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Chemically Synthesized Polyaniline Supercapacitor

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Abstract

Polyaniline (PANI) thin films have been prepared by simple chemical bath deposition at room temperature by polymerization of aniline monomer using ammonium peroxidisulphate (APS). In the present work, PANI films with a number of layers are deposited and comparatively their performance is studied. The PANI film with optimized thickness shows maximum specific capacitance of 670 Fg^{-1}. Surface morphology changes from compact mud like to diffused nanotube structure with increase in thickness. The electrochemical behaviour of PANI film is studied using charge-discharge study. The respective film show energy density of 36 $Whkg^{-1}$ and power density of 1.724 $kWkg^{-1}$.

Keywords: Thickness Dependent Performance, Supercapacitor, Polyaniline, Chemical Oxidation.

Introduction

Nowadays there is the enormous demand for energy due to the population blast. There is an urgent priority to develop a sustainable and clean source of energy. Again industrialization, climate change and the decreasing availability of fossil fuels have resulted in increased demands for energy. Due to these reasons energy storage systems plays a vital role in our lives. In this context, batteries, supercapacitors and fuel cells are the most important electrochemical energy storage devices.

Supercapacitors also named as electrochemical capacitors that store energy more than that of the capacitor and release power more than that of battery [1]. It has long cycle life (> 100 000 cycles) as compared with batteries and fuel cell [2]. Supercapacitors can be used in a variety of energy storage applications. Nowadays supercapacitors are widely used in memory backup system, consumer electronics [3]. They are often used in hybrid electric vehicles, medical electronics and military devices. Recently it has been reported that supercapacitor is used in Airbus A380 within its emergency doors [4].

Depending on charge storage capacity supercapacitor can be classified into three types. i) Electrochemical double layer capacitor (EDLC) ii) Pseudocapacitor iii) Hybrid capacitor formed by the combination of both EDLC and pseudocapacitor [5]. Electrochemical double layer capacitor, where the energy is stored by electrostatic charge separation at the interface between electrode and electrolyte. Pseudocapacitor derives its capacitance from the storage of charge in bulk of material in response to redox reaction. Hybrid capacitor uses both faradic and non-faradic mechanism to store charges. As per requirement of application depending on the type of energy storage, different types of materials are used for making supercapacitors such as metal oxides, carbon materials and conducting polymers. Among them conducting polymers are generally attractive as they have better kinetics, high charge density and low cost [6]. Out of different conducting polymers, polyaniline (PANI) has attracted much attention because of their environment stability, controllable electrical conductivity and easy processability. In recent years nanostructured PANI was synthesized by a variety of approaches including electrochemical deposition [7,8], interfacial polymerization [9], template [10], successive ionic layer adsorption and reaction (SILAR)method [11]. Chemical bath deposition (CBD) has attracted a considerable interest due to an inexpensive, simple and convenient method for large area deposition at relatively low temperature. Hence in the present investigation, CBD method is used to deposit PANI on stainless steel substrates. The change in preparative parameters causes the change in the structure of PANI. The charge storage ability of supercapacitor depends on the high surface area and porous nature that it indirectly depends on the morphology of polymer [12]. Many reports are available in literature in which morphology depends on synthesizing method. The template synthesis method is used to change the PANI morphology from globular particles to nanofibers [13], One-dimensional nanostructured PANI (nanofibers, nanowires, nanobelts, nanotubes, nanorods, nanoneedles and nano sticks) has been studied due to its unique properties and many applications [14], various surfactant changes the morphology of PANI from compact to vertical porous nanostructure and affects the specific capacitance [15], growth of PANI nanofibres using SILAR method [11].

In the present investigation, attempt has been made to increase the amount of active mass of the material by achieving maximum thickness as the pseudocapacitor stores a large amount of charge in the bulk of redox material [6]. The thickness is increased by increasing number of layers for the constant duration. The structural and morphological properties of PANI are presented. The PANI thin films are characterized by X-Ray diffraction (XRD) technique, Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and scanning electron microscopy (SEM). The supercapacitive performance of PANI thin film is investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge studies.

Experimental

Polyaniline (PANI) thin films have been prepared by simple and inexpensive chemical bath deposition (CBD) method at room temperature. All chemicals were purchased in analytical reagent (AR) grade. Aniline, ammonium peroxidisulfate (APS) and sulphuric acid were purchased from S.D.Fine Chemical and used without any further purification.

Synthesis of PANI

In the present investigation, the experiment is carried out with 0.2 M aniline in 1M H_2SO_4 solution and 0.25 APS as an oxidizing agent for polymerization of aniline at various thicknesses. The mirror polished stainless steel (SS) substrates were used for deposition of thin films. The chemical bath was prepared by aniline monomer and APS solution in double distilled water (DDW) at room temperature. The SS substrates were immersed in the bath for 30 min. Initially, the resultant solution is bluish and then turns green in color due to polymerization of aniline. After deposition, a thin film was washed with DDW for 2 to 3 times and then air dried. This is defined as the one layer of deposition. In this case, the thickness of the deposited film is less. To achieve the maximum thickness this process is repeated for four times so as to get the maximum thickness. After 3 layers the thickness of PANI film starts to decrease. Further, a film with one, two and three layers is symbolized as PANI 30-1, PANI 30-2 and PANI 30-3 respectively.

Characterization Techniques

The PANI thin films are characterized by various characterization techniques. The surface morphology was visualized by FE-SEM (Fourier transform scanning electron microscopy) workstation. The thickness of PANI films was measured by conventional weight difference method using sensitive microbalance. A crystallographic study of deposited thin films was performed using D2-Phaser X-ray powder diffractometer with CuKα radiation. The supercapacitive properties of films were studied by cyclic voltammetry (CV) and galvanostatic charge-discharge using Automatic battery cycler (WonAtech WBCS3000). The electrochemical cell consisting platinum as a counter electrode deposited film as working electrode and saturated calomel electrode (SCE) as a reference electrode in 1M H_2SO_4 as an electrolyte. The electrochemical workstation- ZIVE SP5 in the frequency range of 100k-100m Hz with AC amplitude of 10mV.

Results and Discussion

Reaction Mechanism

Chemical bath deposition (CBD) is popular in the synthesis of nanomaterial. Nanomaterials can be synthesized by making chemical reactions in which nucleation and growth process of constituent materials takes place [16]. Basically, Chemical deposition needs three reactants- Aniline, acid and an oxidising agent. In the present work 0.2 M aniline, 1M sulphuric acid and 0.25M ammonium peroxidisulphate ($(NH_4)_2S_2O_8$) are used. For chemical polymerization, monomers have to be oxidized to initiate the reaction. As shown in figure 1, oxidation of aniline monomer by oxidising agent to a radical cation takes place for further polymerization. The main function of the oxidising agent is to remove a proton from aniline molecule. The dimer undergoes chain propagation with oxidation and coupling. Doping of proton takes place by protonic acid (HA) on completion of polymerization[17]. After doping deposited film appear green in colour which is the signature of emeraldine salt. The reaction shows below,

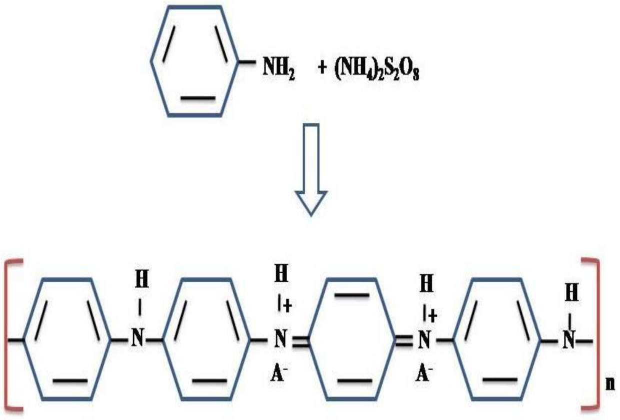

Figure 1: Reaction Mechanism for Polyaniline

Thickness Study

Figure 2 shows the variation of thickness with the number of layers. The thickness of PANI thin film was determined using sensitive microbalance by weight difference method. Thickness can be calculated using the relation,

$$t = \frac{m}{A \times \rho} \qquad (1)$$

Where m is the deposited mass in gram, A is the deposited area and **ρ** denotes the density of deposited material. Thickness plays important role in supercapacitors performance because it changes the materials characteristics. As the thickness increases, the electrical resistivity decreases. [18]. From figure 2, it is observed that initially thickness of PANI film increases with increase in deposition layer. The maximum thickness obtained for third layer was 11.2 µm. For a further increase in deposition layer, there was decrease in thickness of the film which indicates the formation of porous and less adherent film and it may have tensile stress which peeled off the film when the film becomes thick [19,20].

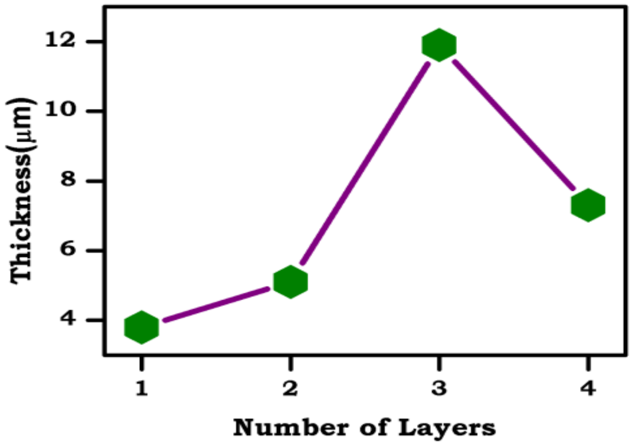

Figure 2: Variation of the thickness of PANI film with number of deposition layers

Structural Study

The structural study of PANI was investigated by using X-ray diffraction (XRD) technique. Figure 3 provides the XRD pattern of PANI on SS substrates recorded in the 2θ range 10-90^0.The peaks marked with the symbol (**Δ**) are assigned to the characteristic peaks of SS substrates. For PANI XRD pattern there is the absence of any sharp peak which indicates that deposited PANI is amorphous in nature. Amorphous nature of PANI film synthesized by SILAR method is already reported [11].

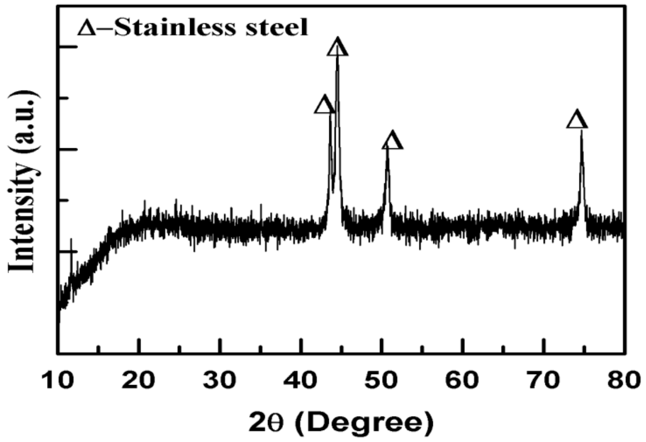

Figure 3: XRD pattern of PANI thin film

Fourier Transform Infrared Spectroscopy study

Figure 4 displays the molecular structure of PANI synthesized samples in the range of 4000-500 cm^{-1} by FTIR spectra. The bands at 1462 cm^{-1} and 1523 cm^{-1} correspond to C=C stretching vibrations of the benzenoid and quinoid rings, respectively[21]. The peak at 1299 cm^{-1} is the characteristic band of aromatic C-N stretching vibration and a weak peak at 3227 cm^{-1} is assigned to stretching mode of N-H [22,23]. The absorption band appears at 1103 cm^{-1}has been explained as vibration band of nitrogen quinone (N=Q=N). In addition, the band at 860 cm^{-1} can be ascribed to C-H out of plane bending vibrations for the aromatic ring which clearly supports the formation of PANI [23].

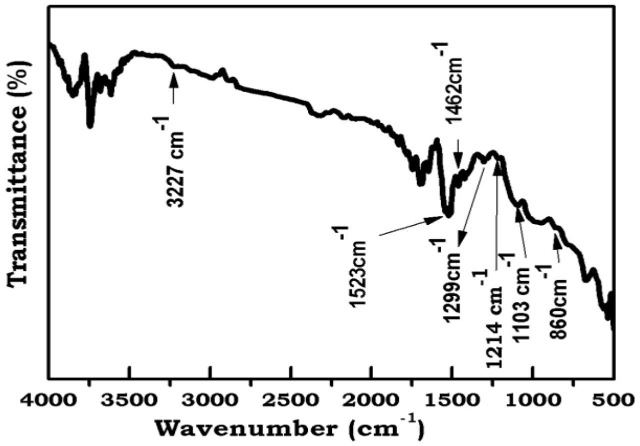

Fig.4 The FTIR spectrum of PANI film

Raman Spectroscopy

Figure 5 displays the Raman spectrum of PANI. The band observed at 1336 cm^{-1} assigned to C-N$^+$ delocalized polaronic structure, which is characteristics of the protonated imine form of PANI [24].The weak peak at 1173 cm^{-1} corresponding to C-H in plane bending [25] in quinoid rings. The sharp peak at 1582 cm^{-1} represents C-C stretching of the benzenoid ring [26].

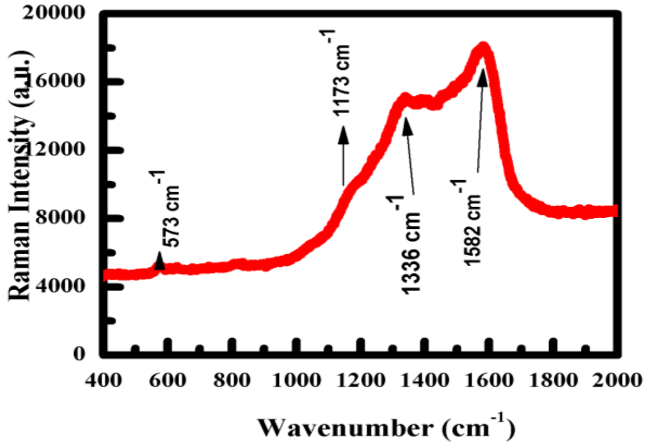

Figure 5: The Raman spectrum of PANI film

Morphological Studies

Surface nature of PANI thin films are studied by field emission electron microscopy (FESM). Figure 6 (a-f) demonstrates the surface morphology of PANI films at different cycles. From the micrographs of 10000x and 50000x magnifications, it is clearly observed that with an increase in cycle number the morphology changes from compact mudlike to diffused nanotube structure. Such porous morphology definitely increases the performance of PANI film [27]. Figure 6 (a-b) shows surface nature of 30-1 layer which looks like mud like compact structure. With the increase in deposition layer the micrographs 6 (c-d) shows porous nanotube structure which may further results in diffused nanotubes as observed in figure 6 (e,f). Such a porous network is essential for better performance of supercapcitor application as it provided improved surface area. Again with an increase in deposition layers active mass increases, which is helpful to store more charge because the bulk of material reacts in pseudo-capacitive material[6].

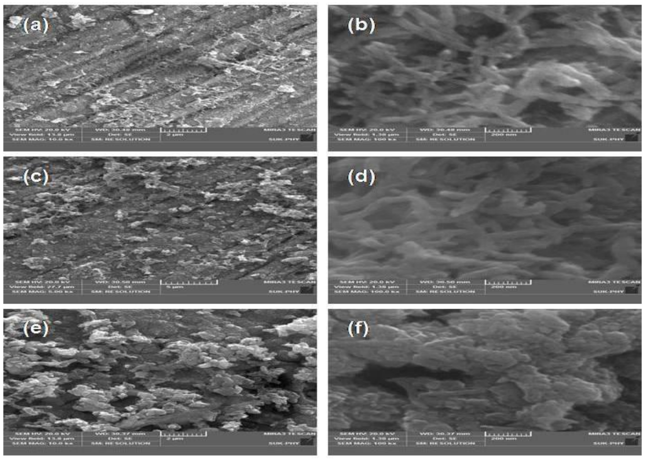

Figure 6: FE-SEM images of PANI (a-b) 30-1, (c-d) 30-2 and (e-f) 30-3 films

Electrochemical Studies

Scan Rate Study

Cyclic voltammetry (CV) is an ultimate tool to analyze the capacitive behavior of synthesized material. Figure 7(a) shows CV of 30-1, 30-2 and 30-3 PANI thin films for the scan rate of 5 mV s^{-1}. It is observed that there is a significant difference in areas of the thin films for different deposition layers. This affects the suprcapacitive performance. The calculated values of specific capacitance for PANI 30-1, 30-2 and 30-3 films at a scan rate of 5 mV s^{-1} are 332, 545 and 670 F g^{-1} respectively. For PANI 30-3 thin film, a maximum specific capacitance is observed which is the effect of a large amount of active mass deposition as seen from the result of thickness measurement. As pseudocapacitive material derives its capacitance from the charge storage in the bulk of redox material in response to redox reaction [6]. The CV curves of PANI 30-1, 30-2 and 30-3 thin films at a scan rate of 5, 10, 20, 50 and 100 mVs^{-1} are shown in fig 7b-d within the potential window -0.2 to 0.8 V/SCE. The redox peaks seen in the curves are due to oxidation and reduction of active sites at the electrode. The appearance of redox peaks indicates the pseudocapacitive nature of PANI material [15].With the increase in scan rate response of current also increases is a sign of ideal capacitive behaviour. The value of specific capacitance decreases with increase in scan rate shows the presence of inner active sites which cannot sustain the redox reactions and also some parts of the surface of the electrode are inaccessible at a high charge-discharge rate [28].

The supercapacitive parameters of PANI film is calculated using following relations

$$C = \frac{I}{dV/dt} \tag{2}$$

Where I is average current and dv/dt is voltage scan rate.

The specific capacitance of polyaniline is calculated by using the relation

$$C_s = \frac{C}{W} \tag{3}$$

Where W is the active weight of PANI film dipped in the electrolyte.

Figure 8 shows a variation of specific capacitance of PANI films with scan rate.

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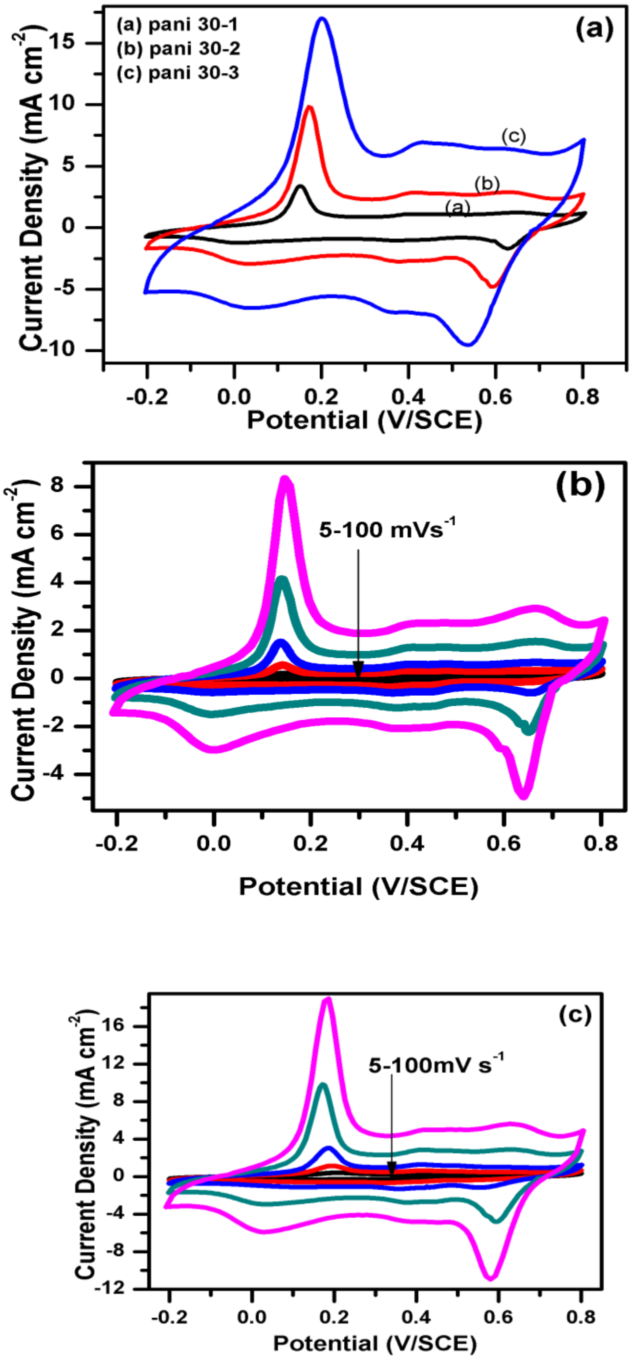

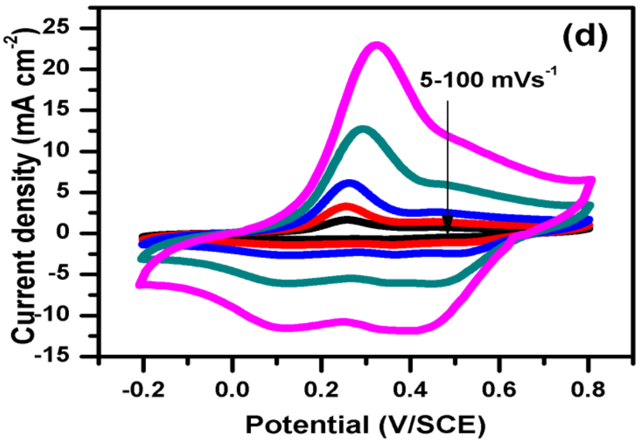

Figure 7: CV curves of (a) PANI 30-1, 30-2, 30-3 for 5 mVs^{-1} scan rate, (b) PANI 30-1, (c) PANI 30-2, (d) PANI 30-3 at different scan rates

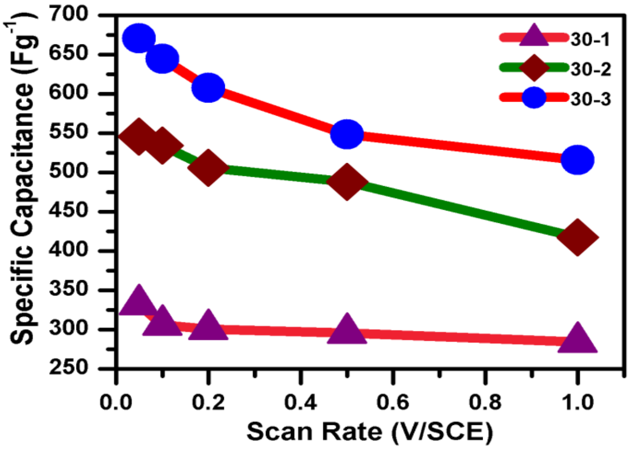

Figure 8: Variation of specific capacitance with scan rate

Galvanostatic charge-discharge study

Figure 9(a-c) displays the galvanostatic charge-discharge curves of PANI 30-1, 30-2 and 30-3 films in 1 M H_2SO_4 electrolyte within potential range -0.2 to 0.8 V/SCE. Galvanostatic charge-discharge study helps to test the performance of supercapacitor. From figure 9 it is clear that the charging and discharging curves are not symmetrical. This represents the pseudocapacitive behavior of PANI electrode. The discharging time is maximum for PANI 30-3 film. The specific capacitance of PANI film from charge-discharge curves is calculated as

$$C_s = \frac{I_d \times T_d}{\Delta V \times W} \quad (4)$$

Where I_d is the discharging current, T_d is the discharging time, V is the potential and W is the weight of deposited PANI film. The value of specific capacitance calculated is maximum for PANI 30-3 film which is 261 Fg^{-1} at a current density of 1 mA cm^{-2}.

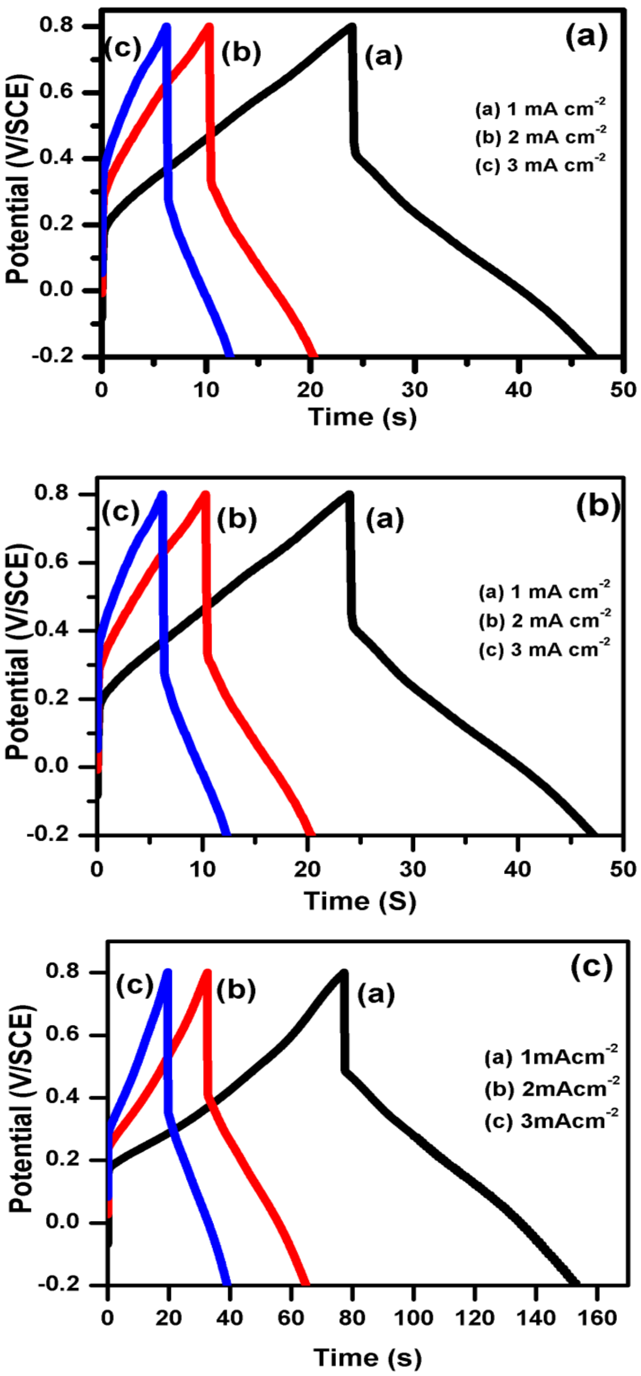

Figure 9: Galvanostatic charge-discharge curves of PANI (a)30-1 (b) 30-2 (c) 30-3 films with current densities in 1 M H_2SO_4 electrolyte

Cycling stability study

Figure 10 shows capacity retention with a number of cycles. In this study, we observe the cycling stability of maximum thickness film 30-3 which shows better supercapacitive performance than the other electrodes. PANI 30-3 film exhibits 67 % of its initial capacity over 500 cycles. From the figure, it is clear that the specific capacitance decreases with a number of cycles. This result indicates that the inexpensive chemical bath deposition method is suitable to deposit PANI for energy storage applications.

Figure 11 shows the Ragon plots of PANI 30-1, 30-2 and 30-3 samples. Study of specific energy density (ED) and specific power density (PD) is essential to examine the efficiency of supercapacitor. From the graph, it is clear that PANI 30-3 film executes higher ED and PD values as 36 Whkg^{-1} and 1.724 kWkg^{-1}. The values of specific energy and specific power are calculated from equations given below

$$SE = I \times t \times (\Delta V/W) \qquad (5)$$
$$SP = I \times (\Delta V/W) \qquad (6)$$

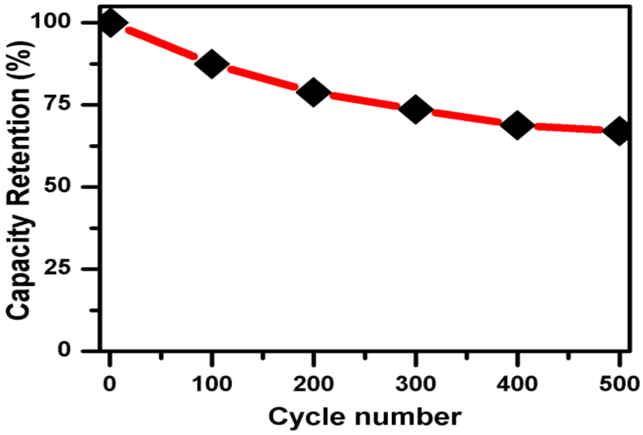

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Figure 10: Capacity retention with number of cycles.

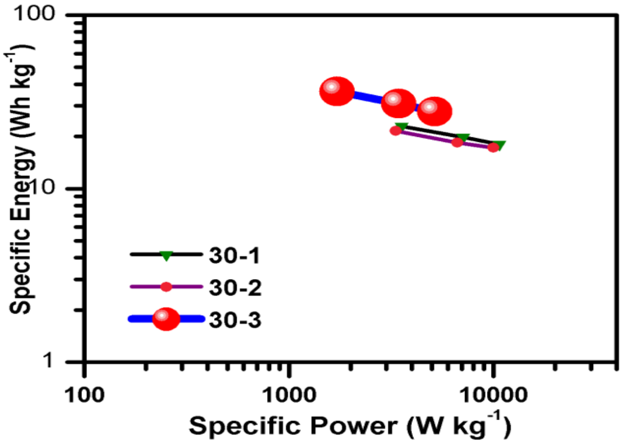

Figure 11: Ragon plot of PANI samples with number of layers.

Electrochemical impedance spectroscopy

Figure 12 reveals the Nyquist plot of PANI 30-1, 30-2 and 30-3 films. An electrochemical impedance spectroscopy (EIS) is a significant study of the fundamental behaviour of material for supercapacitor. Electronic and ionic resistance makes the total impedance of supercapacitor. Impedance spectra indicate semicircular arc in the high-frequency region and a straight line in low-frequency region. The high-frequency intercept of the semicircular arc is due to electrolyte resistance which is called as equivalent series resistance (ESR) and arc diameter denotes charge transfer resistance. The electrolytic resistance is the contribution of ionic resistance of the electrolyte, the resistance of substrate and contact resistance at deposited material and current collector interface. While the charge transfers resistance is the result of faradic reactions and double layer capacitance at the contact interface of the electrode and electrolytic solution [29].

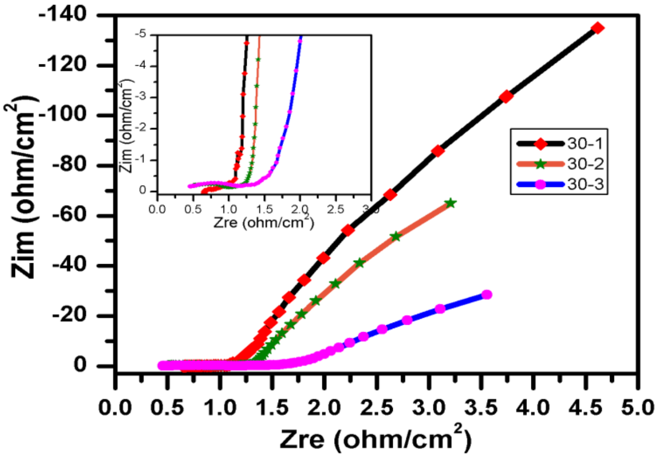

Figure 12: Nyquist plot of PANI 30-1, 30-2 and 30-3 films

An EIS study of PANI film performed in 1 M H_2SO_4 solution operated at a frequency range 100 kHz to 100 mHz. Typical Nyquist plots for PANI 30-1, 30-2 and 30-3 are shown in figure 12. The ESR of 30-1,30-2,30-3 nanostructures of PANI electrodes are calculated to be 0.65 , 0.50 and 0.41 ohm/cm^2 respectively and that of charge transfer resistance is 1.05, 1 and 1.10 ohm/cm^2 respectively. These results point out porous nature of deposited material which provides low impedance and easy access to ions of the electrolyte. The curve in the low-frequency region is steeper in nature that indicates the better capacitive performance [30].

Conclusion

In conclusion, PANI films with a number of layers have been successfully deposited by simple and inexpensive chemical bath deposition method. The thickness of the film affects the performance of material. FTIR spectrum confirms the formation of polyaniline. The CV and charge-discharge curve indicate the capacitive behavior of deposited material. The deposited film with maximum thickness shows specific capacitance of 670 Fg$^{-1.}$ EIS study showed that there is very small resistance which is essential for supercapacitor application.

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