Conducting polymer/carbon nanocoil composite electrodes for efficient supercapacitors

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Herein, we report for the first time, conducting polymer (polyaniline (PANI) and polypyrrole (PPY)) coated carbon nanocoils (CNCs) as efficient binder-free electrode materials for supercapacitors. CNCs act as a perfect backbone for the uniform distribution of the conducting polymers in the composites. In two electrode configuration, the samples exhibited high specific capacitance with the values reaching up to 360 and 202 F g⁻¹ for PANI/CNCs and PPY/CNCs respectively. The values obtained for specific capacitance and maximum storage energy per unit mass of the composites were found to be comparable to one of the best reported values for polymer coated multi-walled carbon nanotubes. In addition, the fabricated PANI/CNC based supercapacitors exhibited a high value of 44.61 Wh kg⁻¹ for maximum storage energy per unit mass. Although the devices exhibit an initial capacitance loss due to the instability of the polymer, the specific capacitance stabilizes at a fixed value after 500 charge–discharge cycles.

1. Introduction

Due to their large power capability, low maintenance cost, high efficiency and long cycle life, supercapacitors have attracted significant research interest in the energy storage field over the past decade.¹⁻² The demand for active electrode materials with high specific capacitance for supercapacitors has stimulated increasing research interest in electronically conducting polymers.³⁻⁶ The capacitance of electronically conducting polymers arises due to the fast and reversible oxidation and reduction processes related to the π-conjugated polymer chains. When used as supercapacitor electrode materials, these conducting polymers undergo fast electrochemical switching and their total mass and volume are involved in charge storage.⁷⁻¹⁰ Polyaniline (PANI) and polypyrrole (PPY) are two of the most extensively studied conducting polymers owing to their high electrical conductivity, ability to exist in various oxidation structures (doped states), environmental stability, excellent capacity for energy storage, lower cost than other conducting polymers and relative ease of synthesis.¹¹⁻¹³ But these materials suffer a serious disadvantage of poor cycling stability during the charge–discharge process as the redox sites in the polymer backbone are not sufficiently stable and they undergo swelling/shrinkage during the doping/redoping process.¹⁴ This causes volume changes and the polymer backbone will be destroyed within a limited number of charge–discharge cycles.⁸ This disadvantage can be overcome to some extent by using polymer/carbon composites, wherein carbon nanomaterials can be used as the substrate to prepare these composites.⁷

Various reports are available on the preparation and supercapacitor properties of polymer/carbon nanocomposite electrodes, wherein activated carbon,¹⁶ mesoporous carbon,¹⁰ carbon nanotubes,¹¹ carbon nanofibers,¹⁷ graphene oxide,¹⁸ graphene nanoplatelets,¹⁹,²⁰ etc. have been widely used as the carbon support material. Recently, carbon nanocoils (CNCs), which are vapor-grown helical carbon nanofibers, have attracted significant research interest because of their helical morphologies, excellent conductivity, corrosion or oxidation resistance nature and high porosity that minimizes the diffusion resistances of various reactants.²¹⁻²² Use of pristine CNCs as supercapacitor electrode materials with a maximum specific capacitance of 40 F g⁻¹ has been reported by Wang et al.²³ In another work they have shown that by purification and activation, specific capacitance of CNCs can be increased to 107 F g⁻¹.²⁴ In one of our earlier works, we have shown that the specific capacitance of CNCs can be increased by proper functionalization.²⁵ To the best of our knowledge, no reports are available on the use of conducting polymer/CNC composites as electrode materials for supercapacitors. CNCs are expected to act as a mesoporous conducting network capable of handling the mechanical stress of conducting polymers during the charge–discharge process.

In the present work, we report the synthesis and supercapacitor behavior of new nanocomposite electrodes, namely PANI/CNCs and PPY/CNCs. CNCs based nanocomposites are prepared through easy and in situ chemical oxidative polymerization on the surface of functionalized CNCs. Symmetric supercapacitors are fabricated using binder-free polymer/CNC
electrodes and performance studies are conducted in the two electrode configuration using cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy measurements. The aim of this study is to investigate the performance of conducting polymer/CNC composites as binder free electrode materials for efficient supercapacitors with special attention to achieve better cycling stability for these electrodes.

2. Experimental methods

2.1 Functionalization of CNCs

1 g of CNCs of purity >90% and electrical conductivity >100 S cm⁻¹, prepared by catalytic decomposition of acetylene over a Ni–Cu catalyst, were refluxed in 100 ml of conc. nitric acid (5 N) at 60 °C for 2 h. This was followed by washing the sample several times with DI water, filtering and drying in air at 100 °C for 30 min.

2.2 Synthesis of polymer/CNC nanocomposites

Polymer coated CNC composites were prepared by immersion of the functionalized CNCs (0.1 g) into an aqueous solution of the corresponding monomer and addition of an oxidant to this solution. PPY was deposited on CNCs by chemical polymerization of 0.5 ml pyrrole with 1.2 g of FeCl₃ in 50 ml 0.1 M HCl. PANI/CNC nanocomposite was synthesized by polymerization of 0.4 ml aniline by 0.4 g K₂Cr₂O₇ in 50 ml of 1 mol HCl over 0.1 g of functionalized CNCs. In either case, the resultant mixture was sonicated for 20–30 min and then magnetically stirred for 6 h at room temperature. The nanocomposite materials were then filtered and washed with a large amount of DI water and subsequently with ethanol to remove residual oxidant. Finally, all composites were washed with acetone and dried at 60 °C. In either case, the proportion of the components was estimated by weighing the final product in the dried state. The schematic of the preparation of polymer/CNCs is illustrated in Fig. 1.

2.3 General characterization of composites

The nanocomposite materials were characterized by a powder X-ray diffraction system (XRD, Bruker, D8 ADVANCE) equipped with Cu-Kα radiation (λ = 0.15406 nm). Raman spectroscopic measurements were carried out using a Lab Ram Aramis Raman spectrometer with a He–Ne laser having an excitation wavelength of 633 nm. BET surface areas of the samples were determined using a surface area and porosimetry system ‘Micromeritics’ (ASAP 2420) at 77 K. Before measurements, the samples were dried at 70 °C for 10 h in a vacuum oven and then degassed at 150 °C for 12 h until the vacuum was less than 2 μm Hg. The surface morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, FEI Helios NanoLab) and transmission electron microscopy (TEM, FEI Titan).

2.4 Preparation of electrodes and electrochemical measurement

Binder-free supercapacitor electrodes of 1.61 cm diameter were prepared using PANI/CNCs, and PPY/CNCs by the following procedure. The composite was dispersed in ethanol and the resulting mixture was homogenized by ultrasonication and coated onto the conductive carbon cloth (ELAT, Nuvant systems Inc.) substrate, which was followed by drying at 100 °C for 12 h in a vacuum oven. Each electrode contained ~4 mg of electroactive material. Two symmetric electrodes, separated by a thin polymer separator (Celgard® 3400) in 1 M H₂SO₄ aqueous electrolyte, were sandwiched in a supercapacitor test cell (ECC-std, EL-Cell GmbH). The electrochemical properties of the supercapacitor electrodes were studied by symmetric assemblies of each material in a two electrode configuration by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) using a Modulab (Solartron Analytical) electrochemical workstation. The two electrode configuration is preferred as it provides the most reliable results of a material’s performance for electrochemical capacitors. Since the measurements are made on symmetric assemblies of materials, by the basic circuit relationship for series capacitors, what is measured is actually 1/2 of the capacitance of the freestanding electrode. The cell capacitance (C in F) was then calculated from the cyclic voltammograms (CVs) according to eqn (1) or from the charge–discharge curves according to eqn (2)

\[
C = \frac{i}{s}
\]

where ‘i’ is the average cathodic current of the CV loop and ‘s’ is the scan rate,²⁷

\[
C = \frac{I}{\Delta V/\Delta t}
\]

where ‘I’ is the constant current for charge–discharge and \(\Delta V/\Delta t\) is the slope of the discharge curve.²⁸

The specific capacitance \(C_{sp} \text{ in F g}^{-1}\) was then calculated as

\[
C_{sp} = \frac{2C}{m}
\]

where ‘m’ is the mass of electroactive material in each electrode.

3. Results and discussion

Fig. 2(a) shows the powder XRD pattern of functionalized CNCs. The peaks are indexed to the reflections of hexagonal
graphite (JCPDS card No. 75-1621). XRD patterns of PANI/CNCs and PPY/CNCs (Fig. 1 (b) and (c)) show diffused peaks from their respective polymers overlapped with the (002) peak of graphitic carbon. Raman spectra of functionalized CNCs, PANI/CNCs and PPY/CNCs are shown in Fig. 3(a–c) respectively. In Fig. 3(a), the band at 1589 cm\(^{-1}\) (G-band) can be assigned to the \(E_{2g}\) vibration of graphitic carbon with an \(sp^2\) electronic configuration and the peak at 1326 cm\(^{-1}\) (D-band) can be attributed to the disordered graphitic carbon. The intensity of the D-band is higher than that of the G-band, as the helical nature and functionalization introduces more defects into CNCs. For PPY/CNCs (Fig. 3(b)), two broad Raman peaks from PPY in the range of 1300–1600 cm\(^{-1}\) due to the ring stretching mode and the \(C=C\) backbone stretching mode overlap with Raman peaks of CNCs.\(^{29-31}\) The Raman spectrum of PANI/CNCs (Fig. 3(c)) prepared in HCl medium shows bands attributable to the PANI oxidation state in the 1700 and 1000 cm\(^{-1}\) regions. The band at 1172 cm\(^{-1}\) is assigned to the \(C=N\) stretching mode of the quinoid units in the range of 1470–1503 cm\(^{-1}\) and the \(C=N\) stretching mode of single bonds at 1226 cm\(^{-1}\) are clearly visible. The broad band at 1250 cm\(^{-1}\) can be assigned to the \(C=N\) stretching mode of the polaronic units.\(^{32}\) From the Raman spectrum of PANI/CNCs, it is clear that a lot of separated, thus localized, single and double bonds exist in the structure of PANI.

The nitrogen adsorption and desorption isotherms of the CNCs, PPY/CNCs and PANI/CNCs are shown in Fig. 4. The isotherm of PANI/CNCs displays a distinct hysteresis loop similar to that of CNCs at a relative pressure of about 0.4–1, which indicates that most mesopores of CNCs are effectively preserved after the PANI polymerization is completed. The hysteresis loop disappears in the case of PPY/CNCs which denotes that the small pores on the walls of CNCs are completely filled upon PPY coating. The calculated values of BET surface area for CNCs, PANI/CNCs and PPY/CNCs are found to be 98.40, 24.58, and 64.23 m\(^2\) g\(^{-1}\) respectively. The decrease in surface area of polymer-coated CNCs as compared to that of CNCs can be attributed to the increase in diameter of CNCs upon the deposition of polymer on the surface of CNCs. But it may not affect the supercapacitor performance of the polymer/CNC composite due to the large pseudocapacitance contribution from the polymer.

Fig. 5(a) shows the typical SEM image of CNCs along with some straight carbon nanofibers. The CNCs are single helical coils with twisted forms similar to \(\alpha\)-helix proteins.\(^{23}\) Fig. 5(b) and (c) show respectively the SEM images of PPY/CNC and PANI/CNC composites. From these images, it is very clear that the entire outer surface of the CNCs has been coated with each of these conducting polymers. TEM observations are used to obtain more detailed structure information of these nanocomposites. Fig. 5(d), (e) and (f) respectively show TEM images of CNCs, PPY/CNCs and PANI/CNCs. The absence of hollow structure in Fig. 5(d) indicates that CNCs are not coiled multiwalled carbon nanotubes (MWNTs), instead these are coiled nanofibers with an average coil diameter 80–100 nm. In the case of PPY/CNCs,
a non-uniform layer of polymer composite is observed (Fig. 5(e)). After an initial period coating on CNCs, PPY tends to preferentially grow on itself rather than on the CNCs. In the PPY composite materials, large amounts of polymer globules are observed on the surface of CNCs. Fig. 5(f) shows that a homogeneous layer of PANI covers the surface of individual CNCs. The sample also shows the presence of independent PANI nanofibres. There is an increase in the outer diameter of the CNCs upon polymer coating. For PPY/CNCs the average outer diameter is found to be nearly 500 nm and for PANI/CNCs it is 100–120 nm. TEM images of the composites provide evidence for the grafting of polymer chains onto CNCs. Polymer/CNC composites prepared by polymerizing the corresponding monomer in the presence of CNCs have a microstructure in which CNCs can be presented as an entrapped mass in a polymer matrix. This increase in the diameter of polymer/CNCs explains the decrease in the BET surface area of CNCs upon polymer coating.

Sheet resistance measurements were performed by the four-probe method for the CNC, PANI/CNC and PPY/CNC based supercapacitor electrodes on conductive carbon cloth having dimensions of 1 cm × 1 cm. The sheet resistance values obtained for CNCs, PPY/CNCs and PANI/CNCs are 1.53, 1.11 and 1.08 Ω □⁻¹ respectively. The sheet resistance values indicate that the conducting polymers made an effective contact with the CNC surfaces which reduced the overall resistance of the electrode composite.

The electrochemical performance of the polymer/CNC composite electrodes is evaluated in real supercapacitors constituted in two electrode cells. The CV curves of the symmetric supercapacitors based on PPY/CNC and PANI/CNC electrode materials measured in a potential range of 0 V to 1 V at different scan rates are shown in Fig. 6(a) and (b) respectively. Each curve is composed of a capacitive current, and the curves at different scan rates show no peaks; this indicates that the electrode is charged and discharged at a pseudo-constant rate over the complete voltammetric cycle. Below a scan rate of 20 mV s⁻¹, both the devices exhibit nearly rectangular CV curves, characteristics for ideal capacitor behavior with good charge propagation. The shape of the CV curves tends to become parallelogram above the scan rate of 50 mV s⁻¹. At a scan rate of 5 mV s⁻¹, values for specific capacitance obtained with respect to the total mass of the composite electrodes are 193 and 332 F g⁻¹ respectively for PPY/CNCs and PANI/CNCs. In comparison, a symmetric supercapacitor made of functionalized CNC electrodes (without polymer) exhibits a specific capacitance of 121 F g⁻¹. Fig. 6(c) shows the variation in the specific capacitance as a function of scan rate. It can be seen that the specific capacitance decreases with an increase in scan rate from 1 to 50 mV s⁻¹.

Galvanostatic charge–discharge curves of symmetric supercapacitors based on functionalized PPY/CNC and PANI/CNC electrodes at a constant current density of 2.5 A g⁻¹ in the potential range between 0 and +1 V are shown in Fig. 7(a) and (b) respectively. Charge–discharge measurements are critical in the analysis and prediction of the active material’s performance under practical operating conditions. It can be seen that the curves are nearly linear and symmetrical, which is another typical characteristic of an ideal capacitor behaviour. Voltage (IR) drop is observed to be very small, which indicates that the electrodes have low internal resistance. Specific capacitance values obtained...

Fig. 5 SEM images of (a) CNCs, (b) PPY/CNCs and (c) PANI/CNCs and TEM images of (d) CNCs, (e) PPY/CNCs and (f) PANI/CNCs.

Fig. 6 Cyclic voltammograms of (a) PPY/CNC and (b) PANI/CNC composite based supercapacitors at a scan rate of 10 mV s⁻¹ in the range of 0 to 1 V and (c) variation in specific capacitance of CNCs and polymer/CNC composites as a function of scan rate.
The specific capacitance of PPY/CNCs is calculated as 17.08, 27.45 and 44.61 Wh kg\(^{-1}\) PPY/CNC and PANI/CNC based symmetric supercapacitors is evaluated by conducting galvanostatic charge–discharge measurements for 2000 cycles at a constant current density of 2.5 A g\(^{-1}\). The enhancement in the specific capacitance of polymer coated CNCs compared to functionalized CNCs may be attributed to the progressive redox reactions occurring at the surface and bulk of conducting polymers through Faradaic charge transfer. It has been reported that compounds built-up with aromatic structures can strongly interact with the basal plane of graphitic surfaces via π-stacking. The effective site-selective interactions between the π-bonds in the aromatic rings of the polymer and the graphitic structure of CNCs facilitate charge-transfer reactions.

The maximum storage energy (\(E\)) per unit mass for CNCs, PPY/CNC and PANI/CNC based symmetric supercapacitors is calculated as 17.08, 27.45 and 44.61 Wh kg\(^{-1}\) respectively, using eqn (4)

\[
E = \frac{1}{2} C_{sp} V_i^2
\]

where \(C_{sp}\) is the specific capacitance and \(V_i\) is the initial voltage (1.0 V) of the discharge curve.

For practical applications, supercapacitors must have long-term cycle stability. The stability of the supercapacitor devices is evaluated by conducting galvanostatic charge–discharge measurements for 2000 cycles at a constant current density of 2.5 A g\(^{-1}\) in the potential range between 0 and +1 V. The specific capacitance and its percentage retention as a function of cycle number are presented in Fig. 7(c) and (d) respectively. After 2000 cycles, PPY/CNCs retain 61% of their initial specific capacitance whereas PANI/CNCs retain nearly 72% of their initial capacitance. In both the cases, the degradation in specific capacitance takes place rapidly up to 500 cycles and after that it remains fairly constant. Cyclic stability of PANI/CNCs is better than that reported for PANI/MWNTs by Zheng \textit{et al.}\(^9\) and Frackowiak \textit{et al.},\(^11\) which may be due to the better adhesion of polymers on the surface of CNCs as compared to MWNTs. We reported that even after 2000 cycles of charge–discharge process, the functionalized CNCs retains nearly 98% of their initial specific capacitance (121 F g\(^{-1}\)). The large capacitance loss for polymer/CNC devices during cycling is probably due to the fact that 80% polymer loading results in the existence of large scale polymer phase and will cause cracking during the charge/discharge process. In addition, part of the polymer deposit loses contact with the CNCs during cycling, resulting in not only poor transport of electrons but also poor ion movement. Nonetheless, the specific capacitance of PANI/CNCs is still markedly higher than CNCs even after 2000 charge/discharge cycles, which makes PANI/CNCs a promising electrode active material. But for PPY/CNCs, the specific capacitance value becomes comparable to that of functionalized CNCs. Use of corrosive liquid electrolytes may cause leakages, which decrease the safety and lifetime of the capacitors. A narrow electrochemical (a maximum voltage of 1 V) window, fast electrolyte evaporation and degradation of conducting polymers at high potentials are the general major disadvantages associated with the aqueous 1 M H\(_2\)SO\(_4\) electrolyte employed in the present study. Therefore, the use of non-aqueous electrolytes with high ion conductivity, nonvolatility, high decomposition temperatures and wide electrochemical stability windows may improve the stability and durability of conducting polymer/CNC based supercapacitors.

Nyquist plots of the PPY/CNCs and PANI/CNCs based symmetric supercapacitors are shown in Fig. 8(a) and (b) respectively. Plots show a semicircular arc in the high frequency region and a straight line in the low-frequency region. The
diameter of the semicircle in the high frequency region is attributed to the charge-transfer resistance of the electrode \( (R_{ct}) \). There are many aggregated polymers observed on the outer surface of PPY/CNC composites as shown in the SEM and TEM images. This aggregated polymer on the outer surface fails to contact with the host CNCs thoroughly. The interaction between the aggregated PPY and CNCs is so weak that it makes few contributions to charge accumulation. Moreover, the aggregated polymer on the outer surface may plug up the pores and block the penetration of electrolyte, which inhibits the contact of active material with the electrolyte. This may increase resistance effects in the PPY/CNC composite electrode. For PANI/CNCs a more uniform coating of polymer over CNCs is observed. This explains the higher \( R_{ct} \) of PPY/CNCs as compared to PANI/CNCs. The straight line in the low frequency region arises from the pseudocapacitance \( (C_p) \). The high-frequency intercept with the real axis is related to the equivalent series resistance \( (R_s) \), which includes the resistance of the bulk electrolyte solution, the intrinsic resistance of the active material and the contact resistance at the active material/current collector interface. ESR data is an important factor in determining the power density of a supercapacitor. Experimental results show that the magnitude of ESR obtained from the \( x \)-intercept of the impedance spectra for PPY/CNC and PANI/CNC composite based electrodes are insensitive to the surface condition of the electrode, and it is consistent with a value of around 1 \( \Omega \) for both devices. In 1 M \( H_2SO_4 \) electrolyte, the same ESR value is obtained for functionalized CNC based symmetric capacitors, indicating that the increasing diameter of CNCs upon polymer loading is not having a negative impact on the ESR value.

The maximum power density \( (P_{max}) \) of the supercapacitor devices is calculated from the low frequency data of the impedance spectra, according to eqn (5)

\[
P_{\text{max}} = \frac{V^2}{4MR_s} \tag{5}
\]

where \( V \) is the initial voltage (here it is 1 V), \( R_s \) is the ESR and \( M \) is the total mass of active materials in two electrodes (in this case \( M = 8 \) mg) with a cell voltage of 1.0 V. Maximum power densities of nearly 31 kW kg\(^{-1}\) are obtained for both polymer/CNC composite based supercapacitors. This value of power density is well-suited for power/surge delivery applications.\(^{1)}\) The equivalent circuit for a polymer/CNC based ideal symmetric supercapacitor cell is illustrated in Fig. 8(c). In the equivalent circuit, a solution resistance \( (R_s) \) is connected in series with a double layer capacitance \( (C_{DL}) \), and the \( C_{DL} \) is connected in parallel with the charge transfer resistance \( (R_{ct}) \) and pseudo-capacitance \( (C_p) \). The parallel \( R_s \) and \( C_{DL} \) configuration accounts for the semicircular feature, while \( C_p \) accounts for the steep line.

For supercapacitors, the majority of their capacitance is available only at low frequency, hence attention should be paid that the impedance data are in this range. Fig. 8(d) presents the frequency response of specific capacitance obtained from EIS measurements of polymer/CNC composite electrodes. The capacitance values were obtained from eqn (6)

\[
C = \frac{1}{2\pi f z''} \tag{6}
\]

Here, \( C \) is the cell capacitance, \( f \) is the frequency, and \( z'' \) is the imaginary part of the impedance. When the frequency increases, the capacitance of all samples decreases, and in the high frequency region the supercapacitors behave like a pure resistor, which indicates that the electrolyte ions cannot penetrate into micropores under high frequencies. It is found that PANI/CNC composites have higher capacitance than PPY/CNC electrodes.

A comparison of the specific capacitance obtained for PPY/CNCs and PANI/CNCs with the data reported for different polymer/carbon composite electrodes is summarized in Tables 1 and 2, respectively. The results obtained in the present study are comparable to or slightly better than those reported for polymer/carbon composites with literature data.

### Table 1 Comparison of specific capacitance of PPY/CNC supercapacitor electrodes with literature data

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Measurement type</th>
<th>Electrolyte</th>
<th>Specific capacitance (F g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPY/carbon aerogel</td>
<td>3-electrode</td>
<td>6 M KOH</td>
<td>433 (@ 1 mV s(^{-1})), 373 (@ 5 mV s(^{-1}))</td>
<td>7</td>
</tr>
<tr>
<td>PPY/SWNT</td>
<td>3-electrode</td>
<td>aqueous</td>
<td>134 (@20 mV s(^{-1}))</td>
<td>35</td>
</tr>
<tr>
<td>PPY/Func. SWNT</td>
<td>3-electrode</td>
<td>Aqueous</td>
<td>200 (@ 200 mV s(^{-1}))</td>
<td>12</td>
</tr>
<tr>
<td>PPYIMWNT</td>
<td>2-electrode</td>
<td>1M H(_2)SO(_4)</td>
<td>192 (@ 5 mV s(^{-1})), 200 (@0.25 A g(^{-1}))</td>
<td>28</td>
</tr>
<tr>
<td>PPY/SWNT</td>
<td>3-electrode</td>
<td>Aqueous</td>
<td>144 (@ 200 mV s(^{-1}))</td>
<td>12</td>
</tr>
<tr>
<td>PPY/graphene</td>
<td>3-electrode</td>
<td>1 M KCl</td>
<td>267 (@10 mV s(^{-1}))</td>
<td>19</td>
</tr>
<tr>
<td>PPY/graphene</td>
<td>3-electrode</td>
<td>2 M H(_2)SO(_4)</td>
<td>267 (@100 mV s(^{-1}))</td>
<td>20</td>
</tr>
<tr>
<td>PPY/CNC</td>
<td>2-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>193 (@5 mV s(^{-1})), 200 (@ 2.5 A g(^{-1}))</td>
<td>Present work</td>
</tr>
</tbody>
</table>

### Table 2 Comparison of specific capacitance of PANI/CNC supercapacitor electrodes with literature data

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Measurement type</th>
<th>Electrolyte</th>
<th>Specific capacitance (F g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/carbon nanofibre</td>
<td>3-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>264 (@ 5 mV s(^{-1}))</td>
<td>17</td>
</tr>
<tr>
<td>PANI/activated carbon</td>
<td>3-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>273 (@50 mV s(^{-1}))</td>
<td>15</td>
</tr>
<tr>
<td>PANI/OMC</td>
<td>3-electrode</td>
<td>6 M KOH</td>
<td>470 (@1 A g(^{-1}))</td>
<td>16</td>
</tr>
<tr>
<td>PANIIMWNT</td>
<td>2-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>344 (@ 2 mV s(^{-1})), 360 (@ 0.2 A g(^{-1}))</td>
<td>28</td>
</tr>
<tr>
<td>PANIMWNT</td>
<td>3-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>305 (@1 mA cm(^{-2}))</td>
<td>36</td>
</tr>
<tr>
<td>PANI/GO</td>
<td>2-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>555 (@ 0.2 A g(^{-1})), 227 (@ 2 A g(^{-1}))</td>
<td>18</td>
</tr>
<tr>
<td>PANI/carbon microfibre</td>
<td>3-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>188 (@ 1 mA)</td>
<td>37</td>
</tr>
<tr>
<td>PANI/CNC</td>
<td>2-electrode</td>
<td>1 M H(_2)SO(_4)</td>
<td>354 (@ 1 mV s(^{-1})), 349 (@ 2 mV s(^{-1})), 332 (@ 5 mV s(^{-1})), 325 (@ 2.5 A g(^{-1}))</td>
<td>Present work</td>
</tr>
</tbody>
</table>
MWNTs in two electrode configuration. From the tables it is also evident that the specific capacitance values obtained in the present study are lower than the values reported for polymer/carbon composites in 3-electrode configuration. But it is well-known that a three electrode measurement configuration can give higher specific capacitance values than a two electrode configuration.  

Khomenko et al. reported the dependence of measured capacitance values of polymer/MWNTs composites on test cell configuration. Their studies revealed that three-electrode cells yield specific capacitance values approximately double those of the two electrode cell. In a recent review on the best practice methods for capacitance measurements of supercapacitors by Stoller and Ruoff, it has been suggested that the two electrode cell configuration is better than the three electrode configuration as the two electrode configuration mimics the physical configuration, internal voltages and charge transfer that occur in a packaged supercapacitor and thus provides the best indication of an electrode material’s performance. From that aspect, the specific capacitance values obtained in the present study, with two electrode configuration, are in the expected range. In addition, the fabricated polymer/CNC composite electrodes have a significant practical advantage that they do not need any additional binder material. From the present study, it is proved that like MWNTs, CNCs can also be used as an effective carbon backbone and that allows excellent dispersion of conducting polymers.

4. Conclusions

PPY/CNCs and PANI/CNCs were successfully synthesized by in situ chemical oxidative polymerization of corresponding monomers on functionalized CNCs to obtain conducting nanocomposites suitable for supercapacitor applications. Raman spectroscopy measurements were used as an effective tool to identify the type of polymer coated over CNCs. The values obtained for specific capacitance and maximum storage energy per unit mass of the polymer/CNC composites were found to be comparable to the best reported values for corresponding polymer dispersed MWNT composites in two electrode configuration. CNCs can be used as an effective carbon backbone as they allow excellent dispersion of conducting polymers. Based on low cost, environmental friendly nature, relative ease of synthesis and excellent capacitive properties with a cycling stability of ~72% after 2000 cycles, the PANI/CNC composites can be considered as promising electrode materials for high performance supercapacitors.

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References