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Organic solvent soluble methyltriphenylphosphonium peroxodisulfate: A novel oxidant for the synthesis of polyaniline and thus prepared polyaniline in high performance supercapacitor

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ABSTRACT

Polyaniline samples are being prepared via chemical polymerization pathway of aniline in water medium. The aim of this work is to carry polymerization of aniline in organic solvent medium. Since the oxidant, methyltriphenylphosphonium peroxodisulfate (MTPPS), is soluble in acetonitrile solvent, aniline was oxidatively polymerized in the presence of *p*-toluenesulfonic acid with MTPPS via solution polymerization pathway (PANI-Sol). For comparison, polyaniline salt was synthesized via emulsion (PANI-Eml) and interfacial (PANI-Int) polymerization pathways. These three polymerization pathways lead the formation of polyaniline-p-toluenesulfonate salt (PANI-p-TSA) in acetonitrile solvent as green solution. Powder form of PANI-p-TSA was isolated from the solution form by precipitating with acetone solvent. Formation of polyaniline was confirmed from infrared and X-ray diffraction spectral results. PANI-Sol, PANI-Eml, and PANI-Int showed nanocrystal, nanopetals, and nanospheres morphology, respectively. The yield and the conductivity of the polyaniline salt prepared in the present study are comparable with those of the conventional polyaniline salt. Specific capacitance of the PANI-Eml, PANI-Sol, and PANI-Int were 460, 424 and 300 F g⁻¹, which was higher than the conventional PANI-p-TSA salt. Energy density was 23, 21.2, and 15 Wh kg⁻¹, respectively at a power density of 200 W kg⁻¹. After 2000 charge-discharge cycles, retention in the specific capacitance values of polyaniline salts was 70.4% (PANI-Sol), 73% (PANI-Eml) and 69.3% (PANI-Int).

Keywords: Polyaniline; Cationic oxidative template; Nanostructured morphology Supercapacitor; Electrochemical characteristics

Introduction

Electrochemical capacitors are a class of energy-storage devices that are able to run at a much higher power density than conventional batteries, at the cost of a considerably lower energy density. In the last decade, research in supercapacitor materials and electrolytes leading to improved energy storage capacities has been motivated by many existing and potential applications. One emerging application of supercapacitors is in electric/hybrid heavy and consumer automotive vehicles, which can use a high power device to supply a surge during startup and to convert the kinetic energy associated with vehicle braking into useful electricity.^{1,2} Conducting polymers as an electrode material in supercapacitor have been proved to be promising electrode materials.³ Among the family of conjugated conducting polymers, polyaniline (PANI) has attracted much attention because of its advantages, such as high conductivity, high electrochemical activity, excellent environmental stability, simple synthesis, controllable chemical and physical properties by the oxidation and protonation state.⁴⁻⁸

Many researchers have been performed with synthesized conducting polymers using Iron(III) salts,⁹ ammonium persulfate,¹⁰ hydrogen peroxide,¹¹ copper(II) salts,¹² potassium dichromate¹³ etc. The chemical oxidative polymerization of aniline in aqueous media is a widely used preparative method, mainly for its technical simplicity. In the literature, mostly water-soluble oxidizing agents are used to oxidize aniline to polyaniline salt. Our group prepared polyaniline salts in a carrier organic solvent via the emulsion & interfacial polymerization pathway by oxidizing aniline with benzoyl peroxide oxidant.¹⁴ Very recently, we have written a chapter on "Recent advances in the approach of polyaniline as electrode for supercapacitor", wherein we have covered the polyaniline materials for supercapacitor application.¹⁵

Our current research is directed towards the polymerization of aniline in organic solvent medium to polyaniline salts via solution, emulsion and interfacial polymerization pathways. These new grades of polyaniline salts are used as electrode materials in supercapacitor application.

Experimental

Materials and instrumentation

All chemicals were purchased from S. D. Fine Chemicals, India. Aniline is purified under reduced pressure. Methyltriphenylphosphonium bromide, ammonium peroxodisulfate were used as received. Solvents were distilled and used. Powder of polyaniline is pressed into a disk of 13 mm diameter and about 1.5 mm thickness under a pressure of 120 Kg/cm². Resistance of the pellet is measured by four probe method using Keithley constant source (Model-6220) and nanovoltmeter (Model-2182A) (Keithley, Cleveland, Ohio, USA). FT-IR spectra of polymer samples were registered on a FT-IR spectrometer (Thermo Nicolet Nexus 670, USA) using the KBr pressed pellet technique. X-ray diffraction profiles for polymer powders were obtained on a Siemens/D-500 X-ray diffractometer, USA using Cu K α radiation, and scan speed of 0.045°/min. Morphology studies (Micro structural and elemental analyses) of the polymer samples were carried out with a Hitachi S-4300 FE-SEM (Tokyo, Japan). The sample is 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. Thermo gravimetric analyses of polymer samples

were carried out using TA Instruments (TGA O500 V20.8, USA) from ambient to 700 °C under nitrogen atmosphere at a heating rate of 10 °C per minute. The electrochemical performances of all the polyaniline samples were investigated using two-electrode Swagelok-type cells without a reference electrode. The polymer sample electrode is fabricated using polyaniline sample (3 mg) on stainless steel mesh by the application of 120 kg/cm² of pressure. Two electrodes with identical polyaniline sample were assembled as supercapacitor and the electrolytic solution is 1 M H₂SO₄ and Cotton Cloth as a separator. Cyclic voltametry and galvanostatic charge-discharge experiments were carried out with a WonATech multichannel potentiostat/galvanostat (WMPG1000, GyeongGi-do, Korea). Cyclic voltammograms were recorded from -0.2 to 0.6 V at various sweep rates and charge-discharge experiments were carried out from 0 to 0.6 V at various current densities. Electrochemical impedance spectroscopy (EIS) measurements were carried out with IM6ex (Zahner-Elektrik, Germany) by applying an AC voltage of 5 mV amplitude in the 40 kHz-10 mHz frequency range at various voltages using three electrode cell configuration i.e., polyaniline salt as working electrode, platinum counter electrode and saturated calomel electrode (SCE) as reference electrode. All electrochemical measurements were carried out at ambient temperature. In this work, all the polymerization reactions are carried out at 25-30 °C and All electrochemical measurements are carried out at ambient temperature.

Synthesis of MTPPS

Methyltriphenylphosphonium peroxodisulfate (MTPPS) was synthesized as per the reported procedure.¹⁶ Aqueous solution of potassium peroxodisulfate ($K_2S_2O_8$) and methyltriphenylphosphonium bromide [C_6H_5)₂CH₃P⁺Br] (1:2 mole ratio) were mixed in a

beaker and stirred. A milky white precipitate formed immediately, indicating the complexation between cationic template and $K_2S_2O_8$. Precipitate (MTPPS) was filtered and washed with water. Sample was dried under vacuum.

Synthesis of polyaniline (PANI-Sol) by solution polymerization pathway

In a typical experiment, aniline (0.93 g, 0.1 M) was dissolved in 50 mL of acetonitrile solvent (CH₃CN). To this solution, 50 mL of CH₃CN solution containing 3.8 g (0.2 M) of *p*-toluenesulfonic acid (*p*-TSA) and MTPPS (1.8 g, 0.025 M) was added as a whole. The reaction mixture was stirred for 4 h. ambient temperature and then the resulting reaction mixture was poured in 250 mL acetone. The green precipitate was filtered, washed with an ample amount of CH₃CN, finally with 250 mL of acetone. The powder sample was dried at 50 °C in an oven until a constant weight.

Synthesis of polyaniline (PANI-Eml) by emulsion polymerization pathway

Polyaniline salt was synthesized by the above procedure except that aniline (0.93 g, 0.1 M) was dissolved in 50 mL of hexane instead of CH₃CN solution.

Synthesis of polyaniline (PANI-Int) by interfacial polymerization pathway

In a typical experiment, aniline (0.93 g, 0.1M) was dissolved in 50 mL of hexane solution. To this solution, 50 mL of CH₃CN solution containing *p*-TSA (3.8 g, 0.2 M) and MTPPS (1.8 g, 0.025 M). This acetonitrile solution was added drop by drop to hexane solution through the sides of the beaker without disturbing the reaction mixture. The reaction was carried out for 24 h. without stirring the reaction mixture. The product was isolated using the above procedure.

Results and discussion

Yield, conductivity and specific capacitance of polyaniline salts

In the chemical polymerization of aniline to polyaniline salts, generally polyanilines are being prepared in aqueous medium with water soluble oxidant, ammonium persulfate.¹⁰ In this work, aniline was oxidized to polyaniline salt by solution polymerization pathway in the presence of *p*-TSA using MTPPS as a novel oxidant in acetonitrile solvent (Scheme 1). Synthesis of polyaniline salt in organic solvent will be very useful for the preparation of conducting polyaniline blend with other insulting polymers via solution polymerization technique. Elements present in polyaniline salt were found out from Energy Dispersive X-ray Spectroscopic technique and showed the presence of elements such as carbon, nitrogen, oxygen and sulfur. The presence of sulfur element indicates that polyaniline salt consists of *p*-TSA dopant and absence of phosphorous element signposts that polyaniline salt does not contain phosphorus group. EDAX result suggests the formation of PANI-*p*-TSA salt in this polymerization pathway.



Scheme 1 Synthesis of polyaniline using MTPPS.

New Journal of Chemistry Accepted Manuscript

In order to find out a better PANI-*p*-TSA system, aniline was oxidized by solution polymerization pathway with increasing concentration of MTPPS. The value of yield, conductivity and specific capacitance from cyclic voltammogram was calculated and the results are reported in Table 1. Value of yield increases with increasing the concentration of oxidant and however, conductivity and capacitance decreases. This may be due to the formation of some amount of leucoemeraldine form. Conductivity and capacitance values are higher with the use of 0.025 M of MTPPS. Further, we focused mainly on three polymerization pathways for the preparation of PANI-*p*-TSA: solution (PANI-Sol), emulsion (PANI-Eml), and interfacial (PANI-Int) polymerization pathways using 0.025 M of oxidant and compared the properties of these systems with those of conventional PANI-*p*-TSA.

Yields of the polyaniline salts (with respect to the amount of aniline used in the reaction) prepared by solution, emulsion and interfacial polymerization pathways are 30, 24, and 10 wt.%, respectively and the values of conductivities are 4.1, 2.9, and 0.1 S cm⁻¹, respectively. The observation of lower yield and conductivity in the case of interfacial polymerization pathway compared to that of the aqueous and emulsion polymerization pathways is because the polymerization occurs at the interface between the two immiscible layers, which is a slow process.

Entry	MTPPS (M)	Yield (g)	Conductivity (S cm ⁻¹)	Cs at 10 mV s ⁻¹ (F g ⁻¹)
1	0.025	0.3	4.1	464
2	0.05	0.5	3.7	452
3	0.1	1.0	0.9	420

Table 1. Yield, conductivity, and specific capacitance of PANI-Sol.

Spectral and thermal characterization

Formation of polyaniline salt (PANI-*p*-TSA) prepared via an alternative polymerization pathway was confirmed from FT-IR spectra. Crystalline nature, morphology and thermal stability of the PANI-*p*-TSA salts were found out from XRD, FE-SEM and TGA measurements respectively and the results are discussed here.

FT-IR spectra of polyaniline salts

Fourier transform infrared spectra of the polyaniline salts prepared by solution, emulsion and interfacial polymerization pathway are shown in Fig. 1. FT-IR spectra of the three polyaniline salts show similar behaviors. As a representative system, PANI-Sol (Fig. 1a) shows major characteristic peaks at 3440 cm⁻¹ (N-H str.), 3200 cm⁻¹ (NH⁺- indicative of doping i.e. salt formation), 2925 cm⁻¹ (C-H str.), 1560 cm⁻¹ (C=C str., quinonoid ring), 1470 cm⁻¹ (C=C str., benzenoid ring), 1300 cm⁻¹ (C-N str., quinonoid ring), 1240 cm⁻¹ (C-N str., benzenoid ring), 1140 cm⁻¹ (N=Q=N vibration, where Q represents the quionoid ring), around 1030 cm⁻¹ (SO₃H group) and 810 cm⁻¹ (1,4-disubstituted benzene), which are very similar to that of the reported polyaniline salt.^{17,18}



Fig. 1 Infrared spectra of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int.

XRD studies of polyaniline salts

X-ray diffraction profile registered for the polyaniline salts prepared by solution, emulsion and interfacial polymerization pathway are shown in Fig. 2. XRD patterns of all three polyaniline salts show similar patterns. As a representative system, PANI-Sol (Fig. 2a) shows three clear peaks around $2\theta = 20$, 25 and 27 ° with corresponding d-spacing of 4.5, 3.5, and 3.3 indicates the semi crystalline nature, which are similar to that of the conventional polyaniline salt.¹⁹



Fig. 2 X-ray diffraction patterns of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int.

FE-SEM images of polyaniline salts

Polyaniline salt prepared by solution polymerization pathway (PANI-Sol) shows nanocrystals (400-500 nm of length and 200-500 nm of width) type morphology (Fig. 3a). Carrying out polymerization in mixture of solvent via emulsion polymerization pathway (PANI-Eml) resulted in petal like morphology (Fig. 3b) and this is changed to sponge nanospheres (400-500 nm diameter) morphology (Fig. 3c) when the reaction is carried out via interfacial polymerization pathway (PANI-Int) due to slow motion of

New Journal of Chemistry

formation of polyaniline. These morphologies are different from the conventional morphology (fibrillar type) of polyaniline-*p*-TSA salt.^{20,21}



Fig. 3 FE-SEM images of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int.

Thermal analysis of polyaniline salts

TGA of polyaniline salts are shown in Fig. 4. TGA thermogram shows two step weight loss processes, first step weight loss is due to moisture present on polyaniline sample and in the second step, and polymer undergoes degradation. Polyaniline salts undergo degradation in the order PANI-Sol (230 °C) > PANI-Eml (215 °C) > PANI-Int (190 °C).



Fig. 4 Thermograms of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int.

Cyclic voltammetric studies of polyaniline salts

Cyclic voltammograms were recorded for the polyaniline samples prepared by three polymerization pathways in symmetric cell configuration between -0.2 to 0.6 V at a scan rate of 10 mV s⁻¹ and are shown in Fig. 5. CV pattern shows almost rectangular shape, reveals the good capacitive behavior. This result implies that the diffusion of ions from the electrolyte can gain access to almost all sites of the electrode. Value of specific capacitance (Cs) was calculated with respect to mass of one electrode. Value of Cs for the polyaniline material prepared by emulsion polymerization pathway (484 F g⁻¹) was higher than that of the polyaniline prepared by solution (464 F g⁻¹) and interfacial (426 F g⁻¹) polymerization pathways. In the conventional polymerization of aniline to polyaniline salt with *p*-TSA by ammonium persulfate via aqueous polymerization pathway leads to the formation of polyaniline salt containing *p*-TSA dopant without impurities. This may be the reason for the superior rate ability of polyaniline-*p*-TSA prepared in the present work.



Fig. 5 CV curves of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int electrode materials in cell configuration at a scanning rate of 10 mV s⁻¹.

12

New Journal of Chemistry

Higher capacitance value was observed for polyaniline salt prepared by emulsion polymerization pathway. Hence, CV of the cell at various scan rates (1, 5, 10, 20, 30, 40, 50 and 100 mV s⁻¹) were carried with PANI-Eml material (Fig. 6) and the corresponding specific capacitance values were 564, 500, 484, 440, 430, 424, 406, and 356 F g⁻¹, respectively. At slower scan rates, the diffusion of ions from the electrolyte can gain access to almost all available materials of the electrode, leading to an effective insertion and de-insertion processes. However, when the scan rate is increased, the effective interaction between the ions and the electrode is reduced, and redox reaction has been limited to the outer surface of electrode; hence, a reduction in capacitance.²² A very important observation is that the curves at different scan rates show no peaks, indicating that the electrode is charged and discharged at a pseudo constant rate over the complete CV cycle or which imply rapid and reversible electrochemical processes. Another observation is that even with high scan rate at 100 mV s⁻¹, the shape of the CV curve still be maintained and this demonstrates high performance of the supercapacitor (Fig. 6).



Fig. 6 CV curves of PANI-Eml electrode material in cell configuration at scanning rates of (a) 1, (b) 5, (c) 10, (d) 20, (e) 30, (f) 40, (g) 50, and (h)100 mV s⁻¹.

Galvanostatic charge-discharge study of polyaniline salts

Charge-discharge behavior is one of the important characteristics for the practical application of supercapacitor. Galvanostatic charge–discharge experiment was performed for the three polyaniline salts. Fig.7 shows the typical charge–discharge plots for the polyaniline electrode at constant specific current density of 0.3 A g^{-1} .



Fig. 7 Charge-discharge curve of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int electrode materials in cell configuration at a current density of 0.3 A g^{-1} .

The values of discharge specific capacitance, energy and power densities were calculated. C_d of the PANI-Eml (460 F g⁻¹) was higher that of the samples PANI-Sol (424 F g⁻¹) and PANI-Int (300 F g⁻¹). Energy density was 23, 21.2, and 15 Wh kg⁻¹, respectively at a power density of 200 W kg⁻¹. Sample prepared by emulsion polymerization pathway was subjected for higher charge-discharge rates and the values are reported in Table 2. The results show that the sample withstands even at higher charge-discharge rate of 1.6 A g⁻¹.

Specific Current Density (A g ⁻¹)	$\begin{array}{c} C_{d} \\ (F g^{-1}) \end{array}$	Energy Density (Wh kg ⁻¹)	Power Density (W kg ⁻¹)	
0.2	460	22.0	200	
0.3	460	23.0	200	
0.6	424	21.2	400	
1.0	414	20.7	600	
1.6	366	18.3	1000	

Table 2. Specific capacitance, energy density and power density at various chargedischarge current densities for PANI-Eml cell system.

Literature reports on the electrochemical performances of PANI-*p*-TSA salts are given in in Table 3 for comparison with the present result. Electrochemical performance of PANI systems are generally carried out for single electrode configuration. However, for practical application, it is necessary to carry out the electrochemical performance of two electrodes cell system. Specific capacitance of PANI-*p*-TSA supercapacitor cell obtained in the present study (460 F g⁻¹) is found to be higher than that of the value (405 F g⁻¹) reported by Sangaranarayanan et al.²⁵ via electrochemical polymerization pathway. However, higher amount of PANI salt cannot be prepared via electrochemical polymerization methods.

Table 3. Literature report on PANI-*p*-TSA based supercapacitor systems.

Synthesis Method	Substrate	Electrode assembly	CV/ CD	Cs (F g ⁻¹)	ED (W kg ⁻¹)	PD (W kg ⁻¹)	Reference
Chemical	Graphite	3	CV	314	-	-	18
Electrochemical	SS	3	CV	431	-	-	23
Solid-state	Graphite	3	CV	593	-	-	24
Electrochemical	Ni	3	CD	405	-	-	25
Chemical	SS	2	CD	460	23	200	This work

The cycle stability for the symmetric supercapacitor cell for the three polyaniline samples in 1 M aqueous H_2SO_4 electrolyte was evaluated by galvanostatic chargedischarge measurement at a current density of 0.3 A g⁻¹ in the potential range between 0 and 0.6 V for 2000 cycles. Retention in specific capacitance of polyaniline salts was 70.4% (PANI-Sol), 73% (PANI-Eml), and 69.3% (PANI-Int), respectively (Fig. 8). After 2000 cycles, the capacitance retention ratio still reaches about 69-73%, indicating high cycling stability of the nanostructured polyaniline electrode. Conductive polymersupercapacitor electrodes often suffer from cycle degradation issues caused by mechanical problems, such as swelling and shrinking, during the doping-dedoping process. A similar behavior was observed by Lokhande et al. for the system, PANI-H₂SO₄ salt.²⁶



Fig. 8 Specific capacitance with cycle number for cell consisting of symmetric samples of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int at 0.3 A g⁻¹ current density.

Electrochemical impedance spectroscopy study of polyaniline salts

EIS experiment was carried for the polyaniline samples in the frequency range from 40 kHz–10 mHz at an applied voltage of 0.7 V (Fig. 9) and the EIS parameters are reported in Table 3. The value of solution resistance for all the samples was in the range of 0.9-1.2 Ω indicating the good conductivity of the electrolyte and very low internal resistance of the electrode. The value of time constant was in the range of 0.6 to 3.0 ms. The value of charge-transfer resistance is the main part of resistance of the supercapacitor. The value of charge transfer resistance was in the range of 2.0 to 8.3 Ω suggests high in electrical conductivity and fast response ability of the electrode. Very low value of R_s, R_{ct}, C_{dl} and τ obtained as 0.9 Ω , 2.0 Ω , 0.6 mF and 0.6 ms indicating fast charge-discharge process, low ESR and high electrical conductivity of the electrode/electrolyte. The value of capacitance obtained at 10 mHz frequency for an applied voltage 0.7 V was in the order: PANI-Eml (386 F g⁻¹) > PANI-Sol (281 F g⁻¹) > PANI-Int (146 F g⁻¹).

Table 3. Solution resistance (R_S), charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) time constant (τ) and specific capacitance (C_S) for polyaniline samples at 0.7 V.

Sample	$R_{s}\left(\Omega\right)$	$R_{ct}(\Omega)$	C_{dl} (mF)	τ (ms)	Cs at 10mHz (F g ⁻¹)
PANI-Sol	1.2	6.2	0.1	1.2	281
PANI-Eml	0.9	2.0	0.1	0.6	386
PANI-Int	1.0	8.3	0.2	3.0	146

Bode plots of frequency versus phase angle for polyaniline samples carried with an applied voltage of 0.7 V are shown in Fig.9 (inset). The value of phase angle at 10 mHz were PANI-Eml (65 °), PANI-Sol (65 °) and PANI-Int (54 °). Ideal supercapacitor

New Journal of Chemistry Accepted Manuscript

gives a phase angle value of 90 $^{\circ}$ and less than 90 $^{\circ}$ shows deviation from ideal capacitor behavior. In the present study, greatest phase angle observed was around 65 $^{\circ}$.



Fig. 9 Impedance spectra in the range 40 kHz to 10 mHz of (a) PANI-Sol, (b) PANI-Eml and (c) PANI-Int at 0.7 V applied potential (inset Phase angle Vs frequency).

Conclusions

Aniline was successfully polymerized in organic solvent using solvent soluble oxidizing agent, methyltriphenylphosphonium peroxodisulfate, for the first time. A systematic and careful electrochemical test was carried out to deeply investigate its potential application for supercapacitor. Among the three polymerization pathways, PANI-Eml showed a higher performance with a capacitance value (460 F g⁻¹), energy density (23 Wh kg⁻¹) and power density of 200 W kg⁻¹ at 0.3 A g⁻¹ current density. After 2000 charge-discharge cycles, retention in the specific capacitance value of polyaniline salt was 73%. Moreover, this methodology will be very useful for the preparation of conducting polyaniline blend with other insulting polymers via solution polymerization technique.

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New Journal of Chemistry

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GRAPHICAL ABSTRACT

Organic solvent soluble methyltriphenylphosphonium peroxodisulfate: A novel oxidant for the synthesis of polyaniline and thus prepared polyaniline in high performance supercapacitor

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Nanostructured polyanilines are successfully prepared using novel oxidant for high performance pseudocapacitor. Methodology will be useful for conducting polyaniline blends.

