Activated Carbon-Polyethylenedioxythiophene Composite Electrodes for Symmetrical Supercapacitors

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ABSTRACT: A symmetrical (p/p) supercapacitor has been fabricated by making use of activated carbon (AC)-polyethylenedioxythiophene (PEDOT)-composite electrodes for the first time. The composite electrodes have been prepared via electrochemical deposition of β-napthalenesulphonate doped PEDOT onto AC electrodes. The characteristics of the electrodes and the fabricated supercapacitor have been investigated using cyclic voltammetry (CV) and AC impedance spectroscopy. The electrodes show a maximum specific capacitance of 158 Fg^{-1} at a scan rate of 10 mV s^{-1}. This indicates that the in situ electro-polymerization of ethylenedioxythiophene (EDOT) onto AC could improve the performance of carbon electrodes for use in supercapacitors. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2165–2170, 2008

Key words: supercapacitors; conducting polymers; polyethylenedioxythiophene; β-napthalenesulphonic acid; activated carbon; cyclic voltammetry; symmetric capacitor

INTRODUCTION

Intrinsically conducting polymers such as polypyrrole (PPy), Polyaniline, and polyethlendioxythiophene (PEDOT) are emerging electro active materials useful for several applications.[1] PEDOT has developed into one of the most successful materials from both fundamental and practical perspectives.[2] It possesses several advantageous properties as compared with other polythiophene derivatives as it has a combination of a low oxidation potential and moderate band gap with good stability in the oxidized state.[2–6] Also, by blocking the β-positions of the heterocyclic ring, the formation of α-β linkages during polymerization is prevented, resulting in a more regiochemically defined material. In addition to a high conductivity (ca. 400–600 S cm^{-1}, for both chemically[2] and electrochemically[5,6] prepared samples), PEDOT is also found to be highly transparent, making it an ideal candidate for several applications including electrode materials. Conducting polymers show oxidation–reduction property and also have high specific surface area. These properties of conducting polymers are utilized in electrode materials of secondary batteries and capacitors.[7,8] However the disadvantages of conducting polymers include a lower cycle life in a charge–discharge process than carbon-based electrodes because of the fact that the redox sites in the polymer backbone are not sufficiently stable for repeated redox process. While activated carbon (AC) has a higher cycle life, its electrical conductivity and capacitance values are lower than those of conducting polymers.[9] To enhance the capacitance and the conductivity of carbon-based supercapacitors, utilization of electronically conducting polymers is considered to be a better option. Further, recently it has been reported that the use of β-napthalenesulphonic (β-NSA) acid medium for polymerization of pyrrole produced nanostructured PPy.[10,11] The nano sized particles, because of their high surface area are very ideal materials for the capacitor electrodes and can yield high capacitance. Hence, fabrication of an AC/PEDOT composite electrode by in situ electropolymerization of ethylendioxythiophene (EDOT) in the presence of β-NSA acid as dopant and electrolyte onto the AC electrodes, may produce novel electrodes with high capacitance. This methodology also permits incorporation of PEDOT onto larger size electrodes similar to the electro deposition of metals. The additional advantage of using PEDOT in the carbon composite would be an increase in the permissible voltage for the symmetrical supercapacitor and an enhanced practical utility.

In view of all this, as a part of our ongoing program on conducting polymer device fabrication,[12] we report in this article, dopant-induced morphology modulation in PEDOT preparation and customization of it onto AC surface to produce a new type of AC/PEDOT composite electrode and evaluation of it as an electrode in a p/p symmetrical hybrid supercapacitor cell configuration using cyclic voltammetry, and electrochemical impedance spectroscopy.

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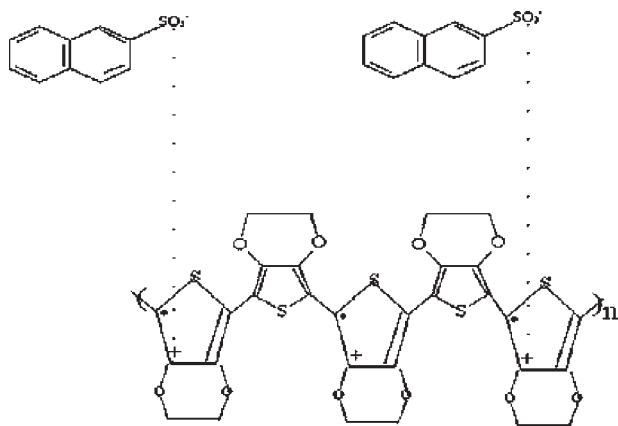
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Figure 1 Structure of β-napthalenesulphonate ion doped PEDOT.

EXPERIMENTAL

Preparation of carbon electrode

AC (Aldrich) was made into a paste by using *N*-methylpyrrolidone along with a binder, polyvinylidiene fluoride, in the ratio of 70 : 30 using a pestle and mortar. This paste was then applied with a brush to a preweighed stainless steel current collector and dried at room temperature.

Electrodeposition of PEDOT onto carbon electrode

Ethylenedioxythiophene (EDOT) (Aldrich) was distilled before use. β-Naphthalenesulphonic acid (β-NSA) (Aldrich) was used as received without further purification, as a dopant and electrolyte. The deposition of PEDOT was carried out at room temperature in a one-compartment cell by galvanostatic polymerization using an AUTOLAB from Eco-Chemie (The Netherlands). A three electrode system was employed with saturated calomel electrode as a reference electrode for p-doping. A platinum foil (5 cm^2) was used as the counter electrode. The typical electrolyte was an aqueous solution of 0.1*M* EDOT and 0.1*M* β-NSA. PEDOT was electrochemically deposited onto the carbon material with a constant current density 0.3 mA cm^{-2} for 500 s. Electrochemical half-cell measurements were conducted in a three-electrode cell equipped with a reference electrode (SCE), platinum foil as counter electrode and carbon/PEDOT composite as the working electrode. FTIR measurements of PEDOT and doped PEDOT were conducted using a NICOLET AVATAR 330 FTIR spectrometer. The surface morphology of the prepared electrodes was examined through scanning electron microscope (SEM) images.

Fabrication of symmetrical (p/p) supercapacitor cell

The capacitor cells were constructed with an electrolyte-impregnated separator sandwiched between two symmetrical AC/PEDOT composite electrodes. The electrodes were prewetted with electrolyte before use. The capacitor performance was characterized by means of cyclic voltammetry using an AUTOLAB from Eco-Chemie, AC impedance measurements were made in the frequency range of 0.1–10^6 Hz. The charge–discharge behavior of the fabricated supercapacitor was tested by using galvanostatic method.

RESULTS AND DISCUSSIONS

The most practically useful polymerization method for EDOT is the so-called BAYTRON P synthesis that was developed at Bayer AG.[13–16] According to this method, the polymerization of EDOT in an aqueous polyelectrolyte (most commonly polystyrenesulphonate) solution using $Na_2S_2O_8$ as the oxidizing agent at room temperature results in a dark blue, aqueous PEDOT/PSS dispersion, which is commercially available from Bayer AG under its trade name BAYTRON P. An interesting aspect of BAYTRON P is that, after drying, the remaining PEDOT/PSS film is highly conducting, transparent, mechanically durable, and insoluble in common solvent. In this article, we report a similar synthesis, employing an aqueous polyelectrolyte solution of (β-NSA) acid and the observed capacitance of the PEDOT/β-NSA film were better compared with previous reports.[17–20] The increased capacitance may be due to the formation of fine PEDOT particles of nanometric size with high surface area and higher conductivity of the film induced by the dopant.[10,11] The structure of the β-napthalenesulphonate doped PEDOT may be represented as shown in Figure 1.
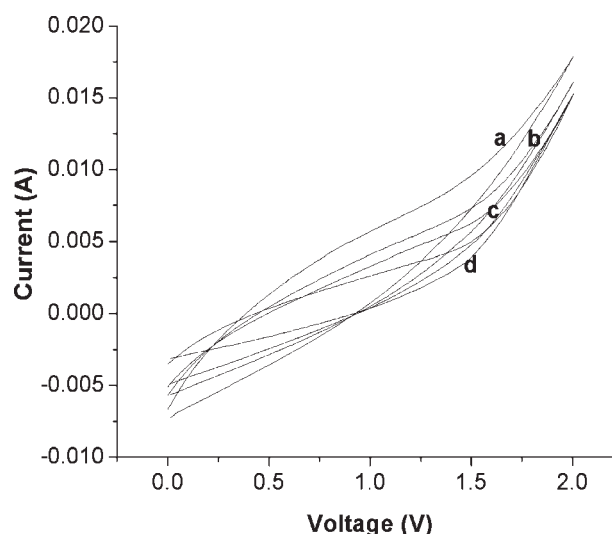

Figure 2 CV of activated carbon on SS electrode at sweep rates of (a) 50 mV s^{-1} (b) 25 mV s^{-1} (c) 20 mV s^{-1} (d) 10 mV s^{-1}.
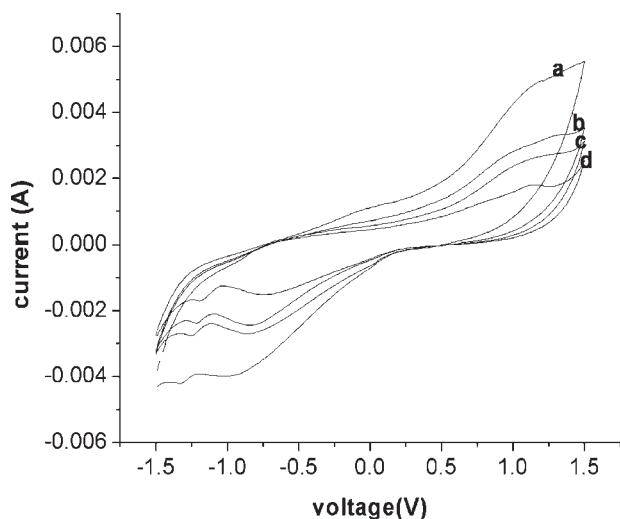
Figure 3 CV of PEDOT deposited on SS electrode at sweep rates of (a) 50 mV s^{-1} (b) 25 mV s^{-1} (c) 20 mV s^{-1} (d) 10 mV s^{-1}.

Figure 5 CV of p/p supercapacitor made of AC/PEDOT composite electrodes at sweep rates of (a) 50 mV s^{-1} (b) 25 mV s^{-1} (c) 20 mV s^{-1} (d) 10 mV s^{-1}.

Cyclic voltammetry responses

Cyclic voltammetry responses for the AC, PEDOT, AC/PEDOT composite single electrode and the p/p supercapacitor at various sweep rates are shown in Figures 2–5. The behavior observed are characteristic of double layer (AC), redox(PEDOT), and a synchronization of double layer and redox (AC/PEDOT composite electrode and p/p supercapacitor) capacitive features. The specific capacitance values of the various electrodes and the supercapacitor (Table I) have been calculated from the respective cyclic voltammograms using the equation:
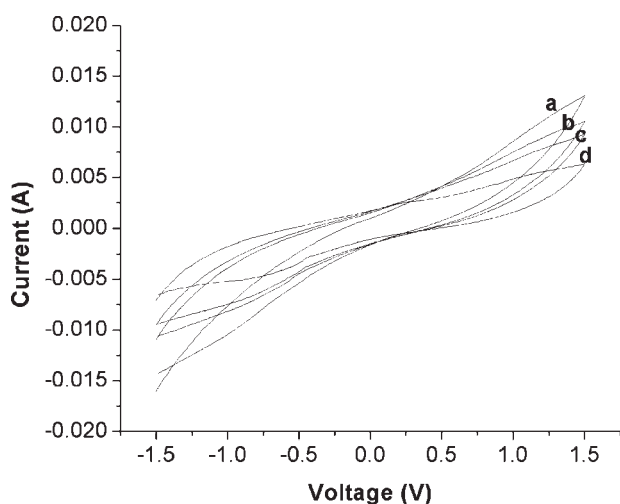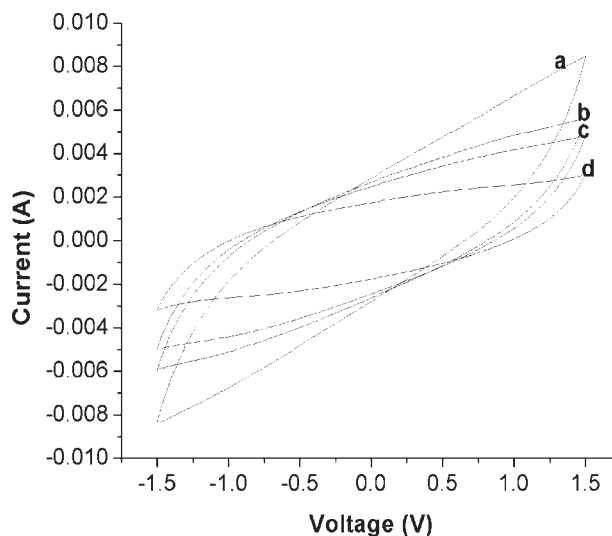
$$C = i/s$$

where 's' is the potential sweep rate and 'i' is the average current.

As shown in Table I, a specific capacitance of 158 Fg^{-1} has been obtained for the composite single electrode at the sweep rate of 10 mV s^{-1}. Whereas, the same for AC and PEDOT single electrodes and p/p AC/PEDOT supercapacitor are 12, 75, and 90 Fg^{-1}, respectively. The data also indicate that the capacitance of the AC/PEDOT single electrode was about twice that of the p/p supercapacitor. This is quite justifiable, as two AC/PEDOT electrodes constitute the electrochemical configuration of a parallel plate condenser connected in series. Specific capacitance

Figure 4 CV of AC/PEDOT composite electrode at sweep rates of (a) 50 mV s^{-1} (b) 25 mV s^{-1} (c) 20 mV s^{-1} (d) 10 mV s^{-1}.

TABLE I
Specific Capacitance Values of Activated Carbon, PEDOT, and Activated Carbon/PEDOT, Elelctrodes and p/p Supercapacitor

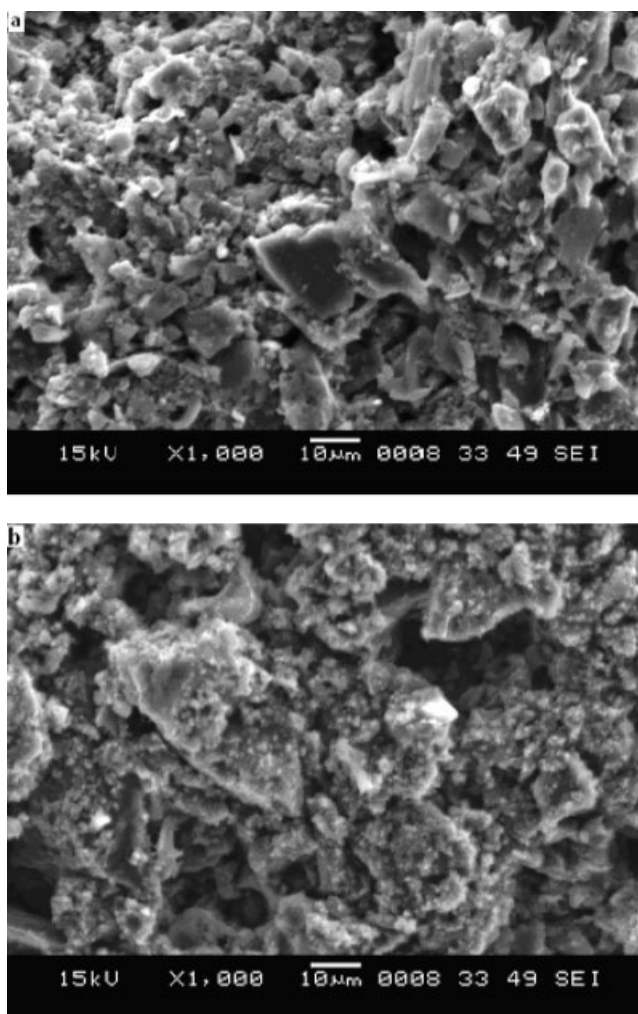| Serial No.	Materials	Scan rate (mV s^{-1})	Specific capacitance (Fg^{-1})
1	Activated carbon	50	8
		25	10
		20	11
		10	12
2	PEDOT	50	28
		25	38
		20	44
		10	75
3	Activated carbon + PEDOT	50	34
		25	67
		20	76
		10	158
4	Symmetrical AC/PEDOT composite electrode supercapacitor	50	17
		25	33
		20	45
		10	90

Figure 6 (a) SEM image of activated carbon on SS electrode. (b) SEM image of AC/PEDOT composite electrode.

of AC/PEDOT composite electrode is higher at all sweep rates compared with the specific capacitance values of individual AC as well as the PEDOT electrodes. The value of capacitance is more than 1 order higher compared with single AC electrode and about twice compared to the single PEDOT electrode, which can be attributed to the combined effect of double layer and redox supercapacitor capacitive behavior. This fact can also be observed in their cyclic voltammograms (Figs. 2–5). Further, it is noteworthy that this composite electrode shows higher capacitance compared with that of the PEDOT electrode reported.[21]

SEM analysis

Figure 6(a) shows the scanning electron microscopic images of the AC pasted on to the SS panel exhibiting irregular granular structure, with particle size varying from 1 to 20 μm. Figure 6(b) presents the SEM image of elelctropolymerized β-napthalene-

sulphonate doped PEDOT particles deposited over AC electrode. The image shows the presence of fine particles dispersed over the surface of AC particles. The sizes of these PEDOT particles are in the range of a few hundred nanometers to a micron. The image also indicates the formation of nano-porous structured deposition of PEDOT on the AC surface. This kind of surface morphology is quite ideal for the fabrication of the electrode as it would be having high surface area and expected to yield good capacitance. We did not probe further into the dependence of the surface morphological features on the concentration of dopant and other conditions of the experiment. More detailed investigation in this regard is required to know the influence of the medium on the morphological features of the electrodeposits.

FTIR analysis

Figure 7 shows the FTIR spectrum of doped PEDOT on AC electrode. The vibrational frequencies of PEDOT are generally seen at frequencies below 1600 cm^{-1}. The peaks observed at 1599, 1498, and 1324 cm^{-1} are due to the C=C and C—C stretching vibrations of quinoid structure of the thiophene ring.[22,23] The bands at 1195 and 1039 cm^{-1} are ascribed to S=O stretching vibrations due to the sulphonate ions of β-NSA.[24,25] The bands at 1143, 1085 cm^{-1} are due to the C—O—C stretching vibrations of the ethylenedioxy group of the PEDOT. The bands at 978, 915, 841, 770, and 682 cm^{-1} are due to the C=S stretching vibrations of PEDOT. The band at 615 cm^{-1} is a characteristic vibration frequency of β-NSA.[24] Similarly the band at 565 cm^{-1} corresponds to the SO_2 scissoring frequency of β-NSA.[25] Hence, the presence of characteristic frequencies of
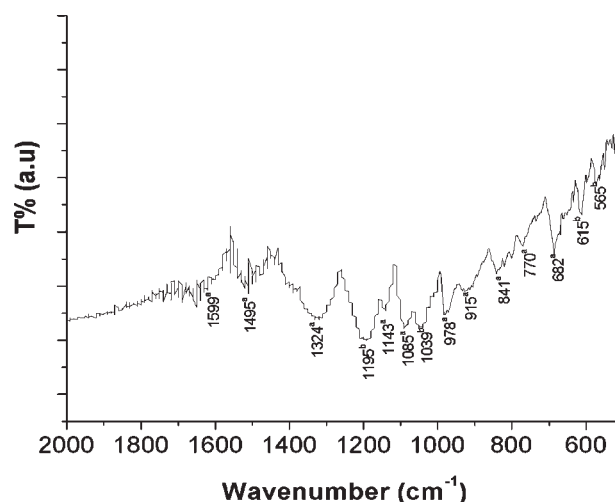

Figure 7 FTIR spectrum of elelctrodeposited PEDOT on activated carbon electrode; (a) Bands corresponding to PEDOT, (b) Bands corresponding to β-NSA.
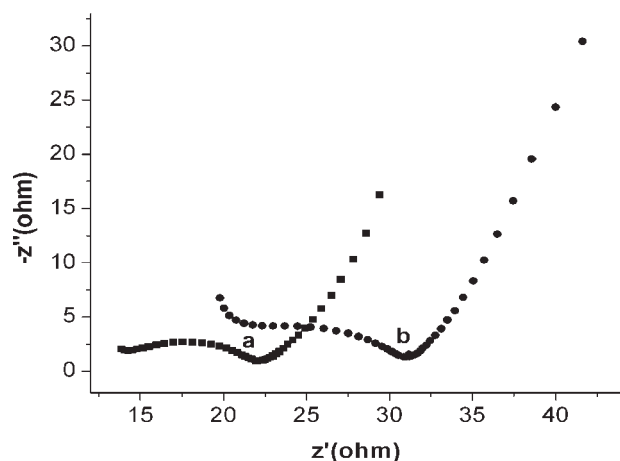
Figure 8 AC impedance responses of single electrodes: (a) Activated carbon (b) AC/PEDOT composite electrode.

both β-NSA and PEDOT in the spectrum indicates the successful formation of β-napthalenesulphonate doped PEDOT on the electrode.

Electrical properties of electrochemical capacitor

The AC impedance responses (Nyquist plots) of AC electrode, AC/PEDOT composite electrode and p/p supercapacitor are shown in Figures 8 and 9. In all cases, a semicircle of large radius is obtained at high frequency in the range and a straight line in the low frequency region. The capacitance value increases at low frequencies because of a larger number of ionic movements, which cause a decrease in the bulk resistance of the capacitor. The semicircle results from the parallel combination of resistance and capacitance and the linear region is because of Warburg impedance. In the low frequency region, the straight line part leans more towards imaginary axis and this
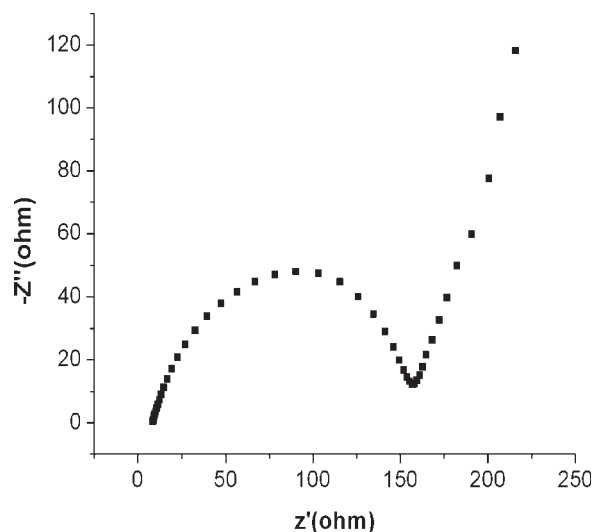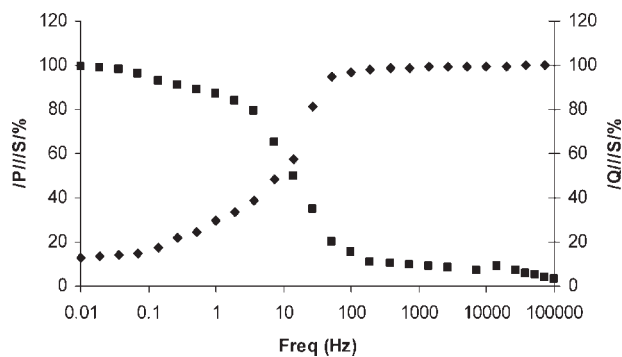

Figure 10 Normalized reactive power $|Q|/|S|\%$ and active power $|P|/|S|\%$ vs. frequency (Hz) for the 1 cm^2 cell p/p supercapacitor.

indicates good capacitive behavior.[26] Hybrid capacitor and carbon capacitor electrodes behave almost similarly in the high frequency region but AC/PEDOT hybrid is more capacitive compared with simple carbon capacitors as is evident in the low frequency region. This is further supported by the specific capacitance calculation of the electrodes and the supercapacitor (Table I). Using Normalized reactive power $|Q|/|S|\%$ and active power $|P|/|S|\%$ versus frequency (Hz) plot (Fig. 10) for the 1-cm^2 cell, the time constant of the fabricated (p/p) supercapacitor has been calculated. The theoretical aspects and other details of this calculation can be found in the literature.[27] The calculated time constant was found to be equal to 7.2 ms. The time constant τ_o, represents a transition for the supercapacitor between a resistive behavior for frequency higher than $1/\tau_o$ and a capacitive behavior for frequencies lower than $1/\tau_o$. Hence, the observed time constant value of 7.2 ms indicated that the present system can be efficiently used up to 150 Hz. Figure 11 shows the
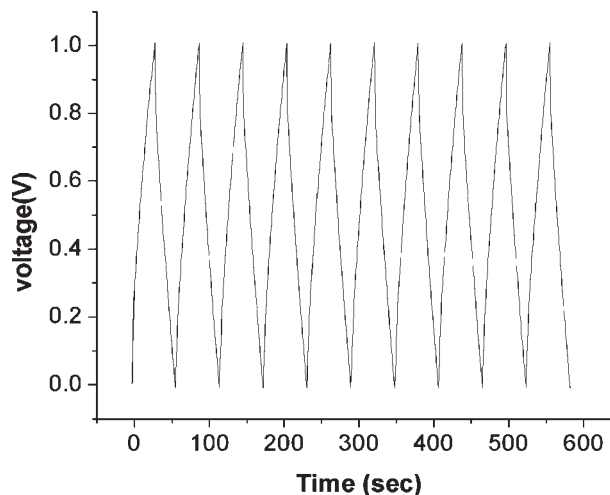

Figure 9 AC Impedance response of p/p supercapacitor.

Figure 11 Galvanostatic charge–discharge curves of p/p supercapacitor at a constant current density of 2 mA cm^{-2}.
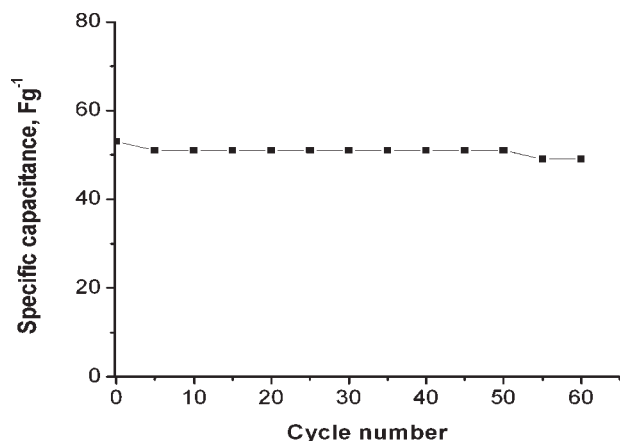
Figure 12 Variation of specific capacitance of p/p super-capacitor with cycle number.

charge–discharge profile of the supercapacitor as measured by galvanostatic method at a constant current density of 2 mA cm^{-2} at different cycles between 0 and 1.0 V, for the first 10 cycles. From the figure, it can be seen that the initial voltage drop during discharge is negligibly small and the voltage of the capacitor varies almost linearly with time during both charging and discharging processes for various cycles. It is evident from the figure that the charging time and also discharging time remained constant with increasing number of cycles. However, there may be a slightly higher voltage drop and decrease in the charging and discharging time with cyclings as well as with current density beyond 4000 cycles because of the degradation possibility of PEDOT redox activity.[28] The couloumbic efficiency of the supercapacitor calculated from charge–discharge cyclings is also high in the range of 98–99%. Figure 12 presents the variation of specific capacitance of the supercapacitor with cyclings. The data reflects that the device exhibited almost constant capacitance during the test. However, at higher cycle numbers the capacitance is expected to decrease slightly because of the decrease of redox activity of the supercapacitor.

CONCLUSIONS

AC–polyethylene dioxythiophene composite electrodes have been prepared via electrochemical polymerization of ethylene dioxythiophene onto AC surface. A (p/p) symmetric supercapacitor has been fabricated using these composite electrodes. The capacitance properties of the composite electrodes and the supercapacitor have been investigated through cyclic voltammetry and AC impedance spectroscopy. The studies showed that the electrodes and the supercapacitor have a specific capacitance of 158 and 90 Fg^{-1}, respectively. The supercapacitor is stable during cyclings and is more suited for applications at low frequency region.

References

1. Kirchmeyer, S.; Reuter, K. J Mater Chem 2005, 15, 2077.
2. Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. Adv Mater 2000, 12, 481.
3. Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. J Electroanal Chem 1994, 369, 87.
4. Winter, I.; Reece, C.; Hormes, J.; Heywang, G.; Jonas, F. J Electroanal Chem 1994, 369, 87.
5. Pettersson, L. A. A.; Carlsson, F.; Inganas, O.; Arwin, H. Thin Solid Films 1998, 313/314, 356.
6. Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. Adv Mater 2003, 15, 855.
7. Feldberg, S. W. J Am Chem Soc 1984, 106, 4671.
8. Carlberg, J. C.; Inganas, O. J Electrochem Soc 1997, 144, L61.
9. Jurewicz, K.; Delpeux, S.; Bertagna, V.; Beguin, F.; Frackowiak, E. J. Chem Phys Lett 2001, 347, 36.
10. Qu, L.; Shi, G. Chem Commun 2003, 206.
11. Qu, L.; Shi, G. Macromolecules 2003, 36, 1063.
12. Krishna Bhat, D.; Selvakumar, M. J Mater Sci 2007, 42, 8158.
13. Jonas, F.; Kraft, W.; Muys, B. Macromol Symp 1995, 100, 169.
14. Jonas, F.; Hey Wang, G. Electrochim Acta 1994, 39, 1345.
15. Jonas, F.; Morrison, J. T. Synth Met 1997, 85, 1397.
16. Jonas, F.; Lerch, K. Kunstsoffe 1997, 87, 1401.
17. Arbizzani, C.; Mastragostino, M.; Menghello, L. Electrochim Acta 1995, 40, 2223.
18. Arbizzani, C.; Mastragostino, M.; Soavi, F. J Power Sources 2001, 100, 164.
19. Ryu, K. S.; Young-Gilee, Hong, Y.-S.; Park, Y. J.; Wu, X.; Kim, K. M.; Kang, M. G.; Park, N.-G.; Chang, S. H. Electrochim Acta 2004, 50, 843.
20. Mastragostino, M.; Arbizzani, C.; Soavi, F. Solid State Ionics 2002, 148, 493.
21. Ryu, K. S.; Kim, K. M.; Park, N.-G.; Park, Y. J.; Chang, S. H. J Power Sources 2002, 103, 305.
22. Kvarnstrom, C.; Neugebauer, H.; Blomquist. S.; Ahonen, H.J.; Kankare, J.; Ivaska, A. Electrochim Acta 1999, 44, 2739.
23. Han, M. G.; Foulger, S. H. Adv Mater 2004, 16, 231.
24. Dutta, P.; De, S. K. Synth Metals 2003, 139, 207.
25. Lambert, J. B.; Shurvell, H. F.; Lighter, G. A.; Cooks, R. G. Introduction to Organic Spectroscopy; Macmilan: New York, 1992.
26. Conway, B. E. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications; Kluwer: New York, 1999.
27. Taberna, P. L.; Simon P.; Fauvarque, J. F. J Electrochem Soc 2003, 150, A292.
28. Muthulakshmi, B.; Kalpana, D.; Pitchumani, S.; Renganathan, N. G. J Power Sources, 2006, 158, 1533.