Carbohydrate Polymers 94 (2013) 487–495

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Functionalisation of fabrics with conducting polymer for tuning capacitance and fabrication of supercapacitor

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ARTICLE INFO

Article history:
Received 14 September 2012
Received in revised form
15 December 2012
Accepted 14 January 2013
Available online 21 January 2013

Keywords:
Conducting polymer
Polypyrrole
Textile electrodes
Composites
Supercapacitor

ABSTRACT

Conducting polymer (polypyrrole (PPy) doped with anion) film has been coated on different textile substrates from a mild, room temperature wet in situ chemical polymerisation method exploiting pyrrole as a monomer and ferric chloride as an oxidant and compared their electrochemical capacitive behaviour by assembling as an unit cell supercapacitor. PPy composites were prepared with carbohydrate polymers like cotton, linen (Natural cellulosic fibre), modified cellulosic fibre-viscose rayon and synthetic polymer polyester fabrics to investigate the influence on electrochemical capacitance. The surface morphology and chemistry of these materials were analysed by SEM, FT-IR, and XRD. It reveals that the PPy has greater interaction with the cellulosic fabrics, but whereas surface deposition only has taken place with synthetic fibres. The capacitive behaviour of the PPy coated textiles were evaluated using cyclic voltammetry, impedance spectroscopy and charge–discharge analysis. A unit cell was fabricated to investigate the capacitive behaviour by assembling two symmetric textile electrodes separated by a solid polymer (PVA/1 M H_2SO_4 gel) electrolyte membrane. The textile electrodes prepared with PPy-Cotton and PPy-Viscose exhibited the highest specific capacitance value of 268 F g^{-1} and 244 F g^{-1}, respectively at a scan rate of 5 mV s^{-1}. The charge–discharge analysis also shows higher specific capacitance value for PPy-Viscose and PPy-Cotton. The focus of this research is to highlight a successful, simple and reproducible method for fabrication of the textile based supercapacitor and the chemistry of surface interaction of PPy molecule with natural and synthetic fabrics.

1. Introduction

Supercapacitors were received great attention in recent years due to their high power and energy densities. These are also called electrochemical capacitors, which store electrical energy using either ion adsorption (electrochemical double layer capacitor) or fast surface redox reactions (pseudocapacitors) (Ali et al., 2011; Jayalakshmi & Balasubramanian, 2008; Wang, Zhang, & Zhang, 2012). Supercapacitor composed of four components such as electrode materials, electrolyte, current collectors and membrane. Electrode materials are important key factor in supercapacitors. Irrespective of the charge storage mechanism, large surface area and conductivity are the two essential properties of the electrode materials. Different materials have been investigated as electrodes, in which conducting polymers (CPs) have greater advantages compared to metal oxides and carbon materials, due to their low cost, high doping–dedoping rate during charge–discharge, high charge densities and ease of synthesis (Ghenaatian, Mousavi, & Rahmanifar, 2012; Graeme, Snook, Kao, & Adam, 2011). A wide variety of conducting polymers such as polypyrrole (PPy), polyaniline (PAn), polythiophene (PT), polyethylenedioxythiophene (PEDOT) and its derivatives have been studied for supercapacitor applications (Fan & Maier, 2006; Liu & Reynolds, 2010; Sivaraman et al., 2006; Wang, Xu, Chen, & Du, 2007). The conducting polymers can store energy by accumulating/releasing counter charges under the electric field arising due to their redox reactions (Arbizzani, Mastragostino, & Meneghello, 1996; Cho & Lee, 2008). These materials show higher conductivity with doping but compared to carbon, have lower surface area. Hence, making of porous conducting polymers or coating of conducting polymer on porous materials will enhance the active surface area (Dubal, Lee, Kim, Kim, & Lokhande, 2012).

Textiles are good choice of materials for coating CP, which increases the surface area of the active material and reduce the weight of the substrate. Several methods are available to coat conducting polymer on textile substrates such as in situ chemical polymerisation, electrochemcial polymerisation and chemical vapour phase polymerisation (Dall'Acqua, Tonia, Varesano, Canetti, & Porzio, 2006; Firoz Babu, Senthil Kumar, Noel, & Anbu Kulandainathan, 2009; Li, Qian, Chen, Ding, & An, 2010; Mo, Zhao, Chen, Niu, & Shi, 2009; Najar, Kaynak, & Foitzik, 2007; Omastov, Trchov, Kovov, & Stejskal, 2003; Tiwari, Jain, & Sharma, 2008).

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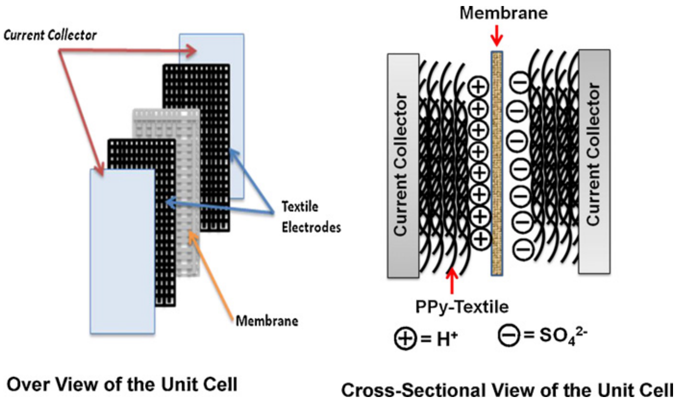
0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.01.021



Scheme 1. Schematic representation of the unit cell supercapacitor prepared using textile electrode.

Various textile fibres and fabrics such as cotton, viscose rayon, nylon lycra, polyester and wool, were also modified with conducting polymers and evaluated (Akif, Saeed, & Richard, 2008; Beneventi, Alila, Boufi, Chaussy, & Nortier, 2006; Lin, Wang, Wang, & Akif, 2005). These composites found number of applications as conductive fabrics, heating devices, electromagnetic interference shielding and antimicrobial fabrics (Hakansson, Amiet, & Kaynaka, 2006; Kaynak & Beltran, 2003; Kim et al., 2003; Lin et al., 2005; Oh, Park, & Kim, 2003). Recently, few reports are available on the conducting polymer-textile composites as the electrodes for the supercapacitor applications (Liew, Thielemans, & Walsh 2010; Seung, Jin, Bo, Tae, & Jun, 2009). Polypyrrole was coated on cellulosic paper based material and evaluated their composite in energy storage devices (Gustav, Aamir, Maria, Leif, & Albert, 2010). The electrodes fabricated by depositing conducting polymer on activated carbon sheets or fibre have investigated as the material for capacitors (Wilson, Looney, & Pandolfo, 2010; Ying et al., 2010). To improve the electrical energy storage self supported composite sheets of conducting polymer and its composites were also developed (Qiong, Yuxi, Zhiyi, Anran, & Gaoquan, 2010; Yueping et al., 2010). Recently, Yue, Caiyun, Xin, and Gordon (2012) demonstrated the performance of PPy-coated nylon lycra textile electrode in supercapacitor application and studied the electrochemical performance while stretching. In addition, Henrik et al. (2012) studied the influence of the cellulosic substrate on electrochemical performance and reported specific charge of 274 C g^{-1} for their paper based polypyrrole electrode.

There are no reports are available by describing the influence of carbohydrate based substrates in the electrochemical performance for the application on supercapacitor. The interaction of conducting polymer with textile material will make much difference in capacitive behaviour. In the present communication, we are able to modify natural and synthetic fibre materials with polypyrrole by in situ chemical polymerisation using pyrrole and ferric chloride as monomer and oxidant, respectively. Modification was made on the natural fibres (cotton and linen), modified fibre (viscose rayon) and synthetic fibre (polyester) and compared the capacitive behaviour of the polypyrrole textile composite. Interaction of conducting polymers with textiles were studied and the successfully fabricated supercapacitor with conductive textile electrodes. Thus a comparative account in relation to their affinity towards PPy surface modification has emerged.

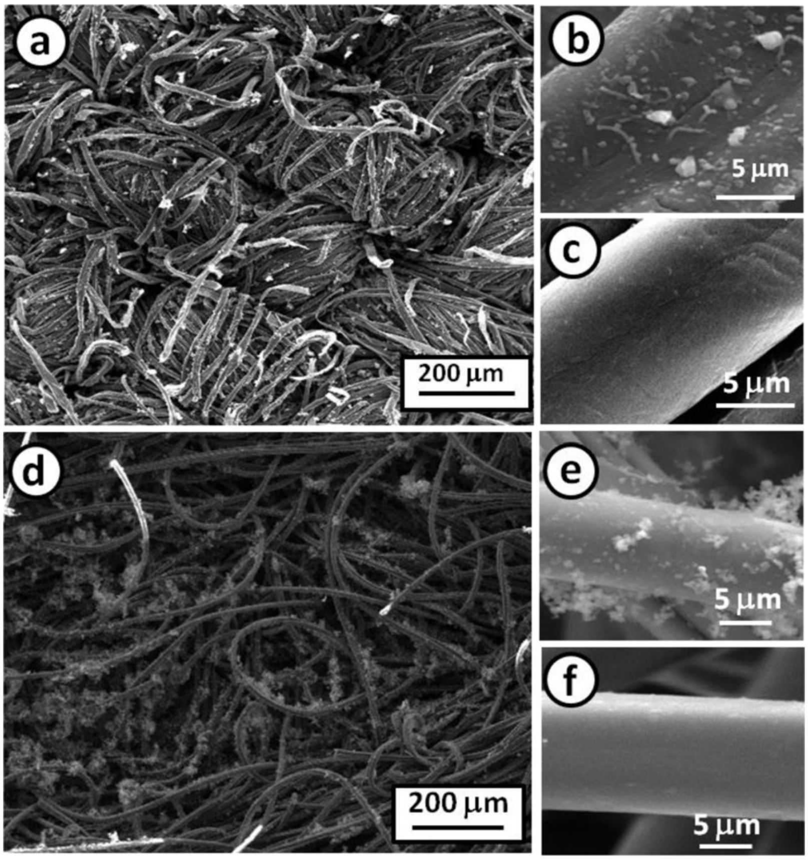


Fig. 1. Scanning electron microscopic images of textiles (a) PPy-Cotton at lower magnification, (b) PPy-Cotton and (c) bare cotton at higher magnification, (d) PPy-Viscose at lower magnification, (e) PPy-Viscose and (f) bare viscose at higher magnification.

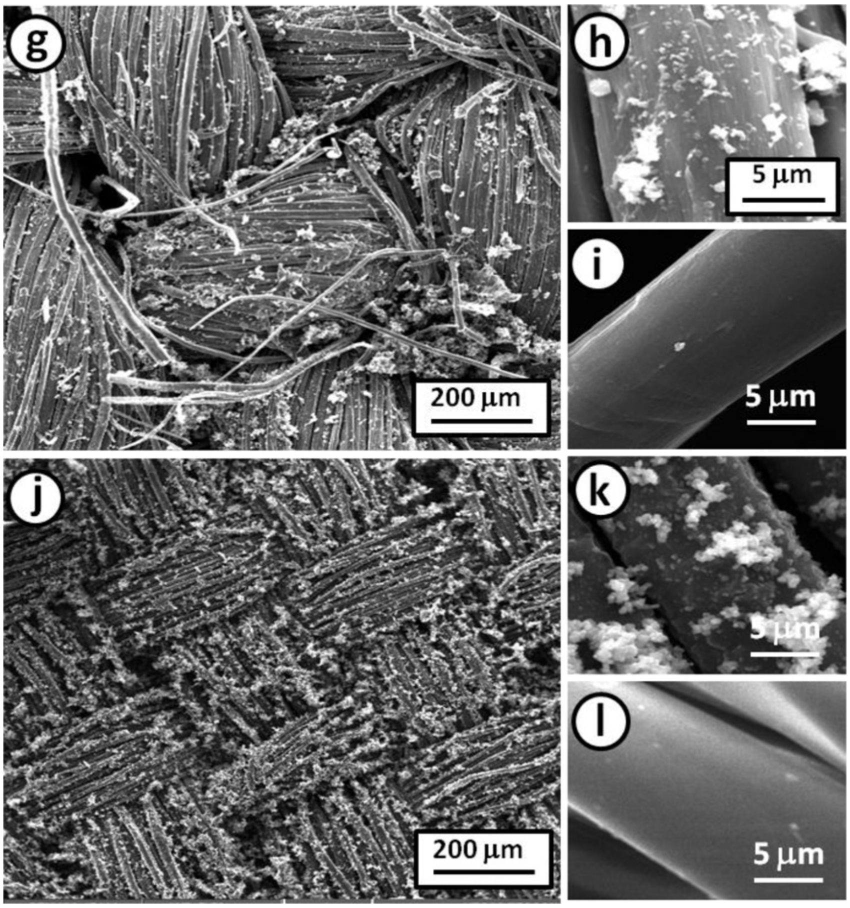


Fig. 2. Scanning electron microscopic images of textiles (g) PPy-Linen at lower magnification, (h) PPy-Linen and (i) bare linen at higher magnification, (j) PPy-PET at lower magnification, (k) PPy-PET and (l) bare PET at higher magnification.

2. Experimental

All the chemicals were of analytical reagent grade and were used without further purification. Polypyrrole-textile (PPy-textile) composites were synthesised using in situ polymerisation of pyrrole with different types of textile materials such as cotton, linen, viscose rayon and polyester, following the methods described previously (Bhat, Seshadri, Nate, & Gore, 2006; Firoz Babu et al., 2009) and the samples were labelled as PPy-Cotton, PPy-Linen, PPy-Viscose and PPy-PET. Initially, the fabric (0.75 g) immersed in 0.2 M $FeCl_3$ solution and stirred at room temperature for 30 min, followed by adding pyrrole drop wise to initiate polymerisation. Polymerisation continued at room temperature for 4 h. After completion of the reaction, samples were washed several times with distilled water and methanol to remove unreacted monomer and oxidant.

The surface morphology of the PPy coated textiles was investigated by scanning electron microscopic (SEM) analysis (VEGA3 Tescan scanning electron microscope). The bare textiles were gold sputtered to get electrical contact. FT-IR spectra were recorded using Nicolet 5DX by attenuated total reflectance (ATR) sampling technique. X-ray powder diffraction (XRD) pattern of the samples were analysed on PANalytical X'PERT PRO system with Bragg-Brentano geometry using Cu $K\alpha_1$ radiation, operating at 40 kV and 30 mA, where as $\lambda = 1.54$ Å for the Cu $K\alpha_1$ line.

Conductivity of PPy coated textiles was measured using four probe conductivity metre, Model: DFP-02 BESTO at room temperature. Conductivity obtained for PPy-Cotton, PPy-Linen, PPy-Viscose and PPy-PET were 2.25×10^{-2}, 1.5×10^{-2}, 2.18×10^{-2} and 0.95×10^{-2} S cm^{-1}, respectively

To study the capacitive behaviour of the textile electrode a unit cell of supercapacitor was assembled. The assembly of supercapacitor was made as given below. Initially, a gel prepared using 2 g polyvinyl alcohol in 20 ml distilled water at 90 °C and 1 M sulphuric acid was added. A polypropylene membrane was dipped in the above prepared gel and used as the membrane for the supercapacitor. Two symmetric PPy-textile of area 1 cm^2 were taken and 1.5 cm^2 membranes were placed between these electrodes. Stainless steel electrodes were used as the current collector. The assembly of the unit cell is shown in Scheme 1. After assembling, the unit cell was pressed using screw clip. Electrochemical characterisation was performed for this unit cell using BAS-IM6 electrochemical analyzer with Thales 4.18 USB software. For EIS, the frequency range was from 100 kHz to 10 mHz with an AC perturbation of 5 mV at open circuit potential.

3. Results and discussion

Polypyrrole-textile (PPy-textile) composites were prepared by in situ polymerisation of pyrrole using ferric chloride ($FeCl_3$) in presence of various textile materials like cotton, linen, viscose and polyester. Ferric chloride acts as an oxidising agent having ability to oxidise the pyrrole monomer, leading to the chemically active cation radicals. The formed Py^+ radical cation can dimerise with expulsion of H^+. The dimers forms cation radicals and react with other monomer molecules, yielding oligomers or insoluble polymers. These polymerised form adsorbed and interact with textiles. Ferric chloride gets reduced to ferrous chloride which can be easily removed by water washings. During the polymerisation process

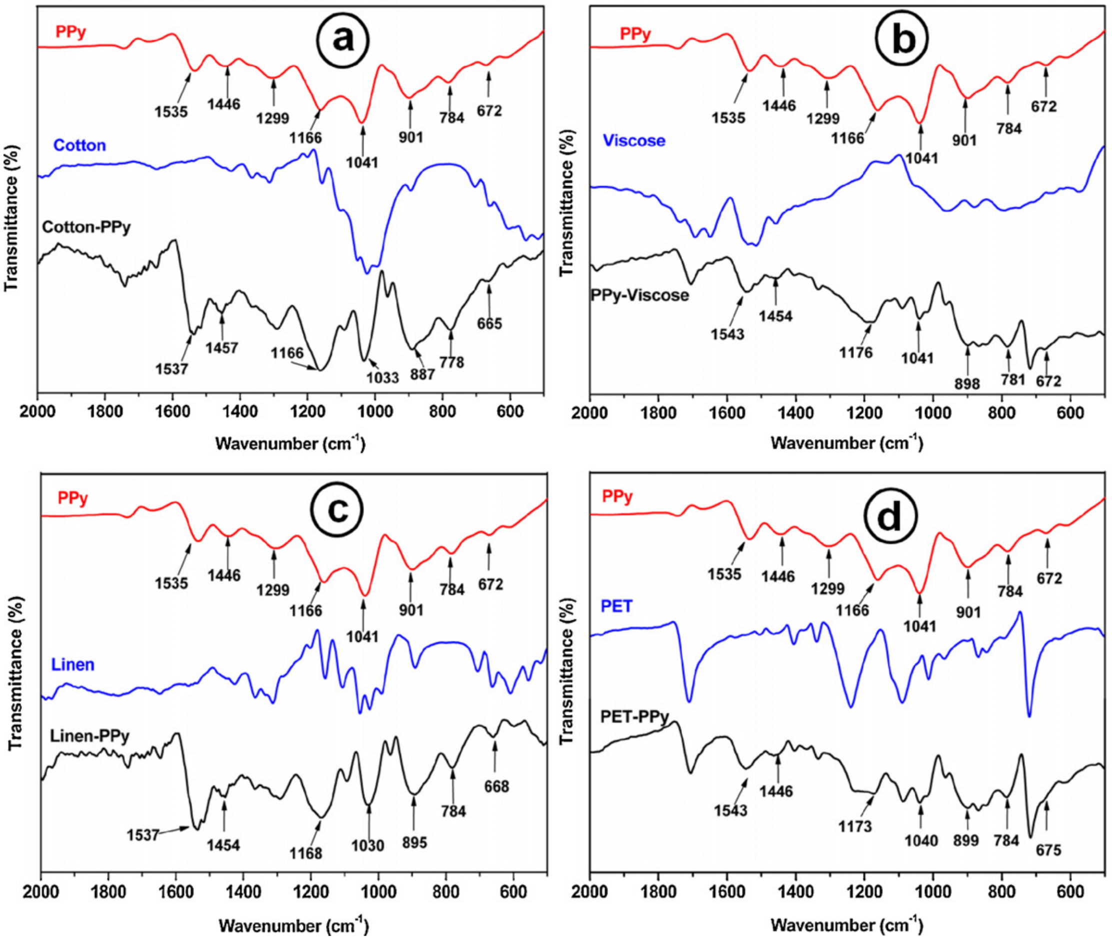


Fig. 3. FTIR spectra of PPy powder and PPy coated textiles (A) cotton, (B) viscose, (C) linen and (D) polyester.

Cl^- ion doped in to PPy backbone. The complete removal of ferric/ferrous chloride from the textile substrate and the presence of doped Cl^- on PPy were confirmed by EDX analysis (Supplementary data, Fig. S1). After in situ polymerisation of pyrrole, colour of the fabric was changed from white to black.

Figs. 1 and 2 show the scanning electron microscopic (SEM) images of the polypyrrole wrapped different textile substrates and demonstrate that polypyrrole uniformly was coated on to the microfibres over the entire sheets of the fabric. The conformed coating of polypyrrole was observed at lower magnifications for polypyrrole coated cotton (Fig. 1a), viscose (Fig. 1d), linen (Fig. 2g) and PET (Fig. 2j) fabric. It can be seen from the SEM images at higher magnifications that the polypyrrole was well coated on to individual fibre after chemical polymerisation. Uniform layer coating over individual fibre were observed for cotton (Fig. 1b) and viscose (Fig. 1e), whereas some bulky deposition of polypyrrole were observed with linen (Fig. 2h) and PET (Fig. 2k) fibre. For comparison, the uncoated fibre at higher magnification of cotton (Fig. 1c), viscose (Fig. 1f), linen (Fig. 2i) and PET (Fig. 2l) were also provided. The mechanical adhesion for these textiles was tested by water washings and the polypyrrole attached to the textiles could withstand several washings indicative of their strong mechanical adherence with the fibre.

To understand the chemical interaction of PPy on to the textiles, FTIR analysis was performed. Fig. 3 shows the FTIR-ATR analysis of the pure PPy, blank textiles and PPy coated textiles in the range of 2000–500 cm^{-1}. The spectral features of PPy were very well understood in the literatures (Yalcınkaya, Demetgul, Timur, & Colak, 2010). PPy spectrum shown in each figure (Fig. 3a–d) was taken for the PPy powder sample prepared at identical condition in the absence of textile substrates. The main characteristic peak at 1535 and 1446 cm^{-1} is assigned to the pyrrole ring vibrations, i.e., the combination of C=C and C—C stretching vibrations. The bands at 1299 and 1166 cm^{-1} is associated with the C—N stretching vibrations. Furthermore, the bands at 1041, 901 and 784 cm^{-1} are ascribed to C—H deformation, C=C in-plane bending vibration of the pyrrole ring and out of plane C—H bending modes, respectively (Grunden & Iroh, 1995; Mecerreyes et al., 2002). The band at 672 cm^{-1} is corresponding to the doped Cl^- ion on the PPy backbone. As the cotton viscose and linen textiles are in the cellulosic background, the FTIR spectrum for these textiles reflects the same behaviour (Fig. 3a–c). The characteristic peaks of cellulose such as $(C—C)_{str}$, $(C—O)_{str}$ and $(C—O—C)_{str}$ are observed between 1140 and 930 cm^{-1} for cellulosic fabrics. A peak also observed at 1637 cm^{-1} is due to a partial oxidation of the alcoholic to carbonyl functional groups as a result of natural ageing of cellulose (Acqua, Tonina, Peilaa, Ferrero, & Catellani, 2004; Brezoi, 2010; Dall'Acqua et al., 2006). The peaks of PPy were overlapped with cellulose peaks (Fig. 3) and some of the bands of PPy were observed with a small shift from the PPy powder for $(C{=}C)_{str}$ at 1537 cm^{-1}, $(C—C)_{str}$ at 1457 cm^{-1}, $(C—N)_{str}$ at 1166 cm^{-1} and C—C in-plane bending vibration at 887 cm^{-1}. FTIR spectrum of synthetic fibre polyester (Fig. 3d) shows the characteristic bands at 1700 (C=O), 1400 (aromatic ring), 1075, 1010 (O=C—O—C or secondary alcohol), 960 (C=C) and 730 (characteristic aromatic ring) cm^{-1}. Most of the bands are unchanged even after modification with polypyrrole on

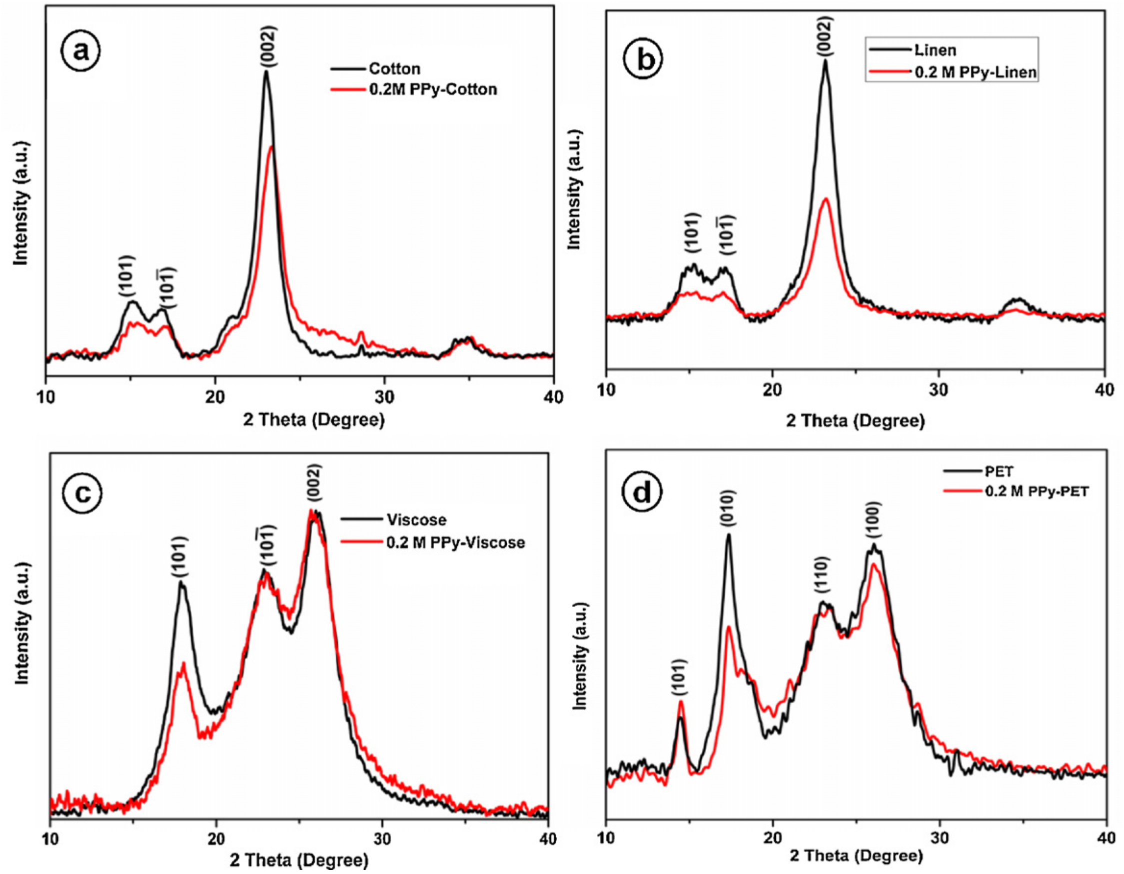


Fig. 4. X-ray diffraction analysis of PPy coated textiles (A) cotton, (B) linen, (C) viscose and (D) polyester.

PET fabric. But some characteristic broad band of PPy are observed at 1543 cm^{-1} for $(C{=}C)_{str}$, 1446 cm^{-1} for $(C{-}C)_{str}$, 1173 cm^{-1} for $(C{-}N)_{str}$ and characteristic bending modes at 784 cm^{-1}. It is noticed that the PPy bands in FTIR spectrum are shifted for PPy-textile composite, indicates the interaction of textile fabrics with PPy in the composites.

Fig. 4 shows the X-ray diffraction (XRD) pattern of uncoated and coated textiles. For cellulosic fibres (cotton, viscose and linen), portions of the fibre were arranged in an orderly fashion or lattice, even though cellulosic fabrics can be differentiated with their crystallinity. As reported in literature, unit cell of the cellulose is monoclinic with three principal place of reflection shown as (0 0 2), (1 0 1) and (1 0 1) (Parikh, Thibodeaux, & Condon, 2007). Here also three peaks are found for both linen and cotton (Fig. 4a and b) as shown (1 0 1) at $2\theta = 15°$, (1 0 1) at $2\theta = 16.6°$ and (0 0 2) at $2\theta = 22.7°$, in the case of viscose (Fig. 4c), three peaks are shown at $2\theta = 18°$ for (1 0 1), 23° for (1 0 1) and 27° for (0 0 2). The XRD spectrum of PPy shows only an amorphous nature 2θ between 20° and 30° (Supplementary data, Fig. S2). After modification with polypyrrole, crystalline nature of the all cellulosic fabrics remains same. Only the plane (1 0 1) was getting affected during the modification and the relative intensity of this plane is reduced accordingly. The polyester samples possessed semi-crystalline and the polyester crystals are orthorhombic in nature. The X-ray pattern of the polyester samples (Fig. 4d) showed strong reflection at $2\theta = 14.4°$, 17.3°, 22.7° and 26.1° which correspond to the orientation of the crystal along (1 0 1), (0 1 0), (1 1 0) and (1 0 0) plane respectively (Talukdar & Achary, 2010), in which a small reduction of relative intensity was observed in the (0 1 0) plane.

The capacitive behaviour of porous/polymeric materials can be investigated using cyclic voltammetry. To perform capacitive study a supercapacitor was composed by using symmetrical textile electrode area of 1 cm^2 separated by polypropylene membrane. These set up was sandwiched between two stainless steel electrodes used as the current collector. 1 M H_2SO_4 was dissolved in PVA solution at 90 °C and after cooling, membrane was dipped in this gel used as the electrolyte as well as separator. Fig. 5a illustrates the cyclic voltammograms of the PPy-Cotton fabric at different scan rates. At low scan rate (5 mV s^{-1}) cyclic voltammogram shows good capacitive behaviour in the voltage range between −1 to 1 V (Fig. 5a, inset) in which a broad anodic peak at ~0.74 V and cathodic peak at ~0.21 V were observed. The redox property of the polypyrrole is related to the anion and cation expulsion/incorporation processes. The SO_4^{2-} ion present in the supporting electrolyte readily diffuses in and out of the polymer during redox processes, in order to neutralise the immobilised charge of the polypyrrole film by the insertion of anions. The anodic and cathodic peaks indicate the release and insertion of sulphate ions (Ansari, 2006; Khalkhali, 2005). The redox reaction can be expressed as Scheme 2.

$$\mathrm{PPy} + \mathrm{A}^- \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} \mathrm{PPy}^+\mathrm{A}^- + e^-$$

Here, A^- is the anions of the electrolyte

Scheme 2. Redox reaction of polypyrrole.

The area of the curve in the cyclic voltammogram increased with increasing scan rate and the redox properties are not clear at higher scan rates. This may be due to the limited ion transport into the PPy matrix.

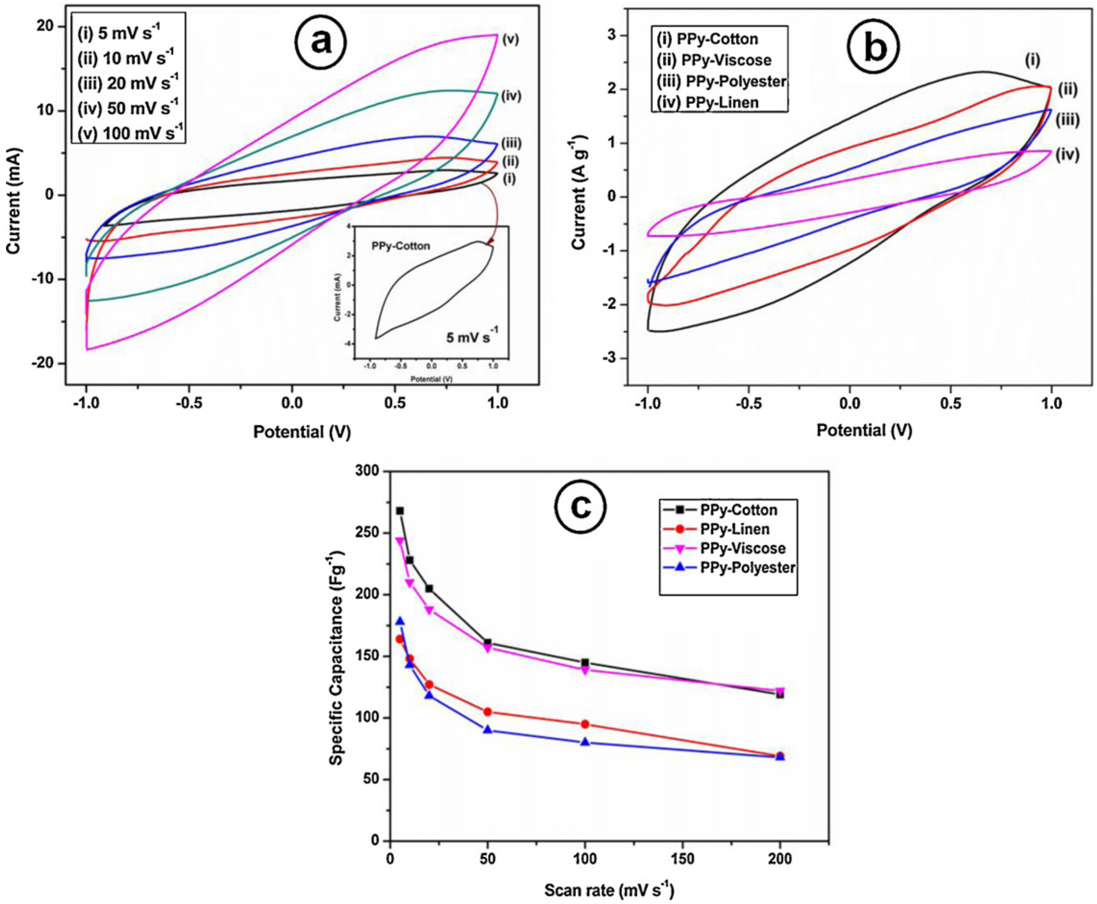


Fig. 5. (a) Cyclic voltammograms of PPy-Cotton fabric at different scan rates (Inset-PPy-Cotton at a scan rate of 5 mV s^{-1}), (b) cyclic voltammograms of 0.2 M PPy coated textile fabrics at 10 mV s^{-1} scan rate (c) specific capacitance calculated from cyclic voltammogramms for PPy coated textiles at different scan rates.

Fig. 5b depicts a plot obtained by cyclic voltammogram of the PPy-Cotton, PPy-Viscose, PPy-Linen and PPy-PET composite electrodes at a scan rate of 10 mV s^{-1}. These cyclic voltammograms demonstrate that the potential range in which current shows capacitive behaviour between −1 to +1 V. The entire PPy coated textile electrodes exhibited nearly rectangular shape with a small redox peaks. The redox peaks are corresponding to the oxidation and reduction of PPy. The quasi rectangular shape of PPy-Cotton and PPy-Viscose is larger than the PPy-Linen and PPy-PET, suggesting a larger capacitive behaviour than that of the later. While increasing the scan rates the current also found to increase. The specific capacitance (SC) of the PPy-textile composites was calculated using Eqn 1 (Aradilla, Estrany, & Aleman, 2011).

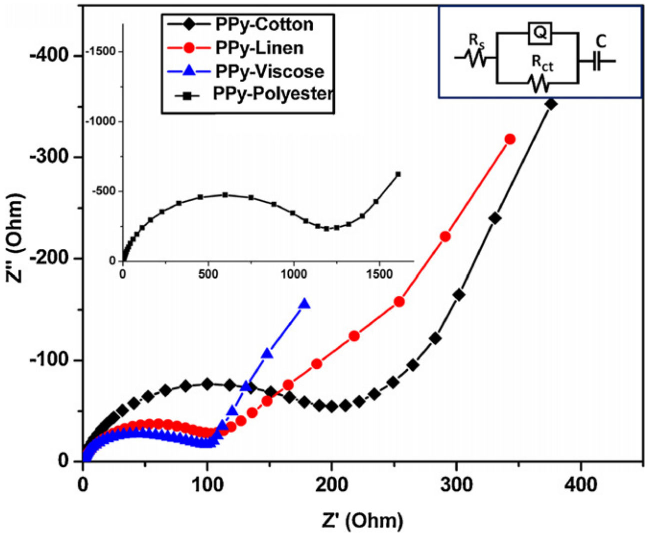


Fig. 6. Impedance spectra of PPy coated textiles at frequency range from 100 kHz to 10 mHz with a sinusoidal signal amplitude of 5 mV and equivalent circuit used to fit the impedance spectrum of PPy-textiles (inset).

$$SC = \frac{Q}{\Delta V \times m} \quad (1)$$

where Q is the voltammetric charge, which is determined from cyclic voltammetric curve, ΔV is the potential window and m is the mass of polymer present in the PPy-textile electrode. The specific capacitance obtained for each fabric at different scan rates are shown in Fig. 5c. The specific capacitance values of the PPy-coated textile decrease as the scan rates increase from 5 to 100 mV s^{-1}. Such decrease in capacitance with scan rate is attributed to the kinetics of the electron transportation in the electrode materials and limited the ion adsorption–desorption process at the interface of the electrode/electrolyte. So the incompletion of the redox transition due to diffusion effect of the ions within the electrode reduced the specific capacitance at higher scan rates (Chen, Rakhi, & Alshareef, 2012; Dubal et al., 2012). It can also be seen in Fig. 5c, that PPy-Cotton and PPy-Viscose shows greater capacitance, reaching the highest value of 268 and 244 F g^{-1} at a scan rate of 5 mV s^{-1}. The specific capacitance values were obtained for these textile electrodes are larger or comparable with the values reported for polypyrrole coated on flexible substrates (Table 1). But increasing the scan rate to 10 mV s^{-1} the specific capacitance value reduced to 228 and 210 F g^{-1}, whereas only 5–6% reduction in

Table 1
Comparison of the specific capacitance between our PPy-textile electrode and several reported polypyrrole coated flexible substrates.

S. no.	Material	Electrolyte	Scan rate	Specific capacitance	Reference
1	PPy coated nylon lycra	1.0 M NaCl	10 mV s^{-1}	123.3 F g^{-1}	Yue et al. (2012)
2	PMAS/PPy template Actitex carbon fibre	1.0 M H_2SO_4	5 mV s^{-1}	152.0 F g^{-1}	Wilson et al. (2010)
3	PPy coated acrylonitrile butadiene rubber	1.0 M Na_2SO_4	5 mV s^{-1}	125.8 F g^{-1}	Hepowit et al. (2012)
4	PPy coated dispersed cladophora cellulose composite	2.0 M NaCl	5 mV s^{-1}	274.0 C g^{-1}	Henrik et al. (2012)
5	Cellulose nanocrystal and polypyrrole composite	0.1 M KCl	0.25 V s^{-1}	336.0 F g^{-1}	Liew et al. (2010)
6	PPy coated cotton	1.0 M H_2SO_4	5 mV s^{-1}	268.0 F g^{-1}	This work
7	PPy coated viscose rayon	1.0 M H_2SO_4	5 mV s^{-1}	244.0 F g^{-1}	This work

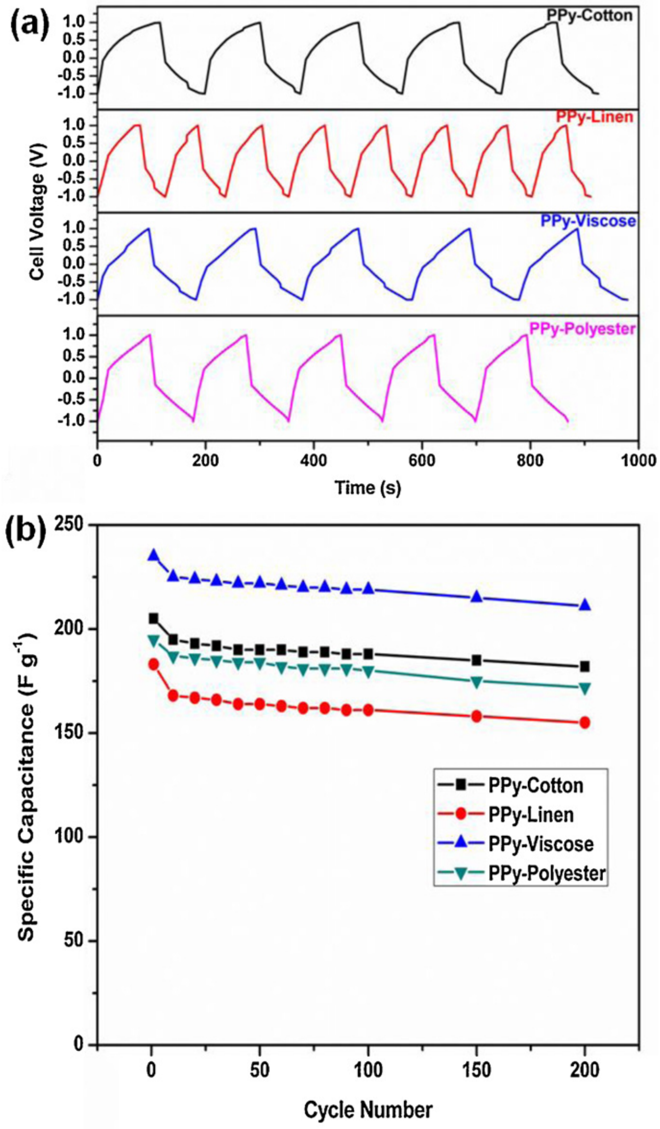


Fig. 7. Galvanostatic charge–discharge curves of polypyrrole coated textiles (a) and specific capacitance calculated from the charge–discharge curve (b).

specific capacitance values were noticed after 100 cycles. The cyclic voltammograms obtained 1st and 100th cycle for PPy-Cotton and PPy-Viscose at a scan rate of 10 mV s^{-1} are shown as supplementary data (Fig. S3). Comparable capacitance values were also obtained for PPy-Linen (164 F g^{-1}) and PPy-PET (178 F g^{-1}) at a scan rate of 5 mV s^{-1}.

Electrochemical impedance spectroscopy was further used to monitor the capacitive behaviour of the PPy coated textile surfaces. Fig. 6 shows the nyquist plot for PPy-Cotton, PPy-Linen, PPy-Viscose and PPy-PET fabrics. The impedance curve of PPy-textile electrodes showed a single semicircle at high frequency and a nearly vertical straight line at low frequency indicating the charge transfer and capacitive processes, respectively. An equivalent circuit is fitted for the impedance spectrum is shown in inset of Fig. 6. The complex equivalent circuit includes a solution resistance from electrolyte, a constant phase element (CPE) arise from double layer capacitance, a charge transfer resistance (R_{ct}) parallel to CPE from ionic charge transfer in electrode/electrolyte interface and a capacitor (C) may be from the capacitance of the electrode in the electrolyte. The electrochemical parameters obtained by fitting the impedance curve for PPy-textiles are summarised in Table 2. Impedance solution resistance (R_s) for PPy-Cotton (0.244 Ω) and PPy-Viscose (0.239 Ω) was lower compared to PPy-Linen and PPy-PET, which can be correlated to the conductivity of the coated textiles and are explained in the experimental section. The ionic charge transfer resistance are low for the former samples which promotes the higher ionic transport and the capacitance values are also found to increase in PPy-Cotton (663 mF cm^{-2}) and PPy-Viscose (300 mF cm^{-2}).

Table 2
Electrochemical parameters obtained from EIS of the unit cell fabricated using PPy-textile electrodes.

Electrode	R_s (()	CPE ((F)	R_{ct} (()	W (()	C (mF)
PPy-Cotton	0.244	106	93	9.96	663
PPy-Linen	0.776	125	187.6	12.5	124
PPy-Viscose	0.239	152	81.5	28.5	300
PPy-PET	0.395	87.4	1270	88.2	22.8

Fig. 7 shows the galvanostatic charge/discharge profiles of PPy-textile electrodes at a current density 3 A g^{-1}. As discussed in literature, here also PPy in different composites show pseudocapacitive behaviour (Davies et al., 2011; Dubal, Patil, Kim, & Lokhande, 2011). The pseudocapacitance of the polymers in the composites is believed to be the main contribution in charge storage. The specific capacitance was calculated from the charge discharge curve for the PPy-textile samples using the following equation.

$$Cm = \frac{I \times \Delta t}{\Delta V \times m} \qquad (2)$$

where C_m is the specific capacitance, I is the charge/discharge current Δt is the discharge time, ΔV is 2 V, and m is the mass of active material within the electrode. PPy-Viscose shows the specific capacitance of 235 F g^{-1}, whereas the capacitance values were found to reduce with PPy-Cotton (205 F g^{-1}), PPy-PET (195 F g^{-1}) and PPy-Linen (183 F g^{-1}) under same current loading range. This observation reveals that the coating of polypyrrole on different textile materials led to different capacitive performances which may be due to the variation in PPy adsorption on the textile material. Cellulosic fabric forms a hydrogen bonding with PPy leads to uniform coating of PPy which enhances redox reaction of the polymer component. The capacitive behaviour of the prototype textile supercapacitors were studied up to 200 cycles. It was observed that a large decrease in specific capacitance around 5–8% for first and second cycle of the discharge curve. But after 200 cycles, only 10–12% loss was observed, which indicates the stability of the PPy-textiles. Further analyses are under progress to study the maximum capacity of these electrodes. The PPy-textile demonstrates the fast charge transfer and redox kinetics.

4. Conclusion

In conclusion, we have successfully prepared polypyrrole-textile (PPy-textile) electrodes by in situ chemical polymerisation and compared their electrochemical capacitive behaviour. SEM analysis shows that the deposited aggregates of PPy on textiles could withstand several washings. The composite formation of conducting polymer with textile materials was confirmed by FTIR analysis. Unit cells based on PPy-textiles were fabricated and studied the electrochemical performance. The cyclic voltammetric analysis clearly demonstrates that PPy-Cotton and Ppy-Viscose had good electrochemical performance than PPy-Linen and PPy-PET in the potential window of -1 to +1 V with 1 M H_2SO_4/PVA coated polypropylene membrane. The specific capacitances of 268 and 244 F g^{-1} were achieved for PPy-Cotton and PPy-Viscose respectively, at a scan rate of 5 mV s^{-1}. This confirms the strong interaction of PPy with textiles leading to high capacitive behaviour. The electrochemical impedance analysis also indicates that the PPy-Cotton and PPy-Viscose provides very low impedance and therefore the intercalation/deintercalation of sulphate ions made easier. These PPy-textile electrodes are comparatively lesser in weight than the usual substrates and are promising materials for fabricating flexible supercapacitors.

Acknowledgements

K. Firoz Babu gratefully acknowledges CSIR-HRDG, New Delhi for the Senior Research Fellowship. Authors also thank CSIR, New Delhi for funding this project under XIIth Five Year plan.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.01.021.

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