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Synthesis of Copolymer of Aniline and Pyrrole by Inverted Emulsion Polymerization Method for Supercapacitor

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ABSTRACT: Copolymer of aniline and pyrrole was synthesized by inverted emulsion polymerization method by oxidizing aniline and pyrrole using benzoyl peroxide in presence of sodium laurylsulphate surfactant and *p*-toluenesulphonic acid. Copolymer samples were characterized by infrared, X-ray diffraction and scanning electron microscopic techniques and compared their properties with the corresponding homopolymers. The optimum reaction conditions for the preparation of copolymer with reasonably good yield (1.72 g) and conductivity (7.3×10^{-2} S/cm) were established. The synthesis procedure was extended to prepare copolymer samples using various protonic acids. Electrochemical characterization such as cyclic voltammetry, charge-discharge and impedance were carried out on symmetrical supercapacitor cell consists of

poly(aniline-*co*-pyrrole)-*p*-toluenesulfonic acid salt, wherein, the copolymer salt was synthesized using equal amount of aniline and pyrrole monomers. The values of specific capacitance, energy and power densities for poly(aniline-*co*-pyrrole)-*p*-toluenesulfonic acid system (PANI-PPy) were calculated from charge-discharge studies and are found to be 21 F/g, 5.7 Wh/Kg and 100 W/Kg respectively. Impedance analysis showed specific capacitance value (57 F/g) at 0.01 Hz at 0.22 V. Among the copolymer salts, copolymer prepared with sulfuric acid showed higher capacitance (66 F/g). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1695–1701, 2010

Key words: conducting polymers; copolymerization; electrochemistry; FTIR; polypyrroles

INTRODUCTION

Electronically conducting polymers have been the subject of numerous investigations in the past three decades, the heightened interest in these polymers are mainly due to their various potential applications.^{1–3} An overview of various technological applications of these novel polymeric materials to electronics, optoelectronics devices and energy storage applications has been presented.¹ Applications such as transparent coating, corrosion protection, printed circuit boards, electromagnetic induction shielding, electro and chemochromic application have been mentioned by Wessling.² In a review article, Paoli et al. have mentioned the conducting polymer blend applications such as photolithography,

electrochromic, photovoltaic, light emitting diode and supercapacitors.³

There has been great interest in developing and refining more energy storage devices. One such device, the supercapacitor, has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. Supercapacitors are particularly useful because of their parameters complement the deficiencies of other power sources such as batteries and fuel cells. Supercapacitors have longer cycle-lives and can be both rapidly charged and discharged at high power densities and find applications in consumer electronics, hybrid electric vehicles, and industrial power management. Supercapacitors can be divided in to two sub type, one is electric double layer capacitors (EDLCs) and another one is pseudocapacitors/electrochemical capacitors (ECs). Three main classes of ECs are based on the materials used such as oxides,^{4,5} carbon materials⁶ and conducting polymers.^{7,8} Supercapacitor consisting of carbon-conducting polymer composites have also been reported.^{9,10} Among these electroactive materials, conducting polymers are promising materials for supercapacitors due to the advantages of high specific capacitance,

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TABLE I
Literature Report on Polyaniline and Polypyrrole Supercapacitors

System	Electrolyte	Capacitance (F/g)	Reference
PANI/MWNTs	1M H ₂ SO ₄	360.0	11
PANI/CNTs	1M NaNO ₃	183.0	12
PANI/activated carbon	1M H ₂ SO ₄	237.5	13
PANI/MWNTs	1M NaNO ₃	224.0	14
PANI/MWNTs	1M NaNO ₃	190.6	15
Ppy-MnO ₂ /CNT	1M Na ₂ SO ₄	281.0	16
Ppy/graphite	1 M KCl	400.0	17
Ppy	1 M KCl	282.0	18
Ppy	1 M TEABF ₄ in acetonitrile	355.0	19
CNTs-PPy	1 M LiClO ₄ acetonitrile	45.0	20

reasonable conductivity, redox properties, environmental stability, eco-friendly and low cost materials.

Among the conducting polymers, polyaniline (PANI) and polypyrrole (PPy) are mostly being studied for supercapacitor application. The literature status of supercapacitor^{11–20} in respect of specific capacitance for PANI and PPy synthesized by chemical polymerization method is given in Table I. Copolymers of aniline and pyrrole have been synthesized by chemical polymerization mostly using aqueous polymerization pathway.^{21–23}

In this work, copolymer of aniline and pyrrole was synthesized by inverted emulsion polymerization method by oxidizing aniline and pyrrole using benzoyl peroxide (BPO) in the presence of sodium lauryl sulfate (SLS) as emulsifier and *p*-TSA as protonic acid. As far as our knowledge is concerned, preparation of copolymer of aniline and pyrrole by inverted emulsion polymerization pathway is the first report. Copolymer samples were characterized by FTIR, XRD and SEM techniques and compared their properties with the corresponding homopolymers. The synthesis procedure was extended to prepare copolymer samples using various protonic acids such as hydrochloric acid (HCl), sulfuric acid (H₂SO₄), β -naphthalenesulfonic acid (NSA), benzenesulfonic acid (BSA), maleic acid (MA), chloroacetic acid (CAA). Electrochemical characterization such as cyclic voltammetry, charge-discharge and impedance analysis were performed on symmetrical supercapacitor cell consists of poly(aniline-co-pyrrole)-*p*-toluenesulfonic acid salt (PANI-PPy), wherein, the copolymer salt was synthesized using equal amount of aniline and pyrrole monomers. Specific capacitance, power and energy densities of the copolymer supercapacitor cell are reported here.

EXPERIMENTAL

Aniline (s.d. finechemicals, India) and pyrrole monomer (spectrochem, India) were purified under

reduced pressure and stored refrigerated before use. All other chemicals including BPO, chloroform, *p*-toluene sulphonic acid (*p*-TSA), SLS, MA, CAA (s.d. finechemicals, India), BSA (Spectrochem, India), NSA (Aldrich) and sulfuric acid H₂SO₄ (Rankem, India) were used as received without further treatment. All the reactions were carried out using distilled water.

Copolymers of aniline and pyrrole were synthesized via inverted emulsion polymerization method. In a typical experiment, 2.0 g of SLS and 3.84 g of *p*-TSA were dissolved in 40 mL of distilled water in 250 mL of round bottom flask and added 30 mL of aqueous solution containing 0.5 mL of aniline and 0.5 mL of pyrrole and stirred the reaction mixture at ambient temperature around 15 min. BPO solution (5.8 g in 30 mL chloroform) was added in to the above reaction mixture. The resulting reaction mixture was stirred at ambient temperature for 24 h. The reaction mixture was poured in to 300 mL of acetone, filtered, washed with water and followed by acetone. The powder sample was dried at 50°C until a constant weight. Copolymer preparation was carried by the changing the concentration of aniline, pyrrole, SLS, *p*-TSA, various acids, reaction time and the results are reported in Table II. Using this procedure, homopolymer of aniline and pyrrole was also prepared for comparison.

Copolymer of aniline and pyrrole (PANI-PPy) samples were pressed in to disks of 13 mm in diameter and about 1.5 mm in thickness under a pressure of 120 kg/cm². The resistance of PANI-PPy samples was measured by a four-probe method with a digital multimeter (Keithely, cleaveland, Ohio, Model 2010). The resistance was calculated on the basis of the average value of three different pellets. The polymer samples for FTIR analysis were mixed with KBr powder and compressed into pellets, wherein, the sample powder was evenly dispersed. Fourier transform infrared spectra were recorded with a GC-FTIR spectrometer (MODEL 670 Nicolet Nexus). Wide angle X-ray diffraction spectra of powder samples were obtained with a Siemens/D-5000

TABLE II
Yield and Conductivity of Copolymer Salts Prepared Under Different Conditions

Variation	Yield (g)	Conductivity (S/cm)
Pyrrole volume in mL ^a		
0.0	0.93	5.1×10^{-4}
0.1	0.58	1.2×10^{-2}
0.2	0.68	1.9×10^{-2}
0.3	1.10	1.2×10^{-2}
0.4	1.22	1.3×10^{-2}
0.5	1.41	4.3×10^{-3}
0.6	1.71	1.3×10^{-3}
0.7	1.47	3.7×10^{-4}
0.8	1.61	1.1×10^{-5}
0.9	1.67	1.3×10^{-6}
1.0	1.67	9.7×10^{-7}
Aniline volume in mL ^b		
0.0	1.55	5.5×10^{-2}
0.1	1.07	3.4×10^{-5}
0.2	1.13	4.7×10^{-4}
0.3	1.07	1.1×10^{-2}
0.4	1.45	1.2×10^{-2}
0.5	1.41	4.3×10^{-3}
0.6	1.71	6.1×10^{-3}
0.7	1.68	4.1×10^{-3}
0.8	1.36	3.6×10^{-3}
0.9	1.41	4.9×10^{-3}
1.0	1.42	2.5×10^{-3}
Time ^c		
1	1.10	2.1×10^{-7}
17	1.75	3.7×10^{-3}
24	1.41	4.3×10^{-3}
Sodium lauryl sulphate ^d		
2.0	1.41	4.3×10^{-3}
2.5	1.23	1.4×10^{-2}
3.0	1.72	7.3×10^{-2}
3.5	1.57	3.6×10^{-2}
4.0	1.30	2.3×10^{-3}
<i>p</i> -toluene sulphonic acid ^e		
2.84	1.46	1.6×10^{-4}
3.84	1.42	4.3×10^{-3}
4.84	1.60	3.3×10^{-3}
5.84	1.53	1.1×10^{-3}
Protonating agent ^f		
2 M HCl	1.58	1.2×10^{-2}
1 M H ₂ SO ₄	1.43	5.9×10^{-3}
2 g NSA	1.30	2.6×10^{-3}
2 g MA	1.21	1.6×10^{-4}
2 g BSA	1.45	7.5×10^{-3}
3 g CAA	0.71	1.0×10^{-6}

^a Reaction conditions: aniline (0.5 mL), SLS (2.0 g), *p*-TSA (3.84 g), BPO (5.8 g), time (24 h), chloroform (30 mL) and various amounts of pyrrole in mL.

^b Reaction conditions: pyrrole (0.5 mL), SLS (2.0 g), *p*-TSA (3.84 g), BPO (5.8 g), time (24 h), chloroform (30 mL) and various amounts of aniline in mL.

^c Reaction conditions: aniline (0.5 mL), pyrrole (0.5 mL), SLS (2.0 g), *p*-TSA (3.84 g), BPO (5.8 g), chloroform and different reaction time.

^d Reaction conditions: aniline (0.5 mL), pyrrole (0.5), *p*-TSA (3.84 g), BPO (5.8 g), time (24 h), chloroform and various amounts of SLS in g.

^e Reaction conditions: aniline (0.5 mL), pyrrole (0.5), SLS (2.0 g), BPO (5.8 g), time (24 h), chloroform and various amounts of *p*-TSA.

^f Reaction conditions: aniline (0.5 mL), pyrrole (0.5), SLS (2.0 g), BPO (5.8 g), time (24 h), chloroform and using different protonating agents.

X-ray diffractometer with Cu K α radiation of wavelength 1.54×10^{-10} m and continuous scan speed of $0.045^\circ \text{ min}^{-1}$. Morphology studies of the polymer samples were carried out using Hitachi S520 scanning electron microscope instrument operating at 10 kV. The sample was mounted on a carbon disc with the help of double sided adhesive tape and sputter-coated with a thin layer of gold to prevent sample charging problems. Cyclic voltammetry and galvanostatic charge–discharge experiments were carried out with a WonATech multichannel potentiostat/galvanostat(WMPG1000, GyeongGi-do, Korea). Electrochemical impedance spectra were recorded with IM6ex Zahner-Elektrik (Germany). PANI-PPy electrode material was prepared by the mixing 80% of polymer material with 20% battery-grade carbon and then pressing the mixture on stainless steel mesh (size, 24 μm) by the application of 100 kg/cm^2 . Three electrode cell measurements were carried out with copolymer as working electrode, platinum electrode as counter electrode, and Ag/AgCl reference electrode in 1M H_2SO_4 electrolyte. Capacitor cell was constructed using two copolymer electrodes in 1M H_2SO_4 electrolyte.

RESULTS AND DISCUSSION

Yield and conductivity

Copolymer of aniline and pyrrole was prepared via inverted emulsion polymerization pathway by oxidizing aniline and pyrrole monomers with BPO in presence of anionic surfactant (SLS) and protonating agent (*p*-TSA). Polymerization was carried out by varying the concentrations of aniline, pyrrole, surfactant, acid and reaction time. Copolymers were also prepared using various acids. The results are reported in Table II. In general, it was observed that the value of conductivity increases with increase in concentration of reactant, attains the maximum, and then decreases. The decrease in conductivity with increasing concentration may be due to the addition of excess dopant to the copolymer which leads to a lower degree of conjugation along the polymer backbone. The optimum reaction conditions for the preparation of copolymer with reasonably good yield (1.72 g) and conductivity ($7.3 \times 10^{-2} \text{ S/cm}$) are: aniline – 0.5 mL, pyrrole – 0.5 mL, BPO (5.8 g), SLS (3.0 g), *p*-TSA (3.84), time (24 h).

A high yield of copolymer salt (173 wt % with respect to the amount of pyrrole and aniline used in the reaction) could be obtained with the use of SLS (0.1 M), *p*-toluenesulphonic acid (0.2 M) and BPO (0.23 M) (Table II). The amount of dopants such as *p*-TSA and DHS present in the polymer chain could not be calculated from the present study. Hence, no quantitative correlations have been made for the

values of the yield and conductivity with the use of different concentrations of acid, emulsifier and oxidant used. Moreover, copolymer samples are not soluble in common organic solvents and thus molecular weight of the polymer could not be calculated. Hence, the yield of the copolymer salt is reported in terms of weight percentage (i.e. 173 wt %) with respect to the total amount of aniline and pyrrole used in the reaction.

FTIR spectra

The FTIR spectrum of PANI salt prepared by inverted emulsion polymerization pathway is shown in Figure 1(a). Characteristic main peaks of PANI are assigned as the bands located at 3235 cm^{-1} due to $-\text{NH}$ str. of PANI, 2920 and 2845 cm^{-1} are symmetrical and asymmetrical stretching of aliphatic C–H of alkyl substituent of dodecylhydrogensulphate, 1570 and 1490 cm^{-1} corresponds to the C=C stretching vibration of the quinoid and benzenoid rings, 1295 and 1235 cm^{-1} bands are characteristics of C–N stretching of the secondary aromatic amine and C–H bending of the benzenoid ring. A similar FTIR spectrum of PANI salt was reported earlier.²⁴ The FTIR spectrum of polypyrrole salt [Fig. 1(c)] prepared by inverted emulsion polymerization pathway is reported earlier.²⁵ Main characteristics peaks are 3435, 2920, 2850, 1545, 1455, 1170, 1695 and 1040 cm^{-1} .²⁵ FTIR spectrum of copolymer [Fig. 1(b)] synthesized by inverted emulsion polymerization method reveals majority of spectral lines matches with that of the homopolymers of aniline and pyrrole.

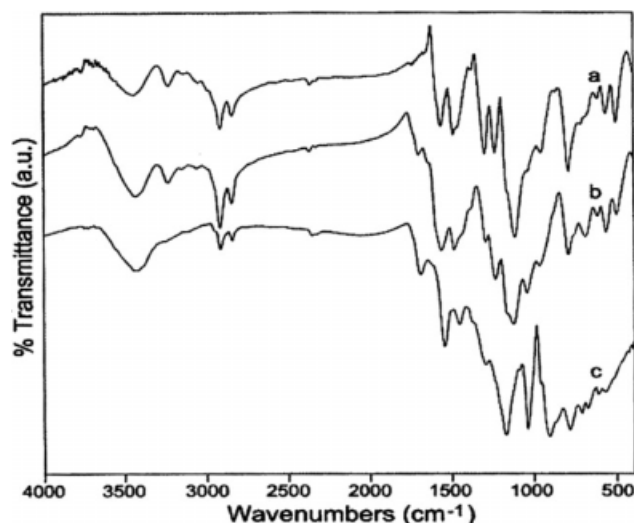


Figure 1 FTIR spectra of (a) polyaniline, (b) copolymer, and (c) polypyrrole.

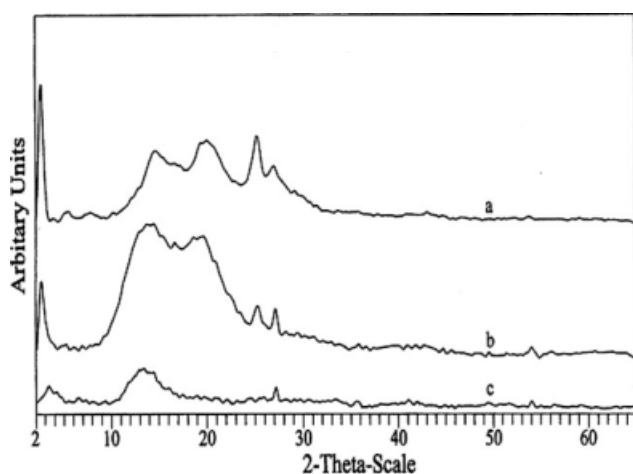


Figure 2 XRD spectra of (a) polyaniline, (b) copolymer, and (c) polypyrrole.

XRD studies

XRD pattern of PANI synthesized by inverted emulsion polymerization technique is shown in Figure 2(a) and it shows peaks at $2\theta = 2.5, 14.8, 19.5, 25.2,$ and 27.0 , corresponding interface distance $d = 35.78, 6.02, 4.55, 3.52,$ and 3.29 , the Bragg peaks centered at $2\theta = 25.2$ and 19.5 (d spacings of 3.52 and 4.55 Å, respectively) correspond to the π stacking distance of the PANI chains and the average separation distance between the alkyl substituents of the SLS dopant. A strong and narrow reflection centered at $2\theta = 2.5$ ($d = 35.8$ Å) indicates the presence of long alkyl chain surfactant. This is similar to the XRD spectrum of PANI salt reported earlier.²⁴ X-ray diffraction patterns of PPy show a broad peak at $2\theta = 14$ [Fig. 2(c)] indicating amorphous structure.²⁵ Typical powder X-ray diffraction profiles, registered for copolymer salt (PANI-PPy) is shown in Figure 2(b), which shows peaks at $2\theta = 2.5, 14.0, 19.9, 25.2$ and 27.2 with corresponding interface distance $d = 35, 6.4, 4.51, 3.52$ and 3.28 respectively. The peaks of copolymer salt are closely matches with that of the peaks due to PANI and polypyrrole indicating clearly the presence of PANI and polypyrrole in the copolymer.

Scanning electron microscopy

The morphology of homopolymer of aniline prepared by inverted emulsion polymerization pathway shows flake like morphology [Fig. 3(a)] and homopolymer of pyrrole shows combination of flake like morphology and agglomerated spherical particles [Fig. 3(c)]. However, the morphology of copolymer [Fig. 3(b)] shows agglomerated spherical sphere with better uniformity.

ELECTROCHEMICAL STUDIES

Electrochemical characteristics of symmetric supercapacitor of copolymer sample (PANI-PPy) were determined from cyclic voltammetry, charge-discharge and impedance measurements and the results are described here.

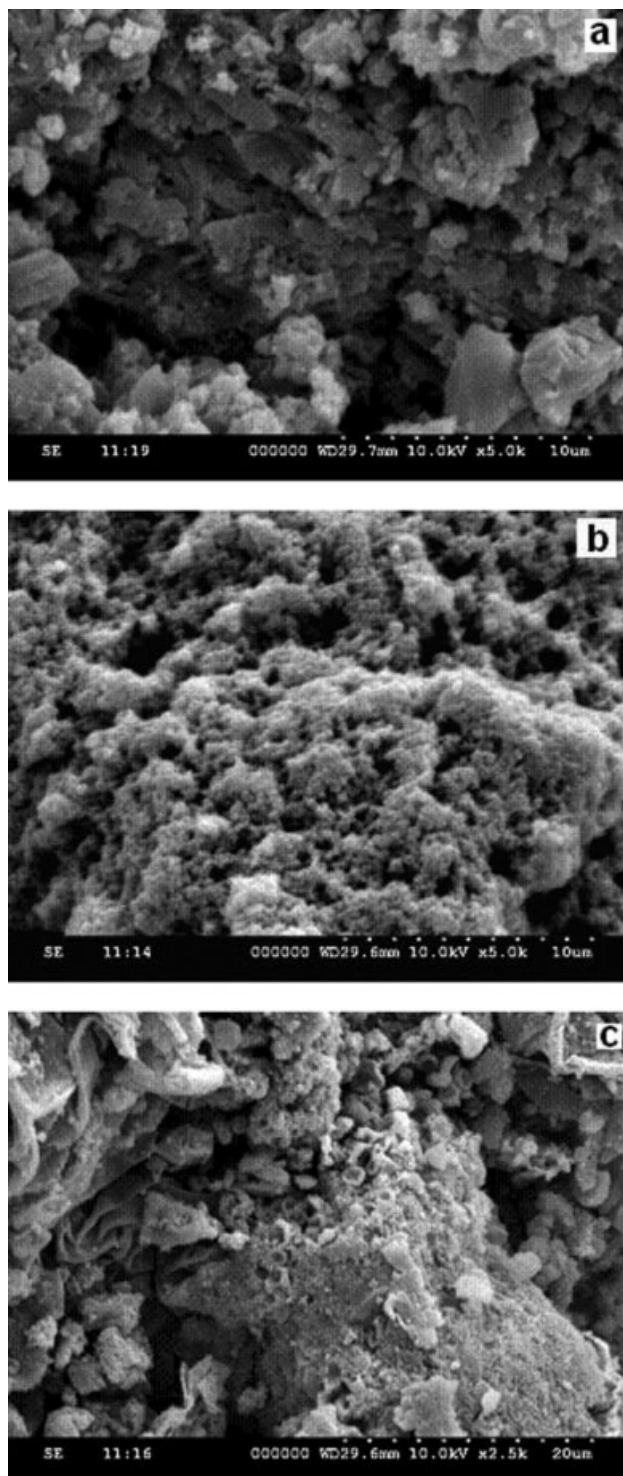


Figure 3 SEM images of (a) polyaniline, (b) copolymer, and (c) polypyrrole.

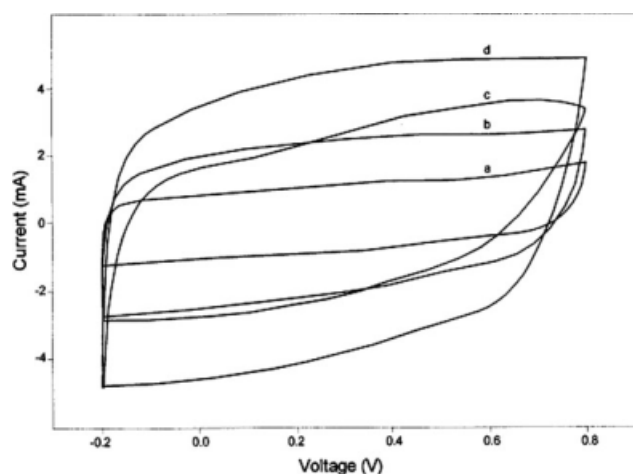


Figure 4 Cyclic voltammetry at different sweep rates of a PANI-PPy supercapacitor with 1M H₂SO₄ electrolyte (a) 1, (b) 2, (c) 5, and (d) 10 mV/s.

Cyclic voltammetry

Symmetric capacitor cells were constructed using PANI-PPy salt electrode and its cyclic voltammogram at different sweep rates is shown in Figure 4. The voltammogram shows more or less rectangular shape. An ideal capacitor should give a perfect rectangular shaped voltammogram. Since the supercapacitors are far away from the ideal capacitor behavior, the voltammogram curves are of slight distorted rectangular shape. The specific capacitance obtained for copolymers of PANI-PPy salts prepared with various protonating agents are reported in Table III. Capacitance value generally decreases with increase in scan rate. As a representative system, PANI-PPy supercapacitor system, the capacitance value decreased as 22.8, 19.1, 14.3, 9.8 F/g with increasing in scan rate as 1, 2, 5, and 10 mV/s. respectively. Among the copolymer salts, copolymer prepared with sulfuric acid showed higher capacitance i.e. 66 F/g at the scan rate of 1 mV/s.

Charge-discharge studies

Galvanostatic charge-discharge behavior of PANI-PPy symmetric capacitor cell was carried out at

TABLE III
Specific Capacitance of Copolymer Salts Prepared using Different Protonating Agents at Four Scan Rates

System	Specific capacitance (F/g)			
	Scan rate (mV/s)			
	1	2	5	10
PANI-PPy - <i>p</i> -TSA	22.8	19.1	14.3	9.8
PANI-PPy -H ₂ SO ₄	66.0	63.4	56.0	46.7
PANI-PPy -NSA	25.9	26.7	25.5	23.0
PANI-PPy -BSA	20.1	20.9	17.2	13.1
PANI-PPy-MA	9.6	9.8	7.9	6.2

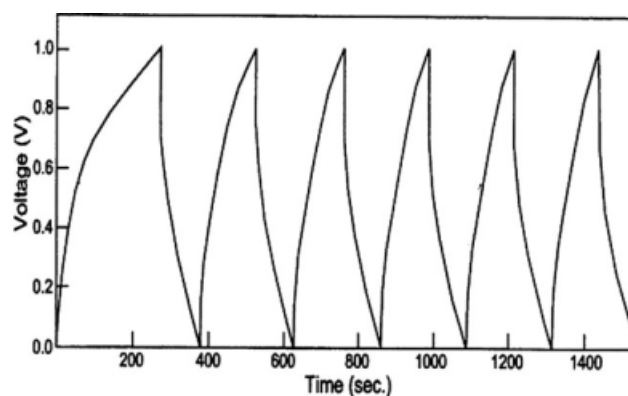


Figure 5 Galvanostatic charge and discharge of copolymer PANI-PPy symmetric capacitor cell at 1 mA current density – 5 cycles.

1 mA current density between voltages of 0 to 1 V up to 5 cycles and shown in Figure 5. The value of specific capacitance, energy and power density were found to be 21 F/g, 5.7 Wh/Kg and 100 W/Kg respectively. The coulombic efficiencies (η) of the capacitors are calculated using the formula (η) = (t_D/t_C) \times 100, where t_D and t_C are expressions of discharge and charge times respectively. Coulombic efficiency is almost remains constant (100–98%) with five cycles.

Impedance analysis of copolymer

Impedance spectroscopy is a powerful tool for mechanistic analysis of interfacial processes and for evaluation of resistance, rate constants, capacitance, etc. Nyquist plot of PANI-PPy symmetric supercapacitor cell in 1.0 M H₂SO₄ electrolyte is shown in Figure 6. The high frequency region usually considered to

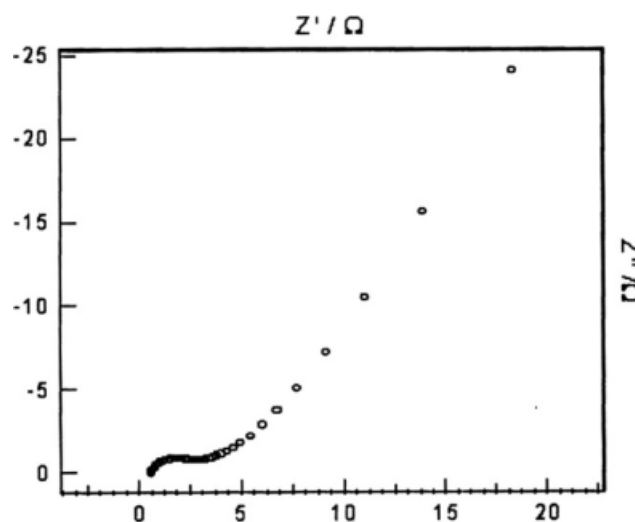


Figure 6 Impedance spectrum in the range 40 kHz to 10 mHz of PANI-PPy symmetric capacitor cell with potential of 0.22 V.

reflect the bulk properties of the electrolyte and the medium frequency region shows the impedance response of the charge transfer between the electrode and electrolyte. In the present work, the value of resistance observed for electrolyte, polymer electrode and charge-transfer resistance are 641 m Ω , 1.8 Ω , and 2.8 Ω respectively. A similar impedance analysis was reported by Carlberg and Inganas for poly(3,4-ethylenedioxythiophene) system.²⁶ Also, the in the high frequency (semicircle portion) can be attributed to double-layer charging/discharging process. The frequency corresponding to the maximum (f^*) of the imaginary component ($-z''$) in the semicircle yields the time constant τ as $\tau = (1/2 \pi f^*)$. PANI-PPy system showed τ value as 1.1×10^{-3} , 1.9×10^{-4} , 1.5×10^{-4} , 1.2×10^{-4} sec with the voltage 0.22, 0.43, 0.55, 0.78 V respectively, and this indicates fast charge-discharge characteristics. At low frequencies, the impedance is usually determined by the diffusion of ions in the polymer film, giving a linear behavior with a frequency independent phase angle of 45°. Impedance approaches a pure capacitive response with a phase angle of 90° directly. In the low frequency region, the slope of the impedance plots increases and tends to become purely capacitive (vertical line characteristic of a limiting diffusion process). The capacitance can be calculated from the following formula: $C = -(2\pi f z_{im})^{-1}$. The capacitance values for PANI-PPy system are calculated at 0.01 Hz frequency and found to be 57.3, 64.9, 46.7, 56 F/g with the voltage 0.22, 0.43, 0.55, 0.78 V respectively. A similar impedance analysis results was reported earlier for PANI salt coated on stainless steel by electrochemical polymerization.²⁷

CONCLUSIONS

Copolymer of aniline and pyrrole was synthesized by inverted emulsion polymerization method using emulsifier and protonic acid. The optimum reaction conditions for the preparation of copolymer with reasonably good yield (1.72 g) and conductivity (7.3×10^{-2} S/cm) were found to be aniline – 0.5 mL, pyrrole – 0.5 mL, BPO (5.8 g), SLS (3.0 g), *p*-TSA (3.84), time (24 h). The synthesis procedure was extended to prepare copolymer samples using various protonic acids such as HCl, H₂SO₄, NSA, BSA, MA, ClCH₂COOH. The value of specific capacitance, energy and power densities for poly(aniline-*co*-pyrrole)-*p*-toluenesulfonic acid system was found to be 21 F/g, 5.7 Wh/Kg and 100 W/Kg respectively with 98–100% coulombic efficiency. The specific capacitance of copolymer was found to be 22.8 F/g at

1 mV/s. scan rate from cyclic voltammetry and 57.3 F/g at 0.22 V from impedance measurement. Among the copolymer salts, copolymer prepared with sulfuric acid showed higher capacitance (66 F/g).

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