CHAPTER - IV

RESULTS AND DISCUSSION

In this chapter, the surfactant assisted dilute polymerization method is adopted for the synthesis of polythiophene with various acid dopants such as tartaric acid (TA), citric acid (CA), $p$-toluene sulphonic acid ($p$-TSA) and anthraquinone sulphonic acid (AQSA) are discussed in detail. Physical and electrochemical properties for supercapacitor applications are also presented.

4.1. SYNTHESIS OF PTh NANOPARTICLES

Polythiophene (PTh) nanoparticles were prepared by surfactant-assisted dilute polymerization method. The polymerization process was initiated by the addition of ferric chloride to the surfactant dispersed thiophene (monomer) solution. When ferric chloride was added, a heavy floccular precipitate instantly appeared, due to electrical neutralization of quaternary ammonium cation of the CTAB and Cl$^-$ of ferric chloride. This surfactant misceller stabilized the droplets against the collision and affected the distribution of the reactants, which altered the course of thiophene polymerization by forming micelle-water interface in this system. This was similar to the organic aqueous interface in interfacial polymerization.
4.1.1. FTIR ANALYSIS

The synthesized polymer powder was confirmed by spectral studies. FTIR spectrum of thiophene and polythiophene are given as Figure 4.1 (a & b). Thiophene spectrum (Figure 4.1.a) showed the aromatic ring characteristic bands, they were (C-H) stretching vibration band at 3089 cm\(^{-1}\); (C=C) stretching band at 1411-1580 cm\(^{-1}\); in-plane bending band at 1036-1080 cm\(^{-1}\); C-H out of plane bending band at 839 cm\(^{-1}\) and (C-S) bending band at 714 cm\(^{-1}\) [1]. The band 830 cm\(^{-1}\) was assigned to (C-S) stretching vibration [2].

The FTIR spectrum of polythiophene (Figure 4.1.b) showed the (C-H) stretching vibration band at 2923 cm\(^{-1}\); (C=C) stretching band at 1458-1596 cm\(^{-1}\); C-H in plane bending band shifted to 1113 cm\(^{-1}\); and (C-S) bending band shifted to 749 cm\(^{-1}\). The doping induced band at 1021 cm\(^{-1}\), was originating from the changes in the conjugated backbone due to the electron withdrawing and electron donating dopants on the polymer chain and the counter ion balancing appeared at 1113, 1309 and 1458 cm\(^{-1}\) [3-5]. The large descending base line in the spectral region of 4000-2000 cm\(^{-1}\) was attributed due to free–electron conduction in the doped polymer. This type of behaviour was not observed in undoped polymer [6]. The increasing conjugation shifted the absorption frequencies of the polymer. These results also supported the polymerization.

4.1.2. UV-VISIBLE ANALYSIS

The UV-Visible absorption spectrum of polythiophene was recorded by using DMSO solvent is shown as Figure 4.2. The main charge carriers in
polythiophene were polarons and/or bipolarons [7]. A new broad absorption band related to bipolaron states appeared around 730-890 nm. The absorption bands were obtained approximately at 306 and 377 nm. The band at 306 nm was associated with the $\pi$-$\pi^*$ interband transition and band at 377 nm was $n$-$\pi^*$ transition, as in the case of other polythiophene homopolymer [8]. Increasing the degree of polymer resulted in a blue shift of $\lambda_{\text{max}}$, confirmed a shorter conjugation length of the polymer [9].

4.1.3. X–RAY DIFFRACTION ANALYSIS

X-ray diffraction study was used to find out the phase purity of PTh (Figure 4.3). There was a partially crystalline broad peak centered at near $2\theta$ value of 22.2°. The strong diffraction peak associated with the chain–to-chain stacking distance of about $2\theta$=22.2° is attributed to both amorphously packed polythiophene main chains [10, 11].

4.1.4. SEM STUDIES

SEM photograph of PTh nanoparticles is shown as Figure 4.4. It can be seen from the photograph that the granular morphology was observed and the average particle size was found to be in the range of 25-45 nm. The image indicated the formation of porous structured PTh. The electrolyte intercalation was much pronounced in this porous structured electrode material.
Fig. 4.1. FTIR spectrum of (a) pure thiophene (b) polythiophene nanoparticles
Fig. 4.2. UV-Visible absorption spectrum of PTh nanoparticles
Fig. 4.3. X-ray diffraction pattern of PTh nanoparticles
Fig. 4.4. SEM photograph of PTh nanoparticles
This kind of surface morphology was ideal for the fabrication of electrode as it would have high surface area and expected to good capacitance.

4.1.5. CONDUCTIVITY MEASUREMENTS

Electrical conductivity measurements were made for the pelletized polythiophene using a four-probe method at 30 °C. The conductivity of polythiophene was found about 0.67 S/cm. This result was comparable with previously reported polythiophene synthesized by FeCl₃ oxidative polymerization [13-17]. The conductivity can be expressed as $\sigma = ne\mu$ ; where ‘e’ is electron charge, ‘n’ is the density of charge carrier and ‘$\mu$’ is the mobility of charge carrier. Thus the doping efficiency depended on the density and mobility of the charge carriers instead of degree of doping alone.

4.1.6. CYCLIC VOLTAMMETRY STUDIES

The capacitors were constructed by polythiophene based symmetric electrodes with PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF₆ in EC/PC (1:1 v/v). The scanning was performed in the voltage range of −1.0 to +1.0 V at various scan rates of 5, 10, 25, 50 and 100 mVs⁻¹ for the capacitor cell (Figure 4.5). The specific capacitances of the capacitor cell were calculated at the scan rates of 5, 10, 25, 50 and 100 mV/s and were approximately 134, 93, 54, 39 and 28 F/g, respectively.
4.5. Cyclic voltammograms of PTh/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1 v/v) /PTh at the sweep rates of a) 5 mV/s, b) 10 mV/s, c) 25 mV/s, d) 50 mV/s and e) 100 mV/s
4.6. Cyclic voltammograms of PTh/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v) /PTh at the sweep rate of 50 mV/s in 5ᵗʰ and 1000ᵗʰ cycles
Specific capacitance as a function of scan rate for PTh/PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh supercapacitor
4.8. Capacitive current as a function of scan rates for PTh/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh supercapacitor
The rectangular form of the voltammogram in which current quickly reached a true horizontal value after the reversal of voltage sweep was seen, if the electrode/electrolyte interface forming the double layer was homogeneous and ideally polarizable. There was an enhanced delay of current to reach a horizontal value, due to the enhancement of distributed capacitance effects in porous electrodes upon increasing the voltage sweep rate. The ohmic resistance in the electrolyte along the axial direction of the micropores of electrode had the effect to charge or discharge faster. Lowering of current would reduce the potential difference resulting from the ohmic resistance between the surface and bottom of the micropores. The potential difference intensified the lag of charge or discharge at the bottom of the micropores and thus enhanced the delay of the currents to reach a horizontal value in the voltammogram.

To investigate the cyclic stability of the system, cyclings (1000 cycles) were carried out at the scan rate of 50 mVs\(^{-1}\) are shown as Figure 4.6. The decaying of current was observed in minimum between 5\(^{th}\) and 1000\(^{th}\) cycles; this ensured that the small capacitance fading of the electrode material. The stability of the electrode material was found as almost moderate.

Ion rearrangement in the redox was not as fast as the rate of potential change (i.e. scan rate) due to microporous nature of the polythiophene. This was especially true for the inner surface area of micropores, which was not freely accessible for solvated ions. Thus these inner surface areas did not completely provide the redox capacitance of higher scan rates of CV.
The discharge capacitance decreased significantly with increasing scan rate up to 50 mVs\textsuperscript{-1} (Figure 4.7) is due to the resistance in the system. This caused a delay the time required to discharge the capacitor [18]. In the PTh/MWCNT composite electrode, the resistance was related to two main factors, namely, the transition of the conducting polymer to an isolated state during the discharge process and the isolating capacity of the template matrix (MWCNT porous structure). The exact time required to discharge the capacitor depended on the resistance (R) and the capacitance (C) in the discharging system.

Above 50 mVs\textsuperscript{-1}, the decreasing of specific discharge capacitance was not so pronounced. The porous structure on the composite allowed a higher swelling of PTh by the electrolyte solution and the formation of parallel ionic and electronic conduction paths. This phenomenon also contributed to maintain the capacitive nature of the composite, despite the increase in scan rate.

The charging currents for both the anode (I\textsubscript{a}) and cathode (I\textsubscript{c}) increased with scan rate. The difference between I\textsubscript{a} and I\textsubscript{c} at current plateaus of the cyclic voltammogram was designed as charging current ($\Delta$I=I\textsubscript{a}-I\textsubscript{c}) and it was plotted against scan rate (Figure 4.8). The capacitance and faradaic current were obtained from the slope and intercept of the graph between $\Delta$I vs scan rate and the values were 2.3 mF and 0.062 mA, respectively.
4.1.7. AC IMPEDANCE STUDIES

In the Nyquist impedance plot, the imaginary part of impedance was plotted as a function of the real component in the frequency range from 10 mHz to 100 kHz. The impedance plot of polythiophene based symmetric redox supercapacitor with PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF₆ in EC/PC (1:1 v/v) electrolyte is shown as Figure 4.9. A non-ideal behaviour of the capacitor was seen; this should be noted that an ideal impedance response from pure capacitor is a straight line parallel to the imaginary axis. The small semicircle at high frequency might be due to diffusion effect of the electrolyte in the electrodes [19-22]. The high frequency impedance associated with the bulk electrolyte resistance and this value was 19 Ω and the mid frequency of spectrum revealed the electrode/electrolyte interface processes. The charged state of impedance response showed the interface affected state, which was caused by diffusion problems indicated by the increase in the internal resistance.

The non-vertical slope of the impedance plot at low frequency of electrochemical capacitor was due to: 1) the micro porosity and redox properties of polythiophene; 2) the low mobility of the ions inside the electrode or the combination of both. The decrease in charge transfer resistance with increasing double layer capacitance confirmed that the redox capacitor using PVdF-co-HFP based microporous polymer electrolyte had good cycle life and low self discharge time (time constant). The charge transfer resistance of the cell was found to be
2.2 $\Omega$ and the specific capacitance was calculated from the impedance spectrum at 10 mHz and it was 124 F/g.

4.1.8. CHARGE-DISCHARGE STUDIES

Galvanostatic charge-discharge experiment was performed to PTh based symmetric redox supercapacitor. The PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF$_6$ in EC/PC (1:1 v/v) acts as electrolyte and separator for the fabrication of capacitor. The charge/discharge process was carried out at a constant current density of 1 mAcm$^{-2}$ upto 2 V of potential limit.

In the charge/discharge profile (Figure 4.10), the charging curves were not exact symmetrical to the discharging curves. This implied that PTh electrode had small lacking of electrochemical reversibility and capacitive characteristics. During the experiments, the amount of charges stored in the capacitor was determined by integrating the current during charge and discharge time. At low discharge potential response of the capacitor approached an ideal linear charge voltage relationship. At higher values of potential the total impedance of the cell gave rise to an initial ohmic drop of the discharge voltage which remained till constant capacitive performances were achieved. However, the initial decrease in capacitance was related to the irreversible charge compensation in faradaic reaction associated with the oxidation/reduction of PTh. The initial sharp change in potential with time, during charging and discharging process was due to the ohmic loss which arose from the internal resistance of the cell. The pseudocapacitance displayed typical charge/discharge performance with small
Fig. 4.9. Impedance spectrum of PTh / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh supercapacitor
Fig. 4.10. Charge and discharge curves of PTh/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh supercapacitor at the constant current density of 1mA/cm$^2$. 
Fig. 4.11. Discharge capacitance as a function of cycle number for PTh/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh supercapacitor
Fig. 4.12. Columbic efficiency and internal resistance as a function of cycle number for PTh/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v)/PTh supercapacitor
discharge capacitance at the working voltage of 2V. The power density was
evaluated by dividing the energy density by discharge time [23]. The observed
ohmic resistance at the potential switching point. To avoid IR drop effect in the
discharge capacitance, the slope was calculated after the IR drop portion of
discharge curve. The capacitance obtained from AC impedance measurements
was lower than charge-discharge measurements, as it was measured at zero
potential of charge and the potential amplitude was also very small (5-10 mV).
This is mainly due to the diffusion of ions in the microporous polymer electrolyte.
The values of the discharge capacitance \((C_m)\) and internal resistance \((R_i)\) of the
capacitor were calculated as 130 Fg\(^{-1}\) and 10.2 Ω cm\(^2\), respectively. The values
of energy and power densities of the capacitors were calculated from the
energy density and power density values were 8 WhKg\(^{-1}\) and 396 W Kg\(^{-1}\),
respectively. In these curves after initial drop in capacity over the first 500 cycles,
there was a slow deterioration in the performance during the cycle period and
over 1000 of continuous cycles. The device provided up to 94 % of the initial
capacitance (Figure 4.11), after 1000 cycles. The coulombic efficiency is the ratio
of charging time to the discharging time. This important parameter was
associated with charge/discharge behaviour of the supercapacitors. The
coulombic efficiency and the internal resistance as the function of the cycle
number are shown in Figure 4.12. The internal resistance increased with cycle
number and the coulombic efficiency was calibrated to 94 %.
4.2. SYNTHESIS OF PTh-TA NANOPARTICLES

Polythiophene–tartaric acid (PTh-TA) nanoparticles were prepared by surfactant-assisted dilute polymerization method by the addition of ferric chloride oxidant to the surfactant (CTAB) dispersed thiophene solution. When ferric chloride was added, a heavy floccular precipitate instantly appeared and the reaction mixture was turned into brownish tint and the colouration became pronounced as polymerization proceeded. This surfactant misceller stabilized droplets against the collisions and affected the distribution of reactants, which altered the course of thiophene polymerization by forming micelle-water interface in this system. As the reaction proceeded, the colour of the organic phase became darken. It could be similar to the organic aqueous interface in interfacial polymerization.

4.2.1. FTIR STUDIES

FTIR spectrum of PTh-TA is shown as Figure 4.13. The $\pi$–electrons and lone pair electrons of TA doped PTh proved the aromatic character by the following absorption peaks; the (C-H) stretching vibration band at 3060 cm$^{-1}$; (C=C) stretching vibration band at 1419-1558 cm$^{-1}$; (C-H) in plane bending band shifted to 1143 cm$^{-1}$ and (C-S) bending band shifted to 793 cm$^{-1}$. The carbonyl group of tartaric acid identified by the band at 1680 cm$^{-1}$. The band at 1077 cm$^{-1}$ denotes (O-H) bending. The band at 2850 and 2921 cm$^{-1}$ showed the (C-H) stretching. The large descending base line in the spectral region of 4000-2000
cm$^{-1}$ is due to free–electron conduction in the doped polymer. This type of behaviour was not observed in undoped polymer [6].

4.2.2. UV-VISIBLE STUDIES

The UV-Visible absorption spectrum of PTh-TA was observed using DMSO solvent is shown as Figure 4.14. The absorption bands were obtained at ~294 and 375 nm. The first absorption band at 294 nm peak was associated with the $\pi-\pi^*$ interband transition and band at 375 nm was $n-\pi^*$ transition as in the case of other polythiophene homopolymer [8]. Polymers showed a maximum of absorption at 250 to 450 nm that could be related to a quite highly conjugated backbone. Increasing the tartaric acid doping in the polymer resulted in a blue shift of $\lambda_{\text{max}}$, implying a shorter conjugation length of the polymer [9]. In the doped state, polymer exhibited a maximum of absorption at 650 to 800 nm.

4.2.3. X–RAY DIFFRACTION ANALYSIS

X-ray diffraction study of PTh-TA was performed by powder XRD method (Figure 4.15). The diffractogram showed the similarity to that of PTh structure. A small broad peak was observed at 2$\theta$ value of 24.2° for the synthesized polymer. This is due to scattering with momentum transfer approximately perpendicular to the polythiophene chain. By examining this pattern at wider angles, the strong diffraction peak associated with the chain–to-chain stacking distance of 2$\theta$=24.2° was inferred.
Fig. 4.13. FTIR spectrum of PTh-TA nanoparticles
Fig. 4.14. UV-Visible absorption spectrum of PTh-TA nanoparticles
4.2.4. SEM STUDIES

The surface morphology of PTh-TA powder is shown as Figure 4.16. The particles were almost uniformly distributed with spherical morphology with the average particle size in the range of 30-45 nm. The porous structured of PTh-TA surface was seen. This kind of electrode material was much pronounced with electrolyte intercalation.

4.2.5. CONDUCTIVITY MEASUREMENT

Electrical conductivity measurements were performed on PTh-TA by four-probe method at 30°C. This study was carried at average of ten different points on the pellet. The intrinsic electrical conductivity of the PTh-TA was found to be 0.77S/cm. This result was comparable with previously reported polythiophene synthesized by FeCl$_3$ oxidative polymerization methods.

4.2.6. CYCLIC VOLTAMMETRY STUDIES

The cyclic voltammograms of polythiophene-tartaric acid (PTh-TA) based symmetric redox supercapacitor using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF$_6$ in EC/PC (1:1 v/v) is shown as Figure 4.17. The optimized potential limit of –1.0 to +1.0 V was used for various scan rates of 5, 10, 25, 50 and 100 mVs$^{-1}$. The specific capacitances of the capacitor cell were calculated by standard formula and the values were 156, 140, 80, 46 and 35 F/g, at the scan rates of 5, 10, 25, 50 and 100 mV/s, respectively.
Fig. 4.15. X-ray diffractogram of PTh-TA nanoparticles
Fig. 4.16. SEM photograph of PTh-TA nanoparticles
Increasing the sweep rate enhanced the delay of current to reach a horizontal value (Figure 4.17). This was due to the enhancement of the distributed capacitance effects in porous electrodes with increasing sweep rate. The slope of the current plateau increased with the sweep rate. An increase in the voltage sweep rate increased the potential difference and intensified the lag of charge or discharge at the bottom of the micropores and thus enhanced the delay of the currents to reach a horizontal value in the voltammogram. To investigate the cyclic stability of the system, cycling (1000 cycles) was done at a scan rate of 50 mVs\(^{-1}\) (Figure 4.18). The defect in current was observed in minimum quantity between 5\(^{th}\) and 1000\(^{th}\) cycles, suggesting that the electrode material was stable.

The ion rearrangement in the redox behaviour was not as fast as the rate of potential change (i.e. scan rate) due to the pores nature of polythiophene-tartaric acid. This is especially true for the inner surface area of micropores not freely accessible for solvated ions. These inner surface areas do not completely provide the redox capacitance at higher scan rates of CV, resulting insignificant decrease in specific capacitance for all pseudocapacitance (Figure 4.19). On the other hand, the comparison of all scan rates with respect to specific capacitances revealed that the decrease was at 5 mV/s > 10 mV/s > 25 mV/s > 50 mV/s > 100 mV/s. The capacitance decreased remarkably with increasing scan rate up to 50 mVs\(^{-1}\) is mainly due to the resistance of the system caused by delay in time required to discharge the capacitor [18]. The porous nature of electrode would have higher swelling with electrolyte, leading to parallel ionic and electronic conduction paths.
4.17. Cyclic voltammograms of PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1 v/v) /PTh-TA at the sweep rates of a) 5 mV/s, b) 10 mV/s, c) 25 mV/s, d) 50 mV/s and e) 100 mV/s
4.18. Cyclic voltammograms of PTh-TA/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v) /PTh-TA at the sweep rate of 50 mV/s in 5th and 1000th cycles
4.19. Specific capacitance as a function of scan rate for
PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh-TA supercapacitor
4.20. Capacitive current as a function of scan rates for PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1 v/v)/PTh-TA supercapacitor
The difference in anodic and cathodic peak currents (\(\Delta I = I_a - I_c\)) were measured for each scan rate is shown as Figure 4.20. Here, \(\Delta I\) value increased significantly with the scan rates. The capacitance and faradaic current were calculated from slope and intercept of the plot, and were 15.6 mF and 0.45 mA, respectively.

4.2.7. AC IMPEDANCE STUDIES

The impedance spectrum of symmetric redox supercapacitor of PTh-TA based cell was carried out at the frequency range of 10 mHz to 100 kHz (Figure 4.21). This impedance spectrum (Nyquist plot) proved a capacitor-like behaviour with small diffusion limitations. The internal resistance (\(R_i\)) was evaluated from the impedance curve intercept at the real axis of high frequency region, and it was 7 \(\Omega\). A semicircle was observed at middle frequency region, revealing charge transfer resistance and it was 1.7 \(\Omega\). The specific capacitance was calculated at 10 mHz and it was 154 F/g.

4.2.8. CHARGE-DISCHARGE STUDIES

TA doped PTh electrode material was tested for galvanostatic charge-discharge study and the symmetric redox supercapacitor is shown as Figure 4.22. The current density of 1 mAcm\(^{-2}\) was applied to the voltage limit of 2 V. The profile of charge curves of each experiment was not exactly symmetrical to that of discharge curves. During the experiments, the amount of charge stored in the capacitor was calculated by integrating the current during charge and discharge
time. At low discharge curve, the response of capacitor approached the ideal linear charge voltage relationship. At higher values of potential curve, the total impedance of the cell gave rise to an initial ohmic drop of the discharge voltage which remained constant till capacitive performance was achieved. The initial sharp change in potential with time, during charging and discharging processes was due to an ohmic loss, which arose from the internal resistance of the cell. The discharge capacitance was calculated from the slope of the discharge curve. The capacitance measured from charge-discharge measurements is mainly due to ions diffusion in the microporous polymer electrolyte with the electrodes. The discharge capacitance and internal resistance ($R_i$) values of the capacitor were calculated as $152 \text{ Fg}^{-1}$ and $6.2 \text{ }\Omega\text{ cm}^2$, respectively. A small capacity fading was found over 1000 cycles by small deterioration in the performance during the cycles. The device provided upto 96 % of the initial capacitance (Figure 4.23). The energy density was calculated from the discharge capacitance at the working voltage of 2 V. The power density was evaluated using the ratio between energy density to the discharge time of capacitor [23]. The calculated energy density and power density values were $14 \text{ Wh Kg}^{-1}$ and $522 \text{ WKg}^{-1}$, respectively. The variation of the coulombic efficiency was calculated by the ratio of charging and discharging time. The coulombic efficiency and the internal resistance as a function of cycle number were plotted (Figure 4.24). The internal resistance increased and the coulombic efficiency decreased with cycle number.
Fig. 4.21. Impedance spectrum of PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh-TA supercapacitor
Fig.4.22. Charge and discharge curves of PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh-TA supercapacitor at the current density of 1mA/cm$^2$
Fig. 4.23. Discharge capacitance as a function of cycle number for PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh-TA supercapacitor
Fig. 4.24. Columbic efficiency and internal resistance as a function of cycle number for PTh-TA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) /PTh-TA supercapacitor
4.3. SYNTHESIS OF PTH-CA NANOPARTICLES

Polythiophene–citric acid (PTh-CA) nanoparticles were prepared by surfactant-assisted dilute polymerization pathway without using any organic solvents. Thiophene was oxidized to polythiophene in presence of cationic surfactant (CTAB) with dopant. When Ferric chloride was slowly added to the surfactant (CTAB) dispersed monomer solution, a heavy floccular precipitate instantly appeared, due to electrical neutralization of quaternary ammonium cation of the CTAB and Cl⁻. During the progress of the reaction, the colourless emulsion turned into brown. This surfactant misceller stabilizes droplets against the collision and affect the distribution of reactants, which altered the course of thiophene polymerization by forming micelle-water interface in this system, could be similar to the organic aqueous interfacial polymerization. As the reaction proceeded, the colour of the organic phase became darken and finally stopped changing, indicating reaction was completed.

4.3.1. FTIR STUDIES

The FTIR spectrum is shown as Figure 4.25. The aromatic characteristics of PTh-CA was described as follows; (C-H) stretching vibration band at 3065 cm⁻¹; (C=C) stretching band at 1415 cm⁻¹; C-H in plane bending band shifted to 1145 cm⁻¹; and (C-S) bending band shifted to 798 cm⁻¹. The carbonyl group of citric acid identified by the band at 1676 cm⁻¹. Band at 1071 cm⁻¹ proved the (O-H) bending; the band at 2851 and 2922 cm⁻¹ showed the (C-H) stretching. The large descending base line in the spectral region of 4000-2000 cm⁻¹ is attributed due to
free–electron conduction in the doped polymer; increasing of conjugation led to shift the absorption frequency of monomer.

4.3.2. UV-VISIBLE STUDIES

UV-Visible absorption spectral study by using DMSO solvent is shown as Figure 4.26. The absorption peaks were observed at approximately 265 and 380 nm. The peak at 265 nm was associated with the $\pi-\pi^*$ interband transition and band at 380 nm was $n-\pi^*$ transition as in the case of other polythiophene homopolymer. The highly conjugated backbone resulted with maximum of absorption at the range of 250 to 450 nm. Increasing the degree of citric acid doped polymer resulted in a blue shift of $\lambda_{\text{max}}$, implying a shorter conjugation length of the polymer. In the doped state, polymers exhibited a maximum of absorption at 650 to 800 nm.

4.3.3. X–RAY DIFFRACTION ANALYSIS

The crystalline purity of PTh-CA was examined by powder XRD analysis (Figure 4.27). The X-ray diffractogram of PTh-CA sample showed, a partially crystalline peak was centered near the 2θ value of 23.1°. A strong diffraction peak associated with the chain–to-chain stacking distance of about $2\theta=23.1^\circ$ was inferred.

4.3.4. SEM STUDIES

The surface morphology of PTh-CA was measured by scanning electron microscope analysis (Figure. 4.28). It has regular spherical morphology with
Fig. 4.25. FTIR spectrum of PTh-CA
Fig. 4.26. UV-Visible absorption spectrum of PTh-CA nanoparticles
Fig. 4.27. X-ray diffractogram of PTh-CA nanoparticles
Fig. 4.28. SEM image of PTh-CA nanoparticles
nano-porous structured surface and the average particle size was found to be in the range of 25-35 nm.

**4.3.5. CONDUCTIVITY MEASUREMENT**

Electrical conductivity measurements by four-probe method at 30 °C were carried out for PTh-CA electrode material. The electrical conductivity of the synthesized polymer was found about 0.72 S/cm and the value was comparable with previously reported PTh samples by FeCl₃ oxidative polymerization [13-17]. The doping efficiency was depended on density and mobility of the charge carriers instead of degree of doping alone.

**4.3.6. CYCLIC VOLTAMMETRY STUDIES**

Cyclic voltammograms for PTh-CA based symmetric redox supercapacitor using PVdF-co-HFP based polymer electrolyte containing 1M LiPF₆ in EC/PC (1:1 v/v) at different scan rates are shown as Figure 4.29. The optimized potential limit was applied to the capacitor cell, in order to determine the maximum operational voltage of the capacitor. There was absence of peaks and the presence of oxidative-reductive processes in this potential range (0-2 V). Almost rectangular like shapes similar to that of typical capacitor are observed at low scan rates (5-25 mV/s) indicating that charge-discharge reversibility occurred at electrode/electrolyte interface. The specific capacitances of the capacitor cell was calculated at the scan rates of 5, 10, 25, 50 and 100 mV/s and were approximately 149, 121, 89, 57 and 45 F/g, respectively.
4.29. Cyclic voltamograms of PTh-CA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v)/PTh-CA at the sweep rates of a) 5 mV/s, b) 10 mV/s, c) 25 mV/s, d) 50 mV/s and e) 100 mV/s
4.30. Cyclic voltammograms of PTh-CA/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v)/PTh-CA at the sweep rate of 50 mV/s in 5th and 1000th cycles
4.31. Specific capacitance as a function of scan rate for PTh-CA/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v)/PTh-CA supercapacitor
4.32. Capacitive current as a function of scan rates for PTh-CA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v)/PTh-CA supercapacitor
The response of capacitor cell was found to be dependant on scan rates, which was a characteristic of capacitor cells [24, 25]. There was a very small current deviation from 5th cycle to 1000th cycle (Figure 4.30). The electrode material had the most stable and higher cycleability to the capacitor application. There was a decrease in specific capacitance for redox super capacitor with scan rate (Figure 4.31). This was due to the increase in sweep rate in delaying the current to reach a horizontal value. This was attributed to the enhancement of the distributed capacitance effects. The CV responses of redox supercapacitor with polymer electrolyte were evaluated in terms of current plateau. The difference between anodic (I_a) and cathodic (I_c) peak currents at current plateaus were considered as ΔI plotted against scan rates is shown as Figure 4.32. The ΔI value increased with scan rate. The capacitance and faradaic current were calculated from the slope and intercept of the curves and were 12.8 mF and 0.37 mA, respectively.

4.3.7. AC IMPEDANCE STUDIES

Nyquist plot of PTh-CA/ PVdF-co-HFP-1M LiPF_6-EC/PC (1:1 v/v) /PTh-CA based capacitor is shown as Figure 4.33. A small semicircle at high frequency region was seen. The impedance values for the capacitor were determined from the spectrum. The intersection of the semicircle with the real axis gave internal resistance (R_i), and it was 12 Ω cm^2. From the low frequency end of the plot, the charge transfer resistance, R_{ct} was determined as 2 Ω cm^2 in 1M LiPF_6. These
values were due to the ohmic resistance between electrodes and the polymer electrolyte. The specific capacitance was calculated as 132 F/g.

4.3.8. CHARGE-DISCHARGE STUDIES

The symmetric redox supercapacitor was constructed by PTh-CA based composite electrodes using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF₆ EC/PC (1:1 v/v). Charge-discharge cycling at current density of 1 mA/cm² is shown as Figure 4.34. The voltage variation was nearly linear during charging and discharging. Further the anodic charging curves were symmetric to the corresponding cathodic discharging counterparts indicating that PTh-CA based electrode exhibited capacitance like behaviour. The discharge capacitance was calculated to 144 F/g, which had good agreement with the value obtained from the cyclic voltammetry. The initial sudden decrease in voltage while discharging of the cell at constant current density was due to the ohmic loss across the internal resistance ($R_i$).

The internal resistance of the capacitor was 6.8 $\Omega$ cm². This has lower inner IR drop which led to higher capacitance than the other systems studied because of higher electrical conductivity of PTh-CA based electrode material. The values of energy and power densities of the capacitor were 11 Wh/kg and 470 W/kg, respectively.

The discharge capacitance as the function of cycle number is shown as Figure 4.35. The specific capacitance of the composite was 144 F/g after 1000 cycles, only decreasing by 6%. The cycle stability of the cell with PTh-CA
composite electrodes is a promising compared with those of other capacitors. The columbic efficiency and internal resistance as a function of cycle number is shown as Figure 4.36. The columbic efficiency of the capacitor cells was found to be in the range of 96% over 1000 cycles. However, it is observed that the IR drop was almost same with the number of cycles up to 1000 cycles.
Fig. 4.33. Impedance spectrum of PTh-CA/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v)/PTh-CA supercapacitor
Fig. 4.34. Charge and discharge curves of PTh-CA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-CA supercapacitor at the current density of 1mA/cm$^2$. 


Fig. 4.35. Discharge capacitance as a function of cycle number for PTh-CA/ PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v)/PTh-CA supercapacitor
Fig. 4.36. Columbic efficiency and internal resistance as a function of cycle number for PTh-CA/ PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v)/PTh-CA supercapacitor
4.4. SYNTHESIS OF PTh-\(\rho\)-TSA NANOPARTICLES

The cationic surfactant-assisted dilute polymerization method was adopted for the synthesis of \(\rho\)-toluene sulphonate doped polythiophene (PTh-\(\rho\)-TSA) nanoparticles. When ferric chloride was added to the monomer with surfactant solution, a heavy floccular precipitate instantly appeared, due to electrical neutralization of quaternary ammonium cation of the CTAB and Cl\(^-\). During the progress of the reaction, the colourless emulsion turned into brown. This surfactant misceller stabilizes droplets against the collision and affects the distribution of reactants, which altered the course of thiophene polymerization by forming micelle-water interface in this system; this is similar to the organic aqueous interfacial polymerization.

4.4.1. FTIR STUDIES

The FTIR spectrum of PTh-\(\rho\)-TSA is shown as Figure 4.37. The \(\pi\) and lone pair electrons delocalization of polythiophene proved the aromatic character by (C-H) stretching vibration band at 3072 cm\(^{-1}\); (C=C) stretching band at 1414 cm\(^{-1}\); C-H in plane bending band shifted to 1144 cm\(^{-1}\); and (C-S) bending band shifted to 793 cm\(^{-1}\). The presence of SO\(_3\) groups in polymer obtained by (S=O) stretching band at 1050 cm\(^{-1}\) and also (S-O) stretching band at 667 cm\(^{-1}\)[26-28]. The band at 2851 and 2922 cm\(^{-1}\) proved the aliphatic (C-H) stretching. The large descending base line in the spectral region of 4000-2000 cm\(^{-1}\) is attributed due to free–electron conduction in the doped polymer. This type of behaviour was not
observed in undoped polymer [6]. These characteristic bands confirmed the formation of PTh-p-TSA compound.

4.4.2. UV-VISIBLE STUDIES

The UV-Visible absorption spectrum of ρ-TSA doped PTh obtained using DMSO solution is shown as Figure 4.38. The absorption bands were approximately observed at 305 and 380 nm. The absorption band at 305 nm is associated with π-π* interband transition and band at 380 nm was n-π* transition. The polymer showed a maximum of absorption at 250 to 450 nm and was related to a quite highly conjugated backbone. Increasing the degree of ρ-TSA doped polymer resulted in a blue shift of λ_{max}, implying a shorter conjugation length of the polymer. In the doped state, polymers exhibited a maximum of absorption at 650 to 800 nm.

4.4.3. X–RAY DIFFRACTION ANALYSIS

The phase purity of the synthesized PTh-ρ-TSA product was investigated by powder X-ray diffraction pattern (Figure 4.39). There was a broad amorphous modest intensity peak centered near 2θ value of 24.3°. The strong diffraction peak associated with the chain–to-chain stacking distance of about 2θ=24.3° was seen and is attributed to amorphously packed polythiophene main chains.

4.4.4. SEM STUDIES

The scanning electron microscopic photograph of the PTh-ρ-TSA powder is shown as Figure 4.40. The particles were uniformly distributed with spherical
Fig. 4.37. FTIR spectrum of PTh-p-TSA
Fig. 4.38. UV-Visible absorption spectrum of PTh-\(\rho\)-TSA nanoparticles
Fig. 4.39. X-ray diffractogram of PTh-\(\rho\)-TSA nanoparticles
Fig. 4.40. SEM photograph of PTh-\(\rho\)-TSA nanoparticles
morphology with the average particle size in the range of 20-25nm. The image also indicated the formation of nano-porous structured PTh-ρ-TSA surface. This caused the higher surface area of electrode material for the energy storage device.

4.4.5. CONDUCTIVITY MEASUREMENT

Electrical conductivity measurement was carried out on the pelletized PTh-ρ-TSA using a four-probe method at 30 °C. The intrinsic electrical conductivity of polythiophene synthesized with similar experimental conditions was found to be 0.98 S/cm. The value was comparable with previously reported polythiophene synthesized by FeCl₃ oxidative polymerization method [13-17].

4.4.6. CYCLIC VOLTAMMETRY STUDIES

Figure.4.41 showed the cyclic voltammograms for PTh-ρ-TSA based redox supercapacitor using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF₆ in EC/PC (1:1 v/v). The scanning was performed in the voltage range of −1.0 to +1.0 V at various scan rates of 5, 10, 25, 50 and 100 mVs⁻¹. The sweep-reversal voltammograms were almost close to an ideal rectangular shape. The specific capacitances of the capacitor cell were calculated at the scan rates of 5, 10, 25, 50 and 100mV/s gives approximately 170, 120, 62, 43 and 26 F/g, respectively. Rectangular shape of the voltammograms was observed even at high scan rate (100 mVs⁻¹) for the redox supercapacitor. At higher scan rates, a deviation from the rectangular shapes
Fig. 4.41. Cyclic voltammograms of PTh-\(\rho\)-TSA / PVdF-co-HFP-1M LiPF\(_6\) in EC&PC (1:1v/v) / PTh-\(\rho\)-TSA at the sweep rates of a) 5 mV/s, b) 10 mV/s, c) 25 mV/s, d) 50 mV/s and e) 100 mV/s
Fig. 4.42. Cyclic voltammograms of PTh-ρ-TSA / PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v) / PTh-ρ-TSA at the sweep rate of 50 mV/s in 5th and 1000th cycles
Fig. 4.43. Specific capacitance as a function of scan rate for PTh-ρ-TSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-ρ-TSA supercapacitor.
Fig. 4.44. Capacitive current as a function of scan rates for PTh-\(\rho\)-TSA / PVdF-co-HFP-1M LiPF₆ in EC&PC (1:1v/v) / PTh-\(\rho\)-SA supercapacitor
was observed for the cell, which was due to a substantial value of equivalent series resistance (ESR) present in real capacitor. Figure 4.42. showed the cyclic voltammogram at 5th and 1000th cycles. There was small deviation in current is due to the capacitance fading. The potential limit of the capacitor was reduced to -0.85 V to +1.0 V with a small current dropping was inferred. Figure 4.43. showed the dependence of specific capacitance with scan rates for PTh-ρ-TSA based redox supercapacitor. Specific capacitance decreased with increasing scan rate.

The difference between $I_a$ and $I_c$ at current plateau of the cyclic voltammogram was evaluated as $\Delta I$ plotted against scan rate, shown in Figure 4.44. The capacitance and faradaic current were evaluated from the slope and intercept of the plot and the values were 36.4 mF and 0.62 mA, respectively.

4.4.7. AC IMPEDANCE STUDIES

Figure 4.45 described the impedance spectrum of PTh-ρ-TSA based redox supercapacitor using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF$_6$ in EC/PC (1:1 v/v). This Nyquist plot showed a good capacitor-like behaviour with small diffusion limitation at low frequency region. A small semicircle observed in the middle high frequency region, revealed the charge transfer resistance and it was 1.4 $\Omega$. The semicircle intersected at the real axis was known as internal resistance ($R_i$) and it was found to be 5 $\Omega$. The specific capacitance was calculated at 10 mHz found to be 161 F/g.
4.4.8. CHARGE-DISCHARGE STUDIES

The supercapacitor cell was tested for charge-discharge experiments with constant current density of 1 mA cm\(^{-2}\). The charge-discharge process of this redox supercapacitor using PTh-\(\rho\)-TSA with PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF\(_6\) in EC/PC (1:1 v/v) is shown as Figure 4.46. The redox supercapacitor was charged up to 0-2 V. The profile of charge curves was not much symmetrical to that of discharge curves. The charge-discharge curve was linear. Ohmic drop was observed for each curve under this condition, which is due to its small internal resistance. The charge-discharge profiles of PTh-\(\rho\)-TSA had the internal resistance as 4.4 Ω cm\(^2\) at the discharge curves. The specific capacitance for redox supercapacitor with PTh-\(\rho\)-TSA was estimated to 167 F/g for 1000 cycles (Figure 4.47). The specific capacitance of the composite was 167 F/g after 1000 cycles, only decreasing by 2%. The energy and power densities of the capacitor were calculated to 19 Wh/kg and 680 W/kg, respectively.

Figure 4.48 showed the evaluation of coulombic efficiency and internal resistance as a function of cycle number for PTh-\(\rho\)-TSA based symmetric redox capacitor. The coulombic efficiency of this cell was found to be in the range of 98%. IR drop increased and the coulombic efficiency decreased with number of cycles about 1000 numbers.
Fig. 4.45. Impedance spectrum of PTh-\(\rho\)-TSA / PVdF-co-HFP-1M LiPF\(_6\) in EC&PC (1:1v/v) / PTh-\(\rho\)-TSA supercapacitor
Fig. 4.46. Charge and discharge curves of PTh-ρ-TSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-ρ-TSA supercapacitor at the current density of 1mA/cm$^2$
Fig. 4.47. Discharge capacitance as a function of cycle number for PTh-\(\rho\)-TSA / PVdF-co-HFP-1M LiPF\(_6\) in EC&PC (1:1v/v) / PTh-\(\rho\)-TSA supercapacitor
Fig. 4.48. Columbic efficiency and internal resistance as a function of cycle number for PTh-$\rho$-TSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-$\rho$-TSA supercapacitor
4.5. SYNTHESIS OF PTh-AQSA NANOPARTICLES

Polythiophene–anthraquinone sulphonic acid (PTh-AQSA) nanoparticles were prepared by surfactant-assisted dilute polymerization method. The polymerization was initiated by addition of ferric chloride solution to the mixture of thiophene and the dopant dispersed with surfactant solution. When ferric chloride was added, a heavy floccular precipitate instantly appeared due to electrical neutralization of quaternary ammonium cation of the CTAB and Cl⁻. This system could be similar to an organic aqueous interface in interfacial polymerization.

4.5.1. FTIR STUDIES

The FTIR spectrum of PTh-AQSA is shown as Figure 4.49. The aromatic nature of PTh-AQSA was confirmed by following absorption bands: (C-H) stretching vibration band at 3076 cm⁻¹; (C=C) stretching band at 1412 cm⁻¹; C-H in plane bending band shifted to 1145 cm⁻¹; and (C-S) bending band shifted to 795 cm⁻¹. The presence of SO₃ groups in the polymer was confirmed by (S=O) stretching band at 1076 cm⁻¹ and also (S-O) stretching band at 660 cm⁻¹ [25-27]. The carbonyl group of quinone was identified by the band at 1674 cm⁻¹; aliphatic (C-H) stretching band obtained at 2850 and 2922 cm⁻¹. The large descending base line in the spectral region of 4000-2000 cm⁻¹ is attributed due to free–electron conduction in the doped polymer. This type of behaviour was not observed in undoped polymer [6].
4.5.2. UV-VISIBLE STUDIES

UV-Visible spectrum of AQSA doped PTh obtained from DMSO solution is shown as Figure 4.50. The absorption bands were obtained at approximately 302 and 383 nm. The band at 302 nm was associated with the $\pi-\pi^*$ interband transition and band at 383 nm was $n-\pi^*$ transition, as in the case of other polythiophene homopolymer. The maximum of absorption at 250 to 450 nm could be related to highly conjugated backbone. Increasing the degree of anthraquinone sulphonic acid doped polymer resulted in a blue shift of $\lambda_{\text{max}}$, implying a shorter conjugation length of the polymer.

4.5.3. X-RAY DIFFRACTION ANALYSIS

The powder XRD pattern of PTh-AQSA is shown as Figure 4.51. The broad intensity peak centered near 2$\theta$ value of 23.9° was observed. The strong diffraction peak associated with the chain-to-chain stacking distance of about 2$\theta$=23.9°, attributed [10, 11] to almost crystalline packed polythiophene main chain. The intensity of the peak increased with the degree of crystallinity. The peaks were in accordance with the earlier reports of the partial crystalline portion of the polymer provided a decrease in resistivity [12].

4.5.4. SEM STUDIES

Scanning electron microscopic image of the PTh-AQSA nanoparticles is shown as Figure 4.52. The granular structure with an average particle size in the
Fig. 4.49. FTIR spectrum of PTh-AQSA
Fig. 4.50. UV-Visible absorption spectra of PTh-AQSA nanoparticles
Fig. 4.51. X-ray diffractogram of PTh-AQSA nanoparticles
Fig. 4.52. SEM photograph of PTh-AQSA nanoparticles
range of 25-40 nm was seen. Uniform porous structured surface of morphology was noticed.

4.5.5. CONDUCTIVITY MEASUREMENT

The four probe electrical conductivity measurement was subjected to PTh-AQSA by making pellet. The conductivity was found to be 1.3 S/cm. This result was comparable with previously reported polythiophene samples [13-17]. The doping efficiency depended on the charge carriers instead of degree of doping alone.

4.5.6. CYCLIC VOLTAMMETRY STUDIES

The specific capacitance and redox behaviour of electrode material was determined by cyclic voltammetry studies. The capacitor was constructed by PTh-AQSA based symmetric electrodes using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF₆ in EC/PC (1:1 v/v). The scanning was performed in the voltage range of –1.0 to +1.0 V at various scan rates of 5, 10, 25, 50 and 100 mVs⁻¹, (Figure 4.53). The specific capacitance values calculated at the scan rates of 5, 10, 25, 50 and 100 mV/s gave approximately about 176, 122, 65, 38 and 25 F/g, respectively. The obtained voltammogram was close to the capacitive like response and there were no visible peaks. This is due to the ideal capacitive nature of electrode material. The featureless characteristic of the voltammogram indicated that electron transfer between electrode and electrolyte
occurred at a constant rate, giving a fairly perfect mirror image during the charging and discharging processes.

To investigate the cyclic stability of the system, cyclings (1000 cycles) were carried out at the scan rate of 50 mVs⁻¹, the cyclic voltammograms are shown as Figure 4.54. The decaying of current was observed in too minimum between 5th and 1000th cycles; this ensured that the capacitance fading of the electrode material is very small. The stability of the electrode material was found as good.

The specific capacitance as a function of scan rate is given as Figure 4.55. The change in capacitance with increase in scan rate is due to the diffusion of ionic species. As the scan rate increased, electric charges might have difficulty to occupy the available sites at electrode/electrolyte interface due to their limited rate of migration and orientation in the electrolyte. Another possible reason was due to the internal resistance of the supercapacitor.

The charging currents for both the anode (I_a) and cathode (I_c) increased with scan rate. The difference between I_a and I_c at current plateaus of the cyclic voltammogram was designed as charging current (ΔI=I_a-I_c) and it was plotted against scan rate (Figure 4.56). From the plot of ΔI vs scan rate of redox supercapacitors the capacitance and faradaic current were calculated from the slope and intercept and their values were about 45.8 F/g and 1.2 mA, respectively.
Fig. 4.53. Cyclic voltammograms of PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA at the sweep rates of a) 5 mV/s, b) 10 mV/s, c) 25 mV/s, d) 50 mV/s and e) 100 mV/s
Fig. 4.54. Cyclic voltammograms of PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA at the sweep rate of 50 mV/s in 5$^{th}$ and 1000$^{th}$ cycles
Fig. 4.55. Specific capacitance as a function of scan rate for PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor
Fig. 4.56. Capacitive current as a function of scan rates for PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor
4.5.7. AC IMPEDANCE STUDIES

Ac impedance spectrum of PTh-AQSA based symmetric redox supercapacitor was measured by using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF$_6$ in EC/PC (1:1 v/v) is shown as Figure 4.57. From the Nyquist plot of PTh-AQSA, the semicircle portion at high frequency region dealt with the charge transfer behaviour and the low frequency or tail region of Warburg portion was due to the pseudocapacitive nature of electrode material. The semicircle intersected with real axis was the internal resistance and the charge transfer resistances were found to be 2 $\Omega$ and 1.2 $\Omega$. These lower values were due to the ohmic resistance between electrodes and the microporous polymer electrolyte. The specific capacitance was calculated about 182 F/g.

4.5.8. CHARGE-DISCHARGE STUDIES

In order to obtain the information about practical feasibility of PTh-AQSA based symmetric redox supercapacitor by using PVdF-co-HFP based microporous polymer electrolyte containing 1M LiPF$_6$ in EC/PC (1:1 v/v), the galvanostatic charge-discharge cycles were recorded at the constant current density of 1 mA/cm$^2$ (Figure 4.58). The voltage variation was nearly linear during charging and discharging. Further the anodic charging curves were symmetric to the corresponding cathodic discharging counterparts indicating that PTh-AQSA based electrodes exhibited capacitance like behaviour. The discharge capacitance was calculated and it was 174 F/g which had good agreement with
the value obtained from the cyclic voltammetry. The curves showed the high reversibility of charging curves to discharging curves indicating the cell had good capacitor behaviour. The charge-discharge curves were in linear shape. This was because of electrode-electrolyte interface and the cell functioned as a good capacitor. There was a minimum of internal resistance loss. A typical charge-discharge performance with internal resistance (3.2 Ω cm²) was calculated from the discharge curves. The specific capacitance of redox supercapacitor with PTh-AQSA was estimated to be 174 F/g for 1000 cycles (Figure 4.59). The stability of the capacitor was maintained even after 1000 cycles. The cycle stability of the cells with PTh-AQSA based composite electrodes was better than others. The values of energy and power densities of the capacitor were calculated as 23 Wh/kg and 760 W/kg, respectively.

Figure 4.60. showed the evolution of coulombic efficiency and internal resistance of PTh-AQSA based capacitor cell. The coulombic efficiency of the capacitor cell was found to be in the range of 98-99% over 1000 cycles. However, it was observed that the IR drop was almost same up to 1000 cycles.
Fig. 4.57. Impedance spectrum of PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor
Fig. 4.58. Charge and discharge curves of PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor at the current density of 1mA/cm$^2$. 
Fig. 4.59. Discharge capacitance as a function of cycle number for PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor
Fig. 4.60. Columbic efficiency and internal resistance as a function of cycle number for PTh-AQSA / PVdF-co-HFP-1M LiPF$_6$ in EC&PC (1:1v/v) / PTh-AQSA supercapacitor
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