material for SCs. The current density of the MnO₂/EVA/40 wt% CNT electrode increases with the increasing MnO₂ deposition time from 15 to 120 s. The 120 s-MnO₂/EVA/40 wt% CNT yields a good electrochemical capacitance of 0.083 F·cm⁻² (0.36 mg·cm⁻²) at the scan rate of 10 mV·s⁻¹. The as-prepared electrode has better performance than the others, because the substrate of EVA/40 wt% CNT has good electrical conductivity (3.7 Ω) and rough. With increasing of the deposition amount of MnO₂, the charge-transfer resistance can increase to 22.9 Ω. If the deposition time of MnO₂ is shortened, a high capacitance will be achieved, which has been confirmed by our experiments [83], as shown in Figure 9.

Figure 10. Electrochemical performance of MnO₂/EBC supercapacitor. (a) CV curves; (b) galvanostatic charge/discharge curves; (c) CV curves at different bending angles; (d) cycle stability at stress–recovery states. (Reproduced with permission from Zhang et al. [84]). © 2013, The Royal Society of Chemistry.

We also report, for the first time, the synthesis of conductive flexible membranes of EVA composites filled with carbon black (CB) and CNT and their application as flexible substrates in SCs [84]. We found that the prepared EVA(49.5wt%)-CB(49.5wt%)-CNT(1wt%) (denoted as ECB) showed the best flexibility and electrical conductivity of 0.17 S·cm⁻¹. To demonstrate the feasibility of the ECB substrate as a conductive substrate for flexible SCs, MnO₂ was grown on the surface of the as-prepared membrane substrate by a simple electrochemical deposition method for 20 min. The ECB substrates after being coated with a layer of MnO₂ are still well flexible, and can even be folded and twisted without any destruction. Electrochemical measurements demonstrated that the MnO₂/ECB composite exhibited a high specific capacitance of 169.5 F·g⁻¹, which is a 2- and 2.5-fold enhancement as compared to the MnO₂/FTO and
MnO$_2$/PETI composites. The shape of charge/discharge curves of the MnO$_2$/EBC electrodes is more symmetrical and their discharge time is substantially more prolonged than the other electrodes, such as the MnO$_2$/Ti, MnO$_2$/FTO, MnO$_2$/PETI. The specific capacitance of the MnO$_2$/EBC electrode increased to 111% during the first 1100 cycles and was almost constant with slight fluctuations during the subsequent 900 cycles. The power density of 10 950 W·kg$^{-1}$ and energy density of 30.4 W h·kg$^{-1}$ were achieved by the MnO$_2$/EBC electrode. By assembling two pieces of the MnO$_2$/EBC composite with a separator, the SC devices were assembled. The device could light a red LED (work voltage: 1.5 V) well for about 10 s after being charged at 2.5 V for 10 s [84]. The bending of the electrodes has no obvious effect on the electrochemical performance, as shown in Figure 10. Similarly, stress-recovery cannot affect the cycle stability obviously, with only less than 5% change. In short, structure of the electrodes will not be destroyed by the bending and stress states. So many good properties of MnO$_2$/EBC electrode will make it applicable in flexible SCs widely spread in the future.

5. Summary

In this chapter, we summarized recent advances in the development of composite electrode materials composed of CNTs and conductive polymer (PANI/PPy/EVA) prepared by electro-deposition. These kinds of composite electrodes can increase energy density without sacrificing their power density. Also, to avoid the use of current collectors, conductive additives and binders, the electrodes are designed to have flexibility that can reduce the total weight of the electrodes. Electrodeposition of conductive polymers onto CNT films can prevent the transmission and deposition of aniline/pyrrole molecules into the internal part of the film. However, electrodeposition often blocks electrolyte channels at the outer surface of CNT film which suffers from ECP aggregation and high resistances due to poor CNT interconnection. High loading mass of conductive polymers and cohesion strength between CNT and conductive polymers are still an important challenge.

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