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Flexible Conducting Polymer-Decorated Nanocomposites for Energy Conversion and Storage Devices

Sivaprakasam Radhakrishnan¹, Danyun Lei¹, Tae Hoon Ko², Byoung-Suhk Kim^{1,2*}

¹Department of BIN Convergence Technology,²Department of Organic Materials & Fiber Engineering,Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 54896, Republic of Korea *Corresponding author

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Introduction

The growing demands for portable devices and electric vehicles which that require high power in short term pulses have prompted a great interest in electrochemical supercapacitors (Figure 5.1). The significance of developing Novel types of energy conversion and storage systems are will playing vital roles due to the fact that global warming and limited resources of fossil fuels. The U.S. Department of Energy Freedom CAR and Vehicle Technologies have estimated the world will require doubling its energy supply to double by 2050 [1]. Recent global research in exploitation of novel technologies for both energy conversion (solar cells and fuel cells etc.) and energy storage (electrochemical capacitors and batteries) are focusing by numerous researchers around the world [2-4]. Stimulated by the needs of high-power energy storage systems in a large spectrum of applications, such as electric and hybrid vehicles, supercapacitors have recently attracted much interest owing to their unique abilities to deliver high power release or uptake in very short time (a Compared with conventional electrostatic capacitors, few seconds). electrochemical supercapacitors can store either hundreds or thousands of times more charge, making them more attractive for meeting the practical demands for energy storage. However, supercapacitors suffer from low energy density compared with Li-ion batteries, which in turn hinders their industrial application [5]. The performance of supercapacitors inclusive of energy density mainly depends on the type and structure of electrode materials. To date, two main acknowledged energy storage principles of supercapacitors have been proposed: the electric double-layer principle and the surface redox reaction-based pseudo-capacitive charge storage principle. Indeed, nanoscale research has enabled a revolution in the development of supercapacitors, which has not only led to substantial improvement of capacitive properties, but the reformation of electrode configuration, and even the device prototype. Conducing polymer based nanocomposite materials have opened up new areas in nano-engineering to meet this energy challenge. Compared with composite materials, the application prospects of single materials are limited due to their poor electrochemical properties. Further, composite nanomaterials with unique structure are of greater interest because of their superior properties compared with their single counterparts [6]. In particular, conducing polymer based nanocomposite materials have been demonstrated to be an enabling technology for developing high-performance energy-storage and conversion systems [7-10]. Recently development in materials science and engineering, particularly conducting polymers (polyaniline, polypyrrole, PEDOT etc.) has facilitated the research and development of energy storage and conversion technologies. Comparing to conventional energy materials, conducting polymers possess some unusual (morphology, electrical conductivity, optical, mechanical, thermal and redox) properties that are useful in enhancing high-performance energy storage systems. Specifically, considerable efforts have been made to utilize the unique properties of polyaniline (PANi) based nanocomposite for high-performance energy-storage applications, due to its relatively high conductivity and largest theoretical pseudocapacitance [11,12], which stores energy by the faradaic reaction involving multiple redox states [13]. However, pseudocapactive reactions occur only on surface layers that are in contact with the electrolyte with the inner part inactive as the dead volume. Therefore, increasing the active sites exposed to the electrolyte is of great importance for increasing the utilization efficiency and the specific capacitance of PANi. Furthermore, a major problem of using polyaniline materials for supercapacitors is that they exhibit poor stabilities during the charge/discharge process [14,15]. A great number of studies have been devoted to increasing the utilization efficiency and specific capacitance of PANi by making it into nanomaterials with small size and good dispersion. At present, PANI is generally grown on various carbon nano-supports such as graphene/CNFs [16], CNTs/CNFs [17], mesoporous carbon [18],

graphene [19], carbon nanotubes (CNTs) [20] and carbon nanofibers (CNFs) [21,22] for improving the dispersion and electrical conductivity. This chapter describes the (i) Chemical and electrochemical synthesis of PANi in presence and absence of surfactant cetyltrimethylammonium bromide (CTAB) and tested for its specific capacitance properties by constructing a supercapacitor using stainless steel electrodes; (ii) dodecyl benzenesulphonic acid (DBSA) doped polyaniline and its magnetite composite (PANi-DBSA/Fe₃O₄) has been prepared and tested for its specific capacitance properties by constructing a symmetric and asymmetric capacitor; (iii) we have fabricated uniform, flexible and transparent electrodes based on PANi nanowire/nylon nanofiber reinforced cellulose acetate (PANi nanowire/PA/CA) thin film for high performance supercapacitor applications; (iv) we have fabricated flexible PANi decorated carbon nanofiber mats (CF) and investigated for its specific capacitance properties and (v) discussion on the challenges and perspective in the research and development of flexible supercapacitors based on conducting polyaniline.



FIGURE 5.1

Schematic diagram for the charge distribution in an electric double-layer capacitor during charge and discharge process

Polyaniline nanocomposite for supercapacitor applications

Polyaniline is a typical phenylene-based polymer having–NH– functional group in a polymer chain flanked either side by a phenylene ring, this structure has a chemical flexibility to yield a high processability. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which has a lone pair of electrons and is responsible for creating great interest in this technology. PANi, the polymer resulting from oxidative polymerization of aniline, is built up from reduced (B-NH-B-NH) and oxidized (B-N=Q=N-) repeat units, where B denotes benzenoid and Q denotes quinoid ring. Thus the ratio of amine to imine yields various structures, such as leucoemeraldine (fully reduced from), emeraldine base (neutral, undoped form), Emeraldine salt (50% oxidized, doped form) and pernigraniline (fully oxidized form) [7]. The simple doping/de-doping phenomenon (Figure 5.2) makes PANi and its composites with other nanomaterials highly suitable for supercapacitor applications. Polyaniline (PANi) and its composite have recently achieved widespread importance in energy storage application because it's unique conduction mechanism, redox properties and high environmental stability [23,24].



Schematic diagram for the structural changes of PANi backbone during charge-discharge process

Phosphoric acid doped Polyaniline as electrode materials for aqueous redox supercapacitor

In this work, phosphoric acid doped polyaniline has been synthesized by chemically (CS) and electrochemically (ES), in the presence (CS-PANi-PA-CTAB &ES-PANi-PA-CTAB) and absence (CS-PANi-PA &ES-PANi-PA) of cetyltrimethylammonium bromide (CTAB) and tested for its specific capacitance properties by constructing a supercapacitor using stainless steel electrodes [7]. The surfactant was added to control and keep the size of the particles small so that the surface area was higher and diffusion of electrolyte ions was greatly improved. Cyclic voltammetry method was used to deposit thin films of PANi by cycling the potential between -0.2 and 1.0 V at a scan rate of 100 mV/s (Figure 5.3a). To study the effect of a surfactant, i.e., CTAB, PANi in presence of CTAB was also been prepared in a similar method by addition appropriate amount of CTAB in the electrolyte mixture (Figure 5.4a).The electrochemical activity of electrodeposited PANi in presence of CTAB (Figure 5.4b) was much better than that of prepared PANi without CTAB (Figure 5.3b).



(a) Electrochemical growth pattern of PANi in the presence of 5 mM aniline in 1M aqueous solution of phosphoric acid as the electrolyte and (b) Cyclic voltammogram of PANi in the absence of monomer, in an aqueous solution of phosphoric acid in the potential window of -0.2 to 0.8 V at different scan rates (50-300 mV/s)



FIGURE 5.4

(a) Electrochemical growth pattern of PANi in the presence of 5 mM aniline in 1M aqueous solution of phosphoric acid containing CTAB as the electrolyte and (b) Cyclic voltammogram of PANi in the absence of monomer, in an aqueous solution of phosphoric acid in the potential window of -0.2 to 0.8 V at different scan rates (50-300 mV/s)

Finally, a capacitor was fabricated using two ES-PANi-PA-CTAB electrodes and was studied for its electrical properties using cyclic voltammetry and galvanostatic charge-discharge test. Due to the smaller particle size of ES-PANi-PA-CTAB materials, as compared to the pure ES-PANi-PA materials, the specific capacitance values obtained in this case are found to be higher. The device exhibited capacitance values between 305 F/g and 248 F/g when current density was varied between 1 mA/cm² and 5 mA/cm² (Figure 5.5a). Repeated charge-discharge studies showed that the capacitor exhibited a specific capacitance of 305 F/g in the first cycle which declined to 197 F/g in the 300th cycle at 1 mA/cm² current density (Figure 5.5b). The chemically prepared samples of CS-PANi-PA & CS-PANi-PA-CTAB were also investigated for the charge-discharge properties. These samples

showed lower specific capacitance value, i.e., 108, 93, 81, 76 and 67 F/g at discharge current densities of 1,2,3,4 and 5 mA/cm², respectively. The lower values are mainly due to the over-oxidation of polyaniline formed by the use of the strong oxidizing agent.



FIGURE 5.5

(a) Plots of specific capacitance versus current densities and (b) Plots of specific capacitance versus cyclic number for electrodeposited PANi electrode

Conducting polyaniline-DBSA/Fe₃O₄composites as electrode materials for supercapacitors

We have prepared dodecyl benzenesulphonic acid (DBSA) doped polyaniline and its magnetite composite (PANi-DBSA/Fe₃O₄) by chemical oxidative polymerization method [6]. The polymer composite products are designated as C-1, C-2 and C-3 for Fe₃O₄ loading of 0.1, 0.2, and 0.3 g, respectively. A control sample (PANi-DBSA) was also prepared without addition of Fe₃O₄ nanoparticles and studied along with the composite for comparison. It is well know that the strong proton donating ability, which is needed for PANi for inducing conductivity, the presence of long chain in DBSA makes it as a good surfactant. Because of this reason, the prepared composites (C-1, C2 and C-3) were partially soluble in chloroform, methanol and good dispersible in water. However, the solubility/dispersibility decreases with increase in Fe₃O₄ nanoparticle incorporation. The electrical conductivity of PANi-Fe₃O₄ (0.597 S/cm) composite showed a higher conductivity than the pristine polymer (0.5 S/cm) due to the presence of magnetite particles.

Electrochemical activity of the composites has been investigated. Figure 5.6A (curve b) shows the cyclic voltammogram of the composite on Pt foil electrode in 1M sulfuric acid. Two anodic oxidation of PANi take place at 0.288 V, 0.784 V, and reductions at 0.651 V and 0.10 V suggesting the presence of conducting PANi. A middle oxidation peak generally observable for pure PANi at about 0.4 V assignable to benzoquinone impurities/degradation products is seen with low intensity and suggests that the impurities are present in lower amounts. Pristine polymer PANi-DBSA (Figure 5.6A; curve a) showed the oxidation peaks at 0.186 V and 0.684 V which are nearly 100 mV less than composite C1. This suggests that electron transfer is more facile in the pristine polymer than in composite C1. Further, the parallelogram shape for the CV with high current suggests that the materials are useful for supercapacitor applications.



(A) Cyclic voltammogram (CV) of pristine polymer (a) PANi-DBSA and (b) composite C1 on Pt electrode recorded at 100 mV/s in 1M sulfuric acid. The figure also shows the transition potentials for LE \leftrightarrow ES \leftrightarrow PE states for the composite. (B) CV of fabricated supercapacitor at the scan rates of 100 to 500 mV/s (a-e)

Figure 5.6B shows the CV behavior of the fabricated capacitor at various can rates. The as-prepared polyaniline (PANi-DBSA) showed a specific capacitance of 160 F/g, whereas its magnetite composite (C1) and the symmetrical capacitor derived from C1 showed enhanced specific capacitance of 228 F/g and 180 F/g respectively at 1mA/cm². Figure 5.7A shows the first three charge-discharge curve of the device at current density from 1mA/cm². Figure 5.7B shows the charge-discharge curves for the 1st, 50th, and 1000th cycles for the capacitor at a current density of 5 mA/cm². The capacitor exhibited a capacitance of 180-135 F/g at 1-5 mA/cm². The capacitance is about 75-79% of the single electrode capacitance value. The capacitor showed a decrease in capacitance to 135 F/g at 5mA/cm². The charge-discharge tests carried for 1000 cycles at this current density showed that the capacitance value falls to 84 F/g in the last charge-discharge cycle. The decrease, from the first to 1000th, is about 35% and indicates that there is a degradation of electrolytes and PANi during the cycling experiment. Figure 5.7D shows the variation of coulombic efficiency of the capacitor with cycle number. Coulombic efficiency (η) is calculated as $\eta = (t_d/t_c) \times 100$ where t_d and t_c are discharge and charge times. The value which is low at 70% for first 100 cycles rises to 97% on further cycling. Further, the capacitor exhibited a power density of 0.407 kW/kg with an energy density of 6.33 Wh/Kg at a discharge current density of 0.44 A/g. The mechanism of the capacitor while charging and discharging is proposed as follow

Charging : PANi + $H_2SO_4 \rightarrow [PANi.H^+] HSO_4$ and Fe_2O_3 . $FeO \rightarrow Fe_2O_3$. $FeO^+ (HSO_4^-)$

Discharging : $[PANi.H^+]$ HSO₄ \rightarrow PANi + H⁺ + HSO₄ and Fe₂O₃. FeO⁺ (HSO₄) \rightarrow Fe₂O₃. FeO + HSO₄

It can be noted here that the specific capacitance of the single electrode of pure PANi-DBSA increased after the addition of magnetite particles (C1) which is also due to the increased surface area (due to lower particle size) apart from the contributions from reversible redox process of magnetite particles. However, the specific capacitance values decreased with further increasing in magnetite for C2 and C3. This may be due to higher particle size (lower surface area) formed with higher loadings of magnetite particles which probably offsets the increase in specific capacitance from redox process of magnetite particles.



(A) Charge-discharge curves for first three cycles exhibited by symmetric capacitor of C1 at current density of 1mA/cm^2 . (B) Charge-discharge curves for various cycles exhibited by capacitor of C1 at current density of 5 mA/cm^2 . (C) Variation of specific capacitance of the capacitor with current density and (D) capacitance and columbic efficiency of the C1 capacitor with cycle numbers

Electrochemical impedance spectroscopy (EIS) was employed to obtain equivalent circuit parameters such as transfer resistance and ohmic resistance which enable mechanistic characterization of the system. Typical Nyquist plots for the capacitor in 1M sulfuric acid at potential of 0.2, 0.4 and 0.6 V are shown in Figure. 5.8. The high-frequency intercept of the semicircle on the real axis provided the value of ohmic resistance (R_{sol}), and the diameter of the semicircule gave an approximate value of the charge transfer resistance (R_{cT}) of the composite/electrolyte interface. The value of R_{sol} is not much change and lie between 0.2 to 0.225 Ω for the voltage 0.2 to 0.6 V of the capacitor. But, the value of RCT increased with the capacitor voltage between 0.2 and 0.6 V which is evident from the increased diameter of the semicircle. It is known that the conductance of PANi maximum between ES and PE states and it decreases when PANi transforms into the LE state. Since the negative electrode of the capacitor gradually changes to the LE state when the voltage of the capacitor is increased, hence RCT value also increased. The electrical parameters deduced from impedance plots using equivalent circuit shown in Figure 5.8 are collected in Table 5.1



Nyquist plots for the capacitor C1 (A) at 0.2 V (B) at 0.4 V and (C) at 0.6 V and (D) equivalent circuit used for the system

TABLE 5.1

System parameters obtained from Nyquist Plots

S.No	Potential (V)	R _{cτ} (Ω cm²)	$CPE_1 (\Omega^{-1} \text{ cm}^{-2} \text{ s})$	$CPE_2 (\Omega/S)$
1	0.2	0.93 ± 0.2	0.00019 ± 0.0005	0.686
2	0.4	1.005 ± 0.2	0.00015 ± 0.0003	0.690
3	0.6	14.89 ± 1	0.0023 ± 0.0001	0.306

Flexible polyaniline-decorated nanofiber membrane for supercapacitor applications

Flexible transparent electrode based on PANi nanowire/nylon nanofiber reinforced cellulose acetate thin film as supercapacitor

Today, thin, light-weight and flexible electronics are being pursued intensively, which has stimulated the investigation of flexible and durable energy storage devices for power generation.

As a result, flexible thin-film electrodes are urgently needed. In recent years, nanoscale engineering technologies have brought many opportunities to fabricate high performance flexible thin-film electrodes. Along this line, transparent electrodes play a vital role in many optoelectronic devices such as touch screens, organic light-emitting diodes, and solar cells. The basic requirements for flexible transparent electrodes are optical transparency, high conductivity, and high levels of bending toughness without significant decrease in the electrical performance. Generally, resistivity and optical transmittance follow opposite trends. A good balance between the electrical resistivity and transmittance is necessary to prepare a highly conductive flexible transparent electrode. Currently, most of the commercial transparent electrodes are made from indium-tin oxide (ITO). However, due to poor mechanical properties, low conductivity in flexible transparent ITO based electrodes, and scarcity of indium prompts the research for materials for next generation optoelectronic devices [25].



FIGURE 5.9

Schematic illustration for the preparation of PANi nanowire-CA nanocomposite film

Recently, several alternative materials for transparent electrodes were reported, for instance, electrodes fabricated using conducting polymers [26-28], CNT [29,30], graphene [31], metal nanowire [32,33], metal nanotrough network [34], and hybrid materials [35-37]. We have fabricated uniform, flexible and transparent electrodes based on PANi nanowire/nylon nanofiber reinforced cellulose acetate (PANi nanowire/PA/CA) thin film for high performance supercapacitor applications [8]. The PANi nanowire/PA/CA thin film transparent electrode was prepared in three steps as shown in Figure 5.9. In this study, the nylon nanofiber-infiltrated cellulose acetate (PA/CA) film was used to develop flexible and transparent conducting electrodes. An *in-situ* polymerization technique was used to prepare the PANi/PA/CA thin film electrode. The surface morphologies of PA/CA thin film (Figure 5.10a) showed the composite infiltration of cellulose acetate into the voids of nylon nanofiber with preserving its fibrous structure. The microstructure of the PANi/PA/CA electrode was observed by FE-SEM. Figure 5.10b shows the morphology of thin film electrode having highly homogenous PANi nanowires. More detailed images were presented in Figure 5.10 (c and d), and further revealed that the average diameters of the PANi nanowires were about 50 nm.



(a) FE-SEM images of precursor PA/CA thin film. (b)-(d) FE-SEM images of in situ polymerized PANi nanowires on PA/CA thin film electrode prepared using 2000 mM of aniline monomer

In general, the optical transmittance of the transparent thin film electrodes is influenced by three key factors such as (i) thickness of the precursor thin film, (ii) total fiber content, and (3) the concentration of the conductive material. In this study, the PA/CA thin films had thickness about 11 μ m with an optical transmittance of 87.2% at 550 nm. The best condition to retain the high optical transparency was to limit the time of electrospinning between 5 and 10 min. Electrospinning [38-41] for over 10 min resulted thin films with significantly lower transparencies. The optical transmittances of the PA/CA and PANi/PA/CA thin film electrodes depending on the aniline monomer concentration were presented in Figure 5.11a. The PANi/PA/CA electrodes exhibited transmittance from 81.3% to 39.0% at 550 nm with respect to aniline concentrations of 25-2000 mM. The transparency and the aniline concentration followed opposite trend. For instance, the electrode prepared using 25 mM of aniline exhibited 81.3% of transparency, whereas the thin film electrode prepared using 2000 mM of aniline possessed only 30% of transparency. This can be easily understood from the optical images of the thin film electrodes shown in Figure 5.11 (b-i).



Optical transmittance of PANi/PA/CA thin films prepared using different concentrations of aniline monomers (a). (b)-(i) are the optical images of precursor PA/CA thin film (b), PANi/PA/CA thin films prepared using different concentrations of aniline 25 mM (c), 200 mM (d), 1000 mM (e), 1400 mM (f), 1600 mM (g), 1800 mM (h), and 2000 mM (i)

The relationship between the average sheet resistivity and optical transmittance of the flexible transparent electrodes was presented in Figure 5.12. The as-prepared PANi/PA/CA electrodes exhibited transmittance from 81.3 % to 39.0 % at 550 nm with respect to aniline concentrations of 25 to 2000 mM. Further, the transmittance and sheet resistance were directly proportional to each other. An electrode with about 81 % of transparency with sheet resistivity of 8700 Ω /sq was achieved using 25 mM of aniline. At higher concentrations of aniline, the sheet resistance drastically decreased despite of reduced transparency. It is obvious that the presence of higher concentrations of PANi nanowire on the PA/CA thin films form a conductive network to decrease the sheet resistivity whereas optical transparency decreases, due to the blocking the transmittance of light. Among the PANi/PA/CA thin films, the electrode prepared using 2000 mM of aniline exhibited as low as 188 ohm/sq, which is corresponding to 5.32 mS/cm. In addition to the optimal transmittance and conductivity, the PANi nanowire/PA/CA thin film electrodes exhibited outstanding toughness. The transparent electrode with low resistivity was subjected to bending test using an in-built measurement kit. In the bending test, the edges of the transparent PANi/PA/CA electrode were fixed between two clamps horizontally. And then the electrode was bent by pushing the two clamps together up to a bending radius of 5 mm at a bending angle between $55^{\circ}60^{\circ}$. A bending cycle in this study consisted of two parts viz (i) bending the electrode to 5 mm

radius and (ii) restoration of the electrode at the radius of 15 mm. The sheet resistivity of the electrode was measured after each 100 bending cycles and did not change over 10% even after 1000 bending cycles (inset in Figure 5.12). Thus the transparent PANi nanowire/PA/CA electrode exhibited excellent flexibility by maintaining its performance.



FIGURE 5.12

Relationship between optical transmittance and sheet resistance for PANi/PA/CA thin films at different concentrations of aniline monomer. PANi/PA/CA thin film prepared using 2000 mM of aniline exhibited resistance as low as 188 ohm/sq with an optical transmittance of 38%.Inset shows bending test results of PANi/PA/CA thin film transparent electrode. The sheet resistance changes versus number of bending at the bends radius of 5 mm

The electrochemical behavior of the flexible PANi nanowire/PA/CA transparent electrode was characterized through cyclic voltammetry and galvanostatic charge-discharge test using a three-electrode system in 1.0 M H_2SO_4 as electrolyte. In order to evaluate the charge storage capacity of the flexible PANi nanowire/PA/CA transparent electrode, a relationship comprising of voltammetric charge, potential window, and mass of active material was used [8]. Since the shape of the CV curves were not an ideal mirror-symmetry, the consideration for anodic and cathodic voltammetric charges were not useful. Therefore, the integral area of CV curve and scan rate were used to represent the voltammetric charge. Thus, the specific capacitance was calculated from CV curves using the following equation (1)[9].

$$C = A/2Vmv \tag{1}$$

Where, C is the specific capacitance of electrode. A is the integral area of the CV curve. V is the potential window. m is the mass of the active material, PANi nanowires. And v is the scan rate. The galvanostatic charge-discharge curves of PANi nanowire/PA/CA thin film transparent electrode was measured in a potential window of 0 - 0.8 V vs Ag/AgCl. Figure 5.13 shows the charge-discharge curves measured at different current densities. Specific capacitance could be also calculated from charge-discharge curves using the following equation (2).

$$C = \frac{I\Delta t}{m\Delta V} \tag{2}$$

Where, *I* (A) is charge or discharge current, Δt (s) is the time for full discharge, *m* (g) is the mass of the PANi nanowires, and ΔV is the potential window during the discharge process. The specific capacitance values decreased as the current density was increased. A maximum specific capacitance of 402 F/g was achieved at a current density of 0.3 A/g. A detailed calculation of specific capacitance is presented in supplementary information.



FIGURE 5.13 Charge-discharge curves of PANi nanowire/PA/CA flexible transparent electrode at different current densities

The flexible PANi nanowire/PA/CA electrode showed a maximum specific capacitance of 400 F/g at a scan rate of 5 mV/s. Upon increasing the scan rate, the specific capacitance decreases. The PANi nanowire/PA/CA electrode was further investigated by galvanostatic charge-discharge test at different current densities. A maximum specific capacitance of 402 F/g was achieved at a current density of 0.3 A/g. The cyclic stability of the PANi nanowire/PA/CA electrode was decreased in the first 400 cycles followed by a slight increase between 400 and 500 cycles (Figure 5.14). Subsequently the capacitance was in decreasing between 500 and 700 cycles and then a very slight decrease was observed for cycles 700-1000. About 61% of the capacitance was retained by the flexible PANi nanowire/PA/CA transparent electrode after 1000 cycles, indicating good capacitance retention of the electrode. The internal resistance of the active material plays important role for the enhancement of specific capacitance. The hydrophilic nature of the CA film was expected to induce the formation of PANi nanowires. Hence, the specific capacitance of PANi nanowire/PA/CA transparent electrode is remarkably higher in this study.



FIGURE 5.14 Capacitive retention of PANi nanowire/PA/CA flexible transparent electrode

Flexible PANi-decorated carbon fiber nanocomposite mats as supercapacitor

In general, the high capacitance requires the electrode material to have a large surface area. In this regard, carbon nanofibers prepared from electrospun precursor polymer nanofibers are potentially useful electrodes for the flexible and bendable supercapacitor applications. We have fabricated carbon nanofiber mats (CF), which are potential materials for supercapacitors, due to their unique properties such as high surface area, electrical conductivity and chemical stability [9]. At first, PAN homopolymer and poly(AN-CA), poly(AN-IA) & poly(AN-IA-CA) copolymers were prepared by a well-known free-radical polymerization method [42]. All the synthesized copolymers were dissolved in DMF and then electrospun followed by carbonization to get carbon nanofiber mats (CF). The CF obtained from poly(AN-IA), poly(AN-CA), and poly(AN-IA-CA) were indicated by CF1, CF2, and CF3, respectively. The stabilization and carbonization of the electrospun copolymer nanofibers were performed at 280 °C at a heating rate of 1.0 °C/min under aerobic condition and 1000 °C at a heating rate of 5.0 °C/min under nitrogen atmosphere[42].Similarly, the CFs were used as substrates for *in-situ* polymerization of aniline to produce the PANi-decorated CFs. The PANi-decorated CFs obtained from poly(AN-IA), poly(AN-CA), and poly(AN-CA), and poly(AN-IA-CA) were indicated by PANi/CF1, PANi/CF3.

The electrochemical properties of PANi/CFs as supercapacitor electrode were investigated in 1M H_2SO_4 as electrolyte. We have observed characteristic redox two peaks of PANi (Figure 5.15). The peaks P1 and P2 were attributed to the redox nature of PANi between leucoemeraldine and emeraldine bases. Whilst, the peaks P3 and P4 were corresponding to the emeraldine-pernigraniline transformations. The cyclic voltammograms of PANi/CFs electrode at different scan rates reveal that the peak current increases linearly with scan rates.SEM image in set shows the typical surface morphology of flexible PANi/CF1 electrode, presenting highly homogeneous decoration of the carbon nanofibers with PANi nanoparticles (Inset in Figure 5.15). It is also noteworthy that the surface of PANi/CF1 and PANI/CF2 exhibited uniform surfaces covered with PANi nanoparticles. On the other hand, in the case of PANi/CF3, the PANi nanoparticles were partly grown along the axis of the carbon nanofibers (data not shown).



Cyclic voltammogram response of PANi-CF1 flexible substrate at different scan rates from 5 to 100 mV/s in 1.0 M H_2SO_4 as electrolyte. SEM image in inset shows the typical surface morphology of flexible PANi/CF1 electrode

The electrochemical impedance spectra were used to investigate the charge-transfer resistance (R_{CT}) of the prepared PANi/CFs. The PANi/CF1 is lower R_{CT} value than that of others. This is due to higher ionic conductivity of the PANi/CF1 electrode, which evidences relatively higher capacitive performance than PANi/CF2 and PANi/CF3. Figure 5.16a exhibited the specific capacitance of PANi/CFs electrode at different scan rates in 1.0 M H₂SO₄. After the incorporated the PANi with CFs, the specific capacitance of the electrodes increased significantly. All electrodes showed a downward trend as the increase of the scan rate. The PANi/CF1 had higher capacitance (113 F/g), which is higher than other two electrodes (PANi/CF2 and PANi/CF3). Further, the cyclic stability of the PANi/CF1 was investigated by cyclic voltammetry measurement (Figure 5.16b). The capacitance of the fabricated PANI/CF1 electrode decreased rapidly in the first 400 cycles. In the range of 400-1000 cycles, the capacitance showed slightly downtrend except PANi/CF3, which had a very slight decrease for cycles 500-600. About 40% of the capacitance was retained by PANi/CF3 electrode after 1000 cycles. The cyclic stabilities of the tested samples were relatively lower which is unclear at present. For the practical application, the cyclic stability of PANi-based supercapacitor is expected to be improved. Blending of highly conductive and electrochemically stable materials such as metal or metal oxides to improve collection of current is an effective method to improve the cyclic stability of the supercapacitor. More hybrid systems [43,44] consisting of PANi are under investigation and we will report the results in near future.



Dependence of specific capacitance at different scan rates (left) and capacitance retention during chargedischarge cycles (right)

Conclusions

Chemically and electrochemically synthesized polyaniline doped by phosphoric acids materials were studied for their supercapacitance properties by fabricating a device. The work demonstrate that cChemically prepared CS-PANi-PA and CS-PANi-PA-CTAB exhibited lower capacitance values due to over-oxidation of the polymer and presence of impurities. Electrochemically grown samples exhibited showed higher capacitance value as compared to the chemically synthesized samples. This due to the high purity of the polymer formed due to repeated cycling of the potential between -0.2 and 1.0 V. Among the electrochemically fabricated devices, the supercapacitor with CTAB (ie., with ES-PANi-PA-CTAB electrode material) shows higher capacitance values, as compared to the ES-PANi-PA capacitor, due to lower size particles, high surface area and porous.

The PANi-magnetite composites are useful as electrode materials for supercapacitor applications. The pristine polymer, PANi-DBSA, showed a lower capacitance of 160 F/g, whereas the single electrode of composite C1 and the symmetrical capacitor of C1 (with a 3.8 wt% loading of magnetite) showed enhanced capacitance of 228 F/g and 180 F/g at 1mA/cm^2 respectively. The capacitance values increased with decreased loading of magnetite particles and also the composites are organically soluble and dispersible in water.

A new transparent substrate, nylon nanofiber-reinforced cellulose acetate film was prepared and used to prepare flexible and transparent electrodes. In situ polymerization of PANi nanowires onto the PA/CA thin film resulted in electrodes with an average sheet resistivity as low as 188 Ω /sq and transmittance up to approximately 40%. In addition to the relatively good transmittance and conductivity, the transparent electrode prepared in this study exhibited outstanding toughness, as it can withstand at least 1000 cycles of bending test. The electrochemical measurements revealed these transparent electrodes have high capacitance up to 400 F/g. This technique of in situ polymerization of PANi on nylon fiber reinforced cellulose acetate films is simple, cost-effective, and time-efficient.

We have also successfully fabricated fl Fexible PANi/CFs hybrid electrode from new carbon fiber precursors have been fabricated. It is noteworthy that and Interestingly, *in-situ* polymerization technique for growth PANi on carbon fiber mats resulted in highly homogeneous coverage of PANi

nanoparticles on the surface of carbon fiber mats. The electrochemical behavior of PANi/CF prepared from poly(AN-IA) was relatively higher than other precursors. However, the cyclic stabilities of the tested samples were relatively lower which is unclear at present. More hybrid systems consisting of PANi are under investigation and results will be reported in the near future. As can be seen from the above work based on conducting polymers, the use of polyaniline and its composite for supercapacitor application is a fascinating research topic. Due to this opportunities remain for developing novel conducting polymer composites for supercapacitor applications with high energy and power densities. Recent developments in the synthesis of conducting polymer nanostructure and its composite with controlled morphology would will speed up the application of conducting polymer for advanced energy storage applications. Further developments in this interesting field are likely to change the way in which future flexible energy systems are developed. These flexible energy storage devices can be subsequently used as power sources for flexible, transparent, portable electronics. With the rapid progress in nanoscience and nanotechnology, we hope the future power sources that combine both an excellent electrochemical and mechanical performance based on conducting polymers will lead to many advances in nanotechnology and boost the development and commercialization of flexible/portable electronics.

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