

# Supercapacitor Studies of Electrochemically Deposited PEDOT on Stainless Steel Substrate

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**ABSTRACT:** There has been increasing interest on various properties and applications of electronically conducting polymers. Polyethylenedioxythiophene (PEDOT) is an interesting polymer of this type as it exhibits very high ionic conductivity. In the present study, PEDOT has been electrochemically deposited on stainless steel (SS) substrate for supercapacitor studies. PEDOT/SS electrodes prepared in 0.1M H<sub>2</sub>SO<sub>4</sub> in presence of a surfactant, sodium dodecylsulphate (SDS), have been found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The effects of concentration of H<sub>2</sub>SO<sub>4</sub>, concentration of

SDS, potential of deposition, and nature of supporting electrolytes used for capacitor studies on SC of the PEDOT/SS electrodes have been studied. SC values as high as 250 F/g in 1M oxalic acid have been obtained during the initial stages of cycling. However, there is a rapid decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on extended cycling. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1160–1171, 2007

**Key words:** conducting polymers; PEDOT; supercapacitor; charge-discharge cycling; AC impedance

## INTRODUCTION

Polymers such as polypyrrole, polyaniline, polyethylenedioxythiophene (PEDOT), etc. possess a high electronic conductivity because of their conjugate bonding structure. They can be prepared by electrochemical oxidation of the corresponding monomers, in addition to chemical oxidation.<sup>1</sup> The electrochemical formation induces high oxidation state to the polymers, which facilitates doping of anions from the electrolyte into the polymer chains. These polymer films can be subjected to reversible electrochemical switching between undoped and doped states by controlling their potentials. The electrochemically induced doping and undoping processes in conducting polymers facilitate their application in electrochemical devices such as batteries, electrochromic devices, etc.

Electrical double-layer formed at the interface between a metallic electrode and an electrolyte has been a topic of innumerable studies in the past.<sup>2</sup> The electrical interface plays a crucial role in kinetics, mechanisms, and applications of a variety of electrochemical reactions. The importance of the interface lays in the fact that the mode of charge-transportation changes from ionic transport in the electrolyte to electronic transport in the metallic electrode at the instance of Faradaic reactions. The electron-transfer

reactions lead to many important applications of electrochemistry, which include energy storage/conversion devices such as batteries and fuel cells. Nevertheless, the electrical charges separated across the interface even in the absence of electron-transfer reactions, can also be utilized for energy through reversible nonFaradaic charge/discharge process.<sup>3</sup> The double-layer capacitance ( $C_{dl}$ ) is defined by Eq. (1):

$$C_{dl} = dq/dE \quad (1)$$

where  $q$  refers to charge on the metal and  $E$  the electrode potential. The energy ( $G$ ) associated with the  $C_{dl}$  is according to Eq. (2):

$$G = C_{dl}E^2/2 \quad (2)$$

Studies on double-layer capacitance, which is due to accumulated excess charges at the interface, for energy storage and conversion process have been investigated in recent years.<sup>4</sup> Double-layer charging and discharging processes occur at faster rates than the electron transfer reaction rates. This fact led to the discovery of electrical double-layer (EDL) capacitors or electrochemical supercapacitors, whose properties differ with those of batteries, for energy-storage and conversion. Batteries are high-energy and low-power devices, where as supercapacitors are low-energy and high-power devices. The faster rate of double-layer charging-discharging processes than the Faradaic reactions reflects in realization of higher power in supercapacitor than in batteries. Supercapacitors

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employing high surface area carbon powders attracted interest in the early stages of the discovery. Subsequently, various other electrode materials such as transition metal oxides, electronically conducting polymers, etc. have been studied.<sup>5</sup> In these materials, in addition to the double-layer capacitance, pseudocapacitance involved in Faradaic reactions also contribute to capacitance.

Conducting polymers are more interesting than carbons and transition metal oxides because of the following merits<sup>6</sup>: (i) conducting polymers have higher electronic conductivity than the metal oxides, (ii) they are cheaper than some oxides, e.g.,  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ , (iii) they can be prepared by using electrochemical methods in a well controlled manners, (iv) electrochemical deposition ensures coherence and adherence to the current collecting substrates, and (v) electrochemical deposition avoids the procedures of electrode-fabrication with suitable binders. Among the conducting polymers, PEDOT is interesting as it is insoluble in most of the solvents, exhibits a high conductivity, changes in color because of applied potential, is stable in the doped state, and exhibits reduced band-gap. Studies on supercapacitor properties of PEDOT are rarely reported.<sup>7-11</sup> Ghosh and Ingnas<sup>7</sup> have reported electrochemical characterization of PEDOT, doped with excess polystyrene-sulfonate (PSS) in the form of a hydrogen conducting network. Because of high ionic mobility in the material, the electrochemical processes were reportedly not limited by ionic diffusion into the polymer, but by the resistance in the conducting network. As the hydrogel showed large capacitance and it was subjected to rapid charge-discharge processes, application of the polymer coated gold electrodes for supercapacitors was envisaged. However, no studies related to supercapacitors were reported in this publication. In another study,<sup>8</sup> PEDOT-PSS films (thickness: 1  $\mu\text{m}$ ) were electrochemically grown on gold electrodes, electrochemical quartz crystal microbalance, and electrochemical impedance spectroscopic studies were carried out. From impedance studies in a nonaqueous electrolyte, a capacitance value of 25  $\text{F}/\text{cm}^3$  is reported. Assuming the density<sup>12</sup> of the film equal to 1.45  $\text{g}/\text{cm}^3$ , this value leads to a specific capacitance (SC) value of about 17  $\text{F}/\text{g}$ . This is not an attractive value for supercapacitor applications. Several thiophene derivatives were polymerized by oxidation of the respective monomers using a  $\text{Fe}^{3+}$  salt, the corresponding polymers were studied for capacitor characteristics.<sup>9</sup> In a nonaqueous electrolyte, a SC value of 103  $\text{F}/\text{g}$  were reported. Electrochemical properties of composites prepared from PEDOT and multiwalled carbon nanotubes were investigated for supercapacitor application.<sup>10</sup> Aqueous as well as nonaqueous electrolytes were employed for capacitor studies. Both chemical oxidation and electrochemical oxida-

tion of EDOT in nonaqueous solutions were carried out for preparation of PEDOT. The values of SC ranged from 60 to 160  $\text{F}/\text{g}$ . Ryu et al.<sup>11</sup> reported capacitance studies of PEDOT and carbon composites in a nonaqueous electrolyte. A maximum SC value of 56  $\text{F}/\text{g}$  is reported. Polymerization of EDOT with a  $\text{Fe}^{3+}$  salt in an aqueous medium was performed by subjecting the reaction mixture to ultrasonic irradiation. Pressed pellets of PEDOT with a binder were used as electrodes and capacitance values up to about 100  $\text{F}/\text{g}$  in a 1M  $\text{H}_2\text{SO}_4$  were reported.

From the above review of literature on supercapacitor studies of PEDOT, the following observations are made: (i) PEDOT is commonly prepared in nonaqueous media, (ii) it is generally prepared in a chemical oxidation route and then electrodes are fabricated using a binder or as pellets, (iii) electrochemical preparation is carried out on noble-metal substrates, (iv) capacitance studies are also commonly made in nonaqueous electrolytes, and (v) SC values are low. It is clear that there exists a scope for various investigations to employ aqueous electrolytes for both preparation of PEDOT and capacitor characterization studies, to use nonplatinum metals as current collecting substrates for electrochemical preparation of PEDOT, and also to obtain higher SC.

In the present study, PEDOT was deposited on stainless steel (SS) substrate from an aqueous solution of the monomer consisting of a surfactant. Several experimental conditions during the electrodeposition of PEDOT films and also during the studies concerning supercapacitor properties were varied with an aim to arrive at the appropriate experimental conditions to obtain high SC. A value of SC of 250  $\text{F}/\text{g}$  was obtained during the initial stages of an extended charge-discharge cycle-life test.

## EXPERIMENTAL

Analytical grade  $\text{H}_2\text{SO}_4$  and oxalic acid were purchased from Merck, and ethylenedioxy-thiophene (EDOT) from Aldrich, Reagent grade sodium dodecylsulphate (SDS,  $\text{C}_{12}\text{H}_{25}\text{NaOSO}_3$ ) from Merck was used as the surface-active agent. A high purity commercial 304 grade SS foil (thickness: 0.2 mm) was used as the substrate for PEDOT deposition. All solutions were prepared in doubly distilled water. A glass cell of about 70 mL capacity with suitable ground-glass joints to introduce a working electrode, Pt foil auxiliary electrodes, and a saturated calomel reference electrode (SCE) was used for electrochemical deposition of PEDOT and also for characterization studies. All potential values are reported against SCE.

Preliminary experiments using a polished and cleaned SS substrate indicated poor adherence of electrodeposited PEDOT. To improve adherence, SS sheet was subjected to sand blasting to generate a noticeable

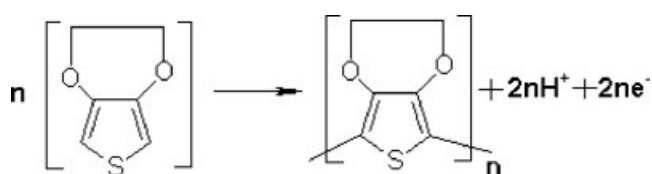
rough surface and washed copiously using a detergent followed by a mild etching in dilute  $\text{H}_2\text{SO}_4$ . A foil of 7-mm width and 6-cm in length was sectioned out of a sandblasted SS sheet,  $1.4 \text{ cm}^2$  area at one of the ends was exposed to the electrolyte and the rest of its length was used as a tag for taking electrical contacts. The SS substrate was again washed thoroughly, rinsed with acetone and dried in vacuum at ambient temperature for about 30 min and weighed before electrodeposition of PEDOT. Some experiments were also carried out on a Pt foil (area:  $1.4 \text{ cm}^2$ ) electrode. An electrolyte of  $0.01\text{M}$  EDOT +  $0.1\text{M}$   $\text{H}_2\text{SO}_4$  was used for PEDOT deposition. For deposition in the presence of surface-active agent, the required quantity of SDS was added followed by a thorough stirring of the electrolyte till a clear solution was obtained. After the electrochemical deposition of the required quantity of PEDOT, the electrode was separated from the cell, rinsed with doubly distilled water, dried at  $50^\circ\text{C}$ , and weighed. Geometric areas of both sandblasted SS and Pt substrates were used for calculation of current density ( $\text{mA}/\text{cm}^2$ ) and specific mass of PEDOT ( $\text{mg}/\text{cm}^2$ ).

A Sartorius balance of model CP225D-OCE with  $0.01 \text{ mg}$  sensitivity was used for weighing the electrodes. The scanning electron microscope (SEM) images were recorded using FEI SEM model Quanta 200 or Sirion. Cyclic voltammetry and galvanostatic charge-discharge cycling were carried out using a potentiostat/galvanostat EG and G PARC model Versastat II or Solartron model 1286. For measuring SC, an electrode was subjected to 10 galvanostatic charge-discharge cycles, and the SC was calculated from the second charge-discharge cycle, unless otherwise stated. UV-visible and FTIR spectra were recorded by Perkin-Elmer model Lambda 35-UV/VIS spectrometer and Bruker FTIR model 66V spectrometer, respectively. For UV-visible spectra, PEDOT was electrochemically deposited on indium tin oxide (ITO) coated glass plate. For recording IR spectra, PEDOT was scrapped carefully from the substrate, the powder was mixed with KBr, and pressed into pellets. All experiments were conducted in an air-conditioned room at  $(22 \pm 1)^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Preparation of PEDOT films

The electrochemical preparation of PEDOT involves oxidation of EDOT molecule at the electrode surface:



The reaction occurs through the formation of cation free-radicals of the monomer, the combination of them resulting in the formation of dimer, further oxidation of dimer, etc., eventually resulting in the formation of the polymer, PEDOT.<sup>13</sup> The polymer is insoluble in aqueous and many common nonaqueous solvents, and therefore forms as a film on the electrode used for oxidation.

### Materials

Electrochemical polymerization of EDOT and other derivatives of thiophene require generally anhydrous organic media.<sup>14</sup> The difficulties for electrooxidation of these monomers in aqueous media include<sup>15</sup>: (i) the monomers are weakly soluble in water, (ii) the oxidation potential of these molecules are close to or higher than the potential of oxygen evolution, and (iii) the electropolymerization process is inhibited by water, because of the formation of thienyl cation radicals, which react rapidly in water. To solve these problems, anionic surfactants such as SDS were added to aqueous solutions of thiophene derivatives.<sup>15</sup> In the presence of SDS, the solubility of the monomers increased and their oxidation potential lowered. Sakmeche et al.<sup>15</sup> electrodeposited PEDOT in the presence of SDS in  $0.1\text{M}$   $\text{LiClO}_4$  aqueous solutions consisting of  $0.05\text{M}$  EDOT on a Pt electrode. It was shown that there was an increase in solubility of EDOT because of SDS and also the oxidation mechanism in aqueous solutions was different from acetonitrile solutions. Strong electrostatic interaction between  $\text{EDOT}^{+\bullet}$  radical cation and SDS anion were reportedly explained the effect of SDS, which resulted in strongly bonded complex between these ions. Furthermore, well-organized and adherent films of PEDOT were formed on Pt at lower potentials than in the absence of SDS in the aqueous medium. PEDOT nanoparticles were also prepared in an aqueous solution in presence of dodecylbenzene sulfonic acid as a surfactant.<sup>16</sup> Vasantha and Phani<sup>17</sup> employed hydroxylpropyl- $\beta$ -cyclodextrin (HP- $\beta$ -CD) as solubilizing agent for EDOT. The cyclic HP- $\beta$ -CD has a hydrophobic interior and hydrophilic outer side, and it forms an inclusion compound with EDOT. Potentiostatic cycling of a Pt electrode in  $0.1\text{M}$   $\text{LiClO}_4$  aqueous electrolyte consisting of  $0.05\text{M}$  HP- $\beta$ -CD and  $0.026\text{M}$  EDOT produced homogenous and adherent PEDOT films on Pt surface. Neutral aqueous media were employed for preparation of PEDOT in most of the reports in the literature. In the present study, preliminary experiments were conducted by preparing PEDOT in neutral and acidic electrolytes, and measuring SC of PEDOT prepared in  $\text{H}_2\text{SO}_4$  medium was greater than the polymer prepared in neutral medium. Hence the rest of the experiments were conducted by preparing PEDOT in  $\text{H}_2\text{SO}_4$  electrolytes. As low concentration

of aniline produced highly porous polyaniline films due to low rate of oxidation,<sup>18</sup> 0.01M was used in the present study although a maximum solubility of 0.05M EDOT was obtained in aqueous neutral media consisting of SDS.<sup>15</sup>

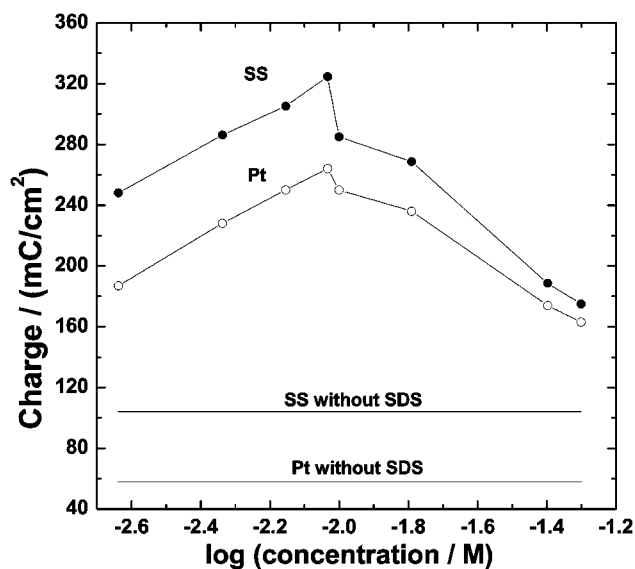
Generally, an inert electrode such as Pt or Au is used for oxidative polymerization resulting in the formation of conducting polymers. However, for application oriented studies, such as supercapacitors, inexpensive, and commonly available metal or alloy substrates are preferred. Therefore, in the present study SS substrate was employed. Electropolymerization of EDOT on non-inert substrates is rarely reported.<sup>19</sup> In this work, it was shown that choice of the electrolyte salts was a determining factor for electropolymerization of EDOT on iron and aluminum in SDS micellar aqueous solution. In the presence of phthalate ions, electropolymerization resulted in passivation of metal surfaces and formation of homogeneous and adherent PEDOT films on iron, whereas the films formed on aluminum were poorly adherent. The adherence of PEDOT films to iron substrate was improved when this metal was pretreated with dilute HNO<sub>3</sub>. Although anticorrosion effect of PEDOT on these reactive metals was studied, capacitor properties were not reported.<sup>19</sup> In the present work also, the adherence of PEDOT on polished and acid-treated SS was poor. However, adherence strongly improved on sand-blasted SS surface.

### Electrochemical oxidation

Electrochemical oxidation of the monomer could be accomplished by galvanostatic, potentiostatic, and potentiodynamic methods. Preliminary experiments were carried out by depositing galvanostatically (c.d: 2–5 mA/cm<sup>2</sup>), potentiostatically ( $E = 0.8$ – $1.2$  V) and potentiodynamically in the potential range of 0– $1.2$  V (sweep rate = 2–50 mV/s), and measuring capacitance. It was found that the potentiostatically prepared PEDOT/SS electrodes yielded higher SC. This may be because of difference in morphology of PEDOT films obtained methods. Therefore, the experiments were carried out with potentiostatically prepared PEDOT/SS electrodes.

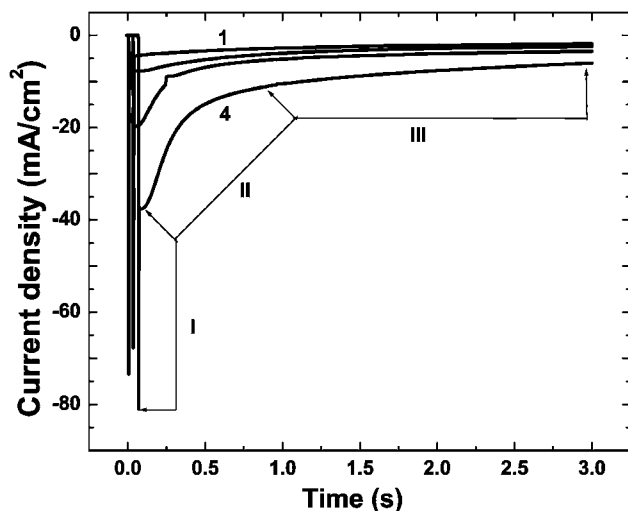
### The influence of concentration of surfactant

The influence of concentration of SDS on the rate of electrodeposition was studied. PEDOT/SS and PEDOT/Pt electrodes were prepared in 0.01M EDOT + 0.1M H<sub>2</sub>SO<sub>4</sub> with varying concentration of SDS in 0–0.50M range at 0.9 V for 300 s. The quantity of charge passed in each solution was taken as a measure of the rate of polymerization. A plot of charge density ( $q$ ) against the concentration of SDS is shown in Figure 1. In the absence of the surfactant, the values of  $q$  obtained for Pt and SS are about 60 and 105 mC/cm<sup>2</sup>, respectively.



**Figure 1** Amount of charge passed in 300 s after stepping the electrode potential to 0.9 V versus SCE as a function of SDS concentration for the electropolymerization of EDOT on SS (●) and Pt (○) in electrolyte of 0.1M H<sub>2</sub>SO<sub>4</sub> + 0.01M EDOT + 0.01M SDS. The horizontal lines represent the polymerization charges for Pt and SS in the absence of SDS.

Higher value of  $q$  for SS is due to greater surface area, which resulted from the sand blasting. The values of  $q$  for both Pt and SS increase with an increase in concentration of SDS from 0.002 to 0.01M. Further increase in SDS concentration results in a decrease in  $q$ . Thus maximum  $q$  values are obtained at 0.01M of SDS. The increase in charge of SS electrode is from 105 to 320 mC/cm<sup>2</sup> when concentration of SDS is increased from 0 to 0.01M in the electrolyte. The corresponding values of  $q$  for Pt are 60–250 mC/cm<sup>2</sup>. At all concentrations of SDS, the rate of deposition of PEDOT on SS is greater than that of Pt because of greater surface area. The rates of deposition on both SS and Pt increase by about 3–4 times due to the presence of 0.01M SDS. The influence of concentration of SDS on polymerization rate of EDOT may be explained on the basis of formation of complex between micells of SDS and EDOT<sup>+</sup>• cation free radicals.<sup>15</sup> The critical micellar concentration (CMC) of SDS in water is 0.008M.<sup>20</sup> There is a substantial decrease in CMC if the medium is changed to dilute H<sub>2</sub>SO<sub>4</sub>. The CMC of SDS in 0.5M H<sub>2</sub>SO<sub>4</sub> is 0.07mM, which is about 100 times less than the CMC in water. Thus at all concentration of SDS used in the present work, micelle formation exists, and the micelles tend to accumulate on the electrode/electrolyte interface. As the concentration of SDS increases from 0.001 to 0.01M, the surface concentrations of micelle-EDOT<sup>+</sup>• cation radical concentration increases, which facilitates increased rate of PEDOT film formation. By further increasing the concentration of SDS, which exceeds the concentration of the monomer, it is likely



**Figure 2** Current transients for electrodeposition of PEDOT on Pt electrode at (1) 0.9, (2) 1.0, (3) 1.1, and (4) 1.2 V versus SCE in 0.1M H<sub>2</sub>SO<sub>4</sub> + 0.01M EDOT + 0.01M SDS.

that the surface concentration of uncomplexed micells increases. As a result, the rate of PEDOT formation decreases.

### Deposition mechanism and morphology

In preparation of electrodeposited films, the nature of growth can affect the properties of the resulting films. The potential step chronoamperometric technique, where the change in current is followed with time after stepping the potential to a desired value, is useful for studying phase formation kinetics and the growth mechanism.<sup>21</sup> A series of current-time transients were recorded for a Pt electrode at different stepping potentials, as shown in Figure 2. The transients are found to have three regions. When the potential is stepped up, there is an increase in current due to double-layer charging (region I in Fig. 2). The current decreases with time in the II region where the electron-transfer process starts occurring. The pattern of the current variation in this region depends on the mechanism of charge-transfer step. The nature of the current-time curve in this region corresponds to nucleation and growth of the electrodeposits. There is a steady flow of current in the III region due to the growth of electrodeposited polymer.

The relationship between current and time in the II region is different for different mechanisms of growth.<sup>22</sup> By establishing the power-law relationship of the current and time corresponding to this region (Fig. 2), the respective mechanism can be predicted:

$$i = kt^n \quad (3)$$

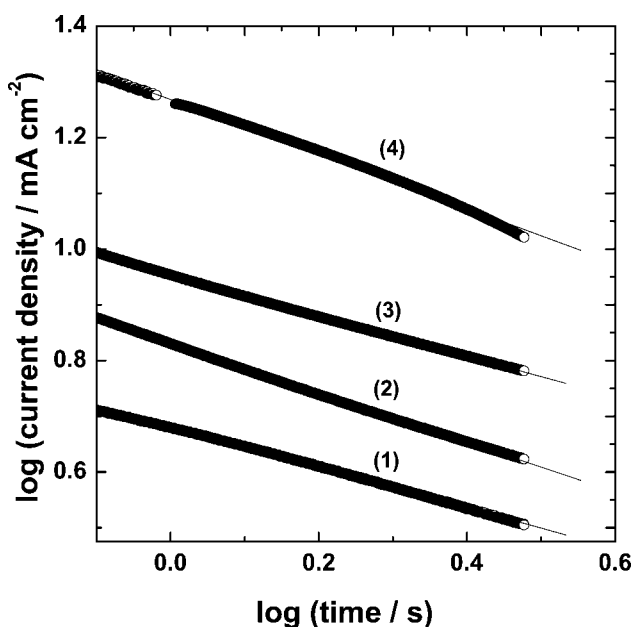
where  $k$  is constant, which generally includes the parameter such as diffusion coefficient, concentration,

etc. For determination of the value of  $n$ , Eq. (3) is rewritten as:

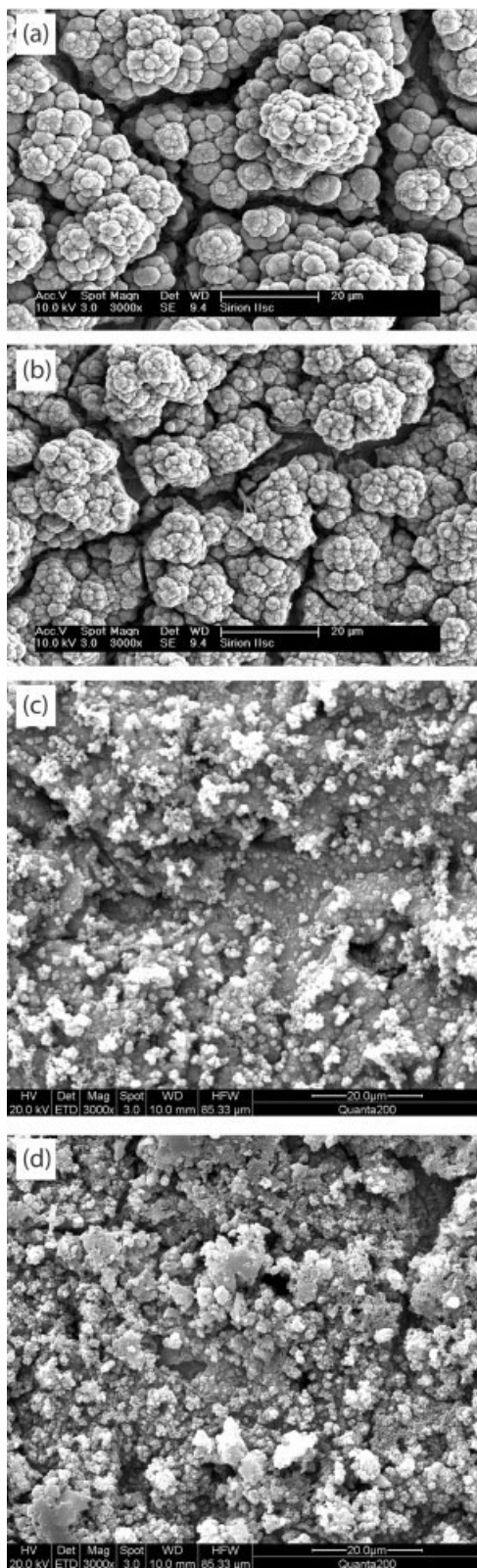
$$\log i = \log k + n \log t \quad (4)$$

For the data presented in Figure 2,  $\log i$  versus  $\log t$  plots were constructed and shown in Figure 3. The plots are linear for the data recorded in the potential range 0.9–1.2 V and the value of slope [equal to  $n$  in Eq. (2)] is about  $-0.5$ . This value suggests that the electrocrystallization of PEDOT involves three-dimensional growth of the nuclei.<sup>23</sup>

The nature of PEDOT electrodeposits obtained at different potentials on SS substrate was examined by scanning electron microscopy (Fig. 4). It is seen that at 0.9–1.0 V, globular deposits of PEDOT are obtained, thus confirming three-dimensional growth. The size of the globules decreases with an increase in potential from 0.9 to 1.0 V. At potential 1.1–1.2 V, the PEDOT deposits were powdery with poor adherence to the substrate. A few electrodes were prepared in the potential range from 0.8 to 1.1 V with a mass density of 0.6 mg/cm<sup>2</sup>, and their capacitance values were measured as detailed later. The data in Figure 5 show that there is a marginal decrease in SC by increasing the potential from 0.8 to 1.0 V. However, there is a drastic decrease of SC from about 160 F/g for PEDOT/SS electrode prepared at 1.0 V to about 90 F/g for the electrode prepared at 1.1 V. This is probably due to powdery PEDOT deposits formed at the potential >1.0 V. In view of obtaining a high capacitance and also preparing the PEDOT at a reasonable



**Figure 3** A log–log plot of region II of current transients data shown in Figure 2 at (1) 0.9, (2) 1.0, (3) 1.1, and (4) 1.2 V versus SCE.



**Figure 4** SEM images of PEDOT/SS prepared at (a) 0.9, (b) 1.0, (c) 1.1, (d) 1.2 V versus SCE in 0.1M H<sub>2</sub>SO<sub>4</sub> + 0.01M EDOT + 0.01M SDS.

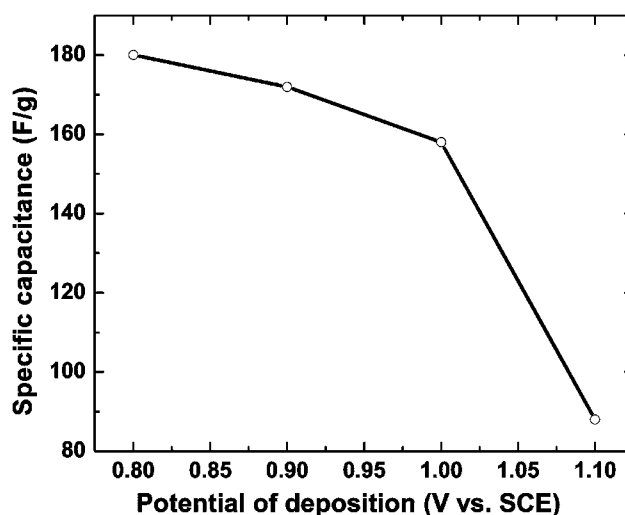
fast rate, 0.9 V was chosen as the suitable potential for further studies.

**Capacitance studies in HClO<sub>4</sub> + NaClO<sub>4</sub> solutions**

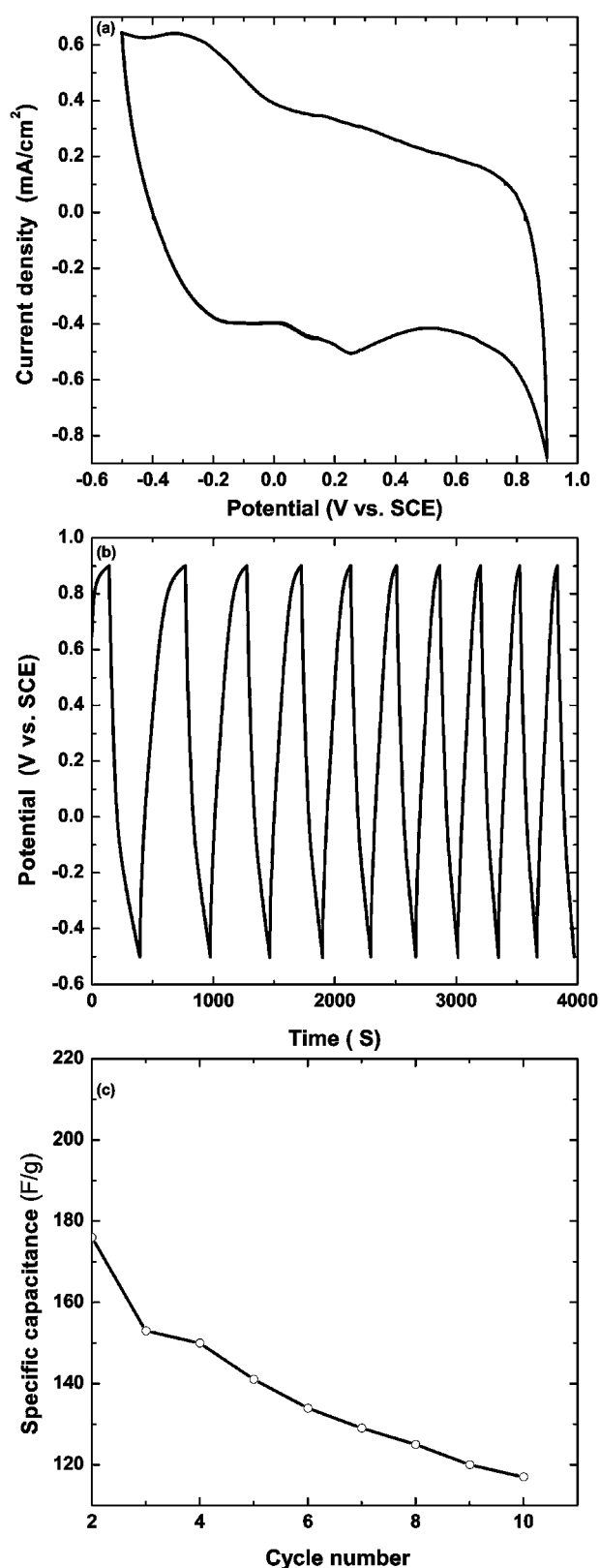
Capacitance properties of PEDOT are studied and reported either in an organic medium or a dilute H<sub>2</sub>SO<sub>4</sub> aqueous medium. The SC values varied from study to study, and a maximum value of ~ 103 F/g is reported.<sup>19</sup> The charges involved in doping/undoping processes with in the conducting polymers strongly depend on the nature of the electrolyte, and accordingly SC values also differ from electrolyte to electrolyte. For instance, a mixed electrolyte of HClO<sub>4</sub> + NaClO<sub>4</sub> was reported to be a better electrolyte than a few other electrolytes for obtaining stable capacitance values of polyaniline.<sup>24</sup> Accordingly, in the present studies also, 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> mixed electrolyte was employed for electrochemical characterization of PEDOT/SS electrodes. Capacitance behavior of PEDOT/SS electrodes was studied by subjecting them to cyclic voltammetry and galvanostatic charge-discharge cycling. As a result of several preliminary studies, a potential window of 1.4 V from -0.5 to 0.9 V was found to be appropriate for capacitance studies. In this region of potential, the cyclic voltammograms in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> mixed electrolyte are broad and the potential variation with charge/discharge time is linear, as shown in Figure 6(a,b), respectively. The value of SC was calculated from the discharge data using Eq. (5).

$$SC = It / (1.25 m) \tag{5}$$

where *I* is the discharge current, *t* is discharge time, and *m* is mass of PEDOT. The value of SC obtained

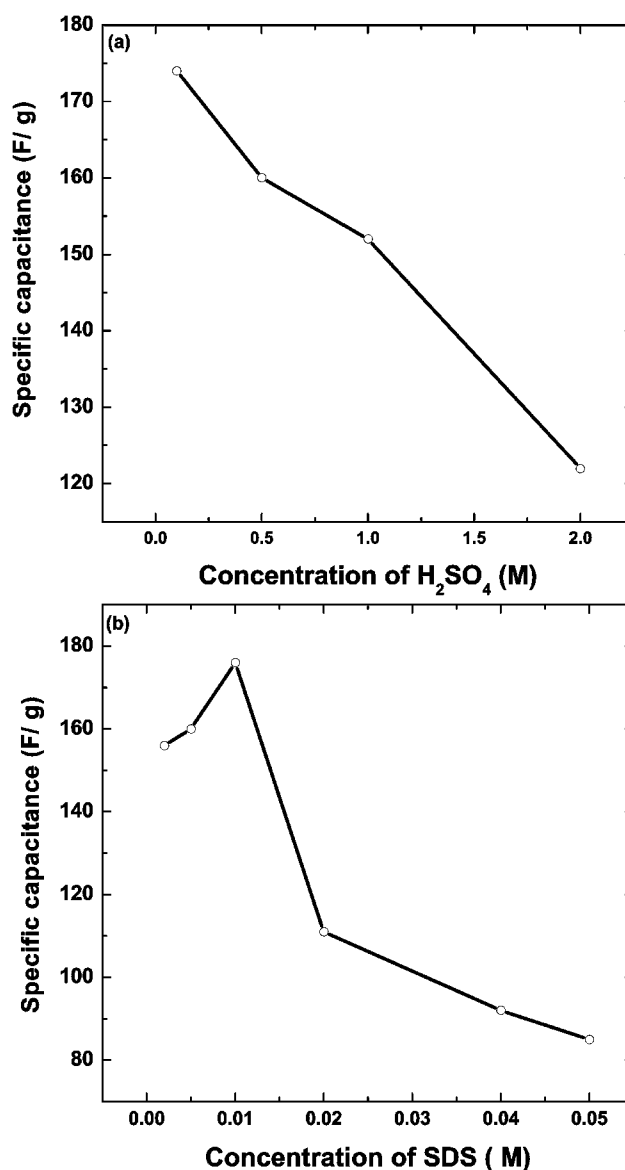


**Figure 5** The effect of potential of deposition of PEDOT/SS on specific capacitance. The mass of the material was 0.6 mg/cm<sup>2</sup>. Charge-discharge current: 0.7 mA/cm<sup>2</sup> (1.17 A/g).



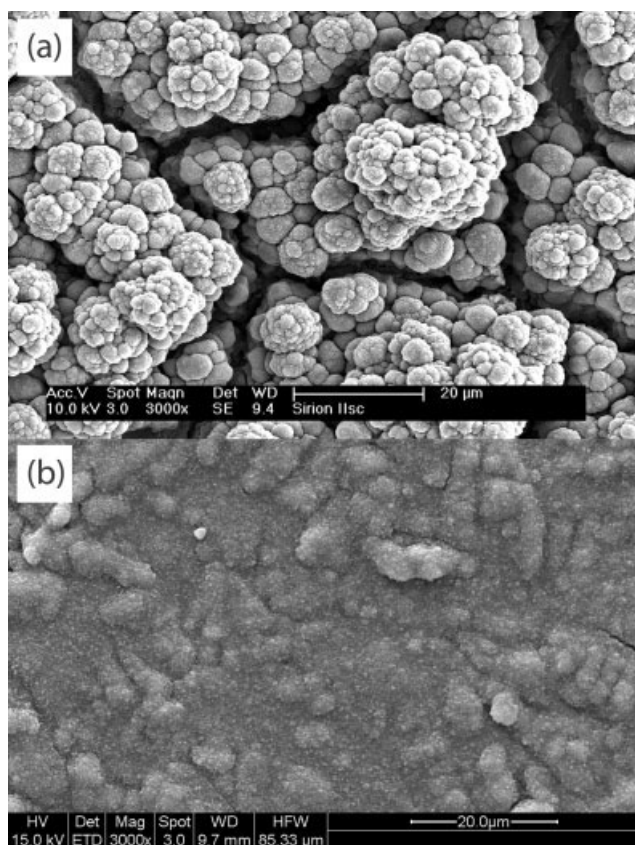
**Figure 6** (a) Cyclic voltammogram recorded at a scan rate of 10 mV/s of PEDOT/SS, (b) galvanostatic charge-discharge curve at 0.7 mA/cm<sup>2</sup> (1.17 A/g of PEDOT/SS in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> mixed electrolyte, and (c) variation of SC during 10 charge-discharge cycles. Mass of the PEDOT was 0.6 mg/cm<sup>2</sup>.

from the data of second cycle in Figure 6(b) is 176 F/g. This value is greater than 103 F/g generally reported for PEDOT in the literature.<sup>9</sup> The experimental conditions in the present work are conducive for obtaining higher values of SC. The variation of SC during the initial 10 charge-discharge cycles is shown in Figure 6(c). There is a substantial decrease in SC from 175 F/g obtained in the second cycle to 120 F/g in the tenth cycle. A considerable decrease in SC of PEDOT based polymer is reported in the literature on repeated charge-discharge cycling.<sup>9</sup>



**Figure 7** (a) Variation of specific capacitance of PEDOT with concentration of H<sub>2</sub>SO<sub>4</sub> used as the supporting electrolyte for PEDOT deposition (mass of PEDOT = 0.6 mg/cm<sup>2</sup>) and (b) dependence of specific capacitance on concentration of SDS of PEDOT/SS. Charge-discharge current: 0.7 mA/cm<sup>2</sup> (1.17 A/g).

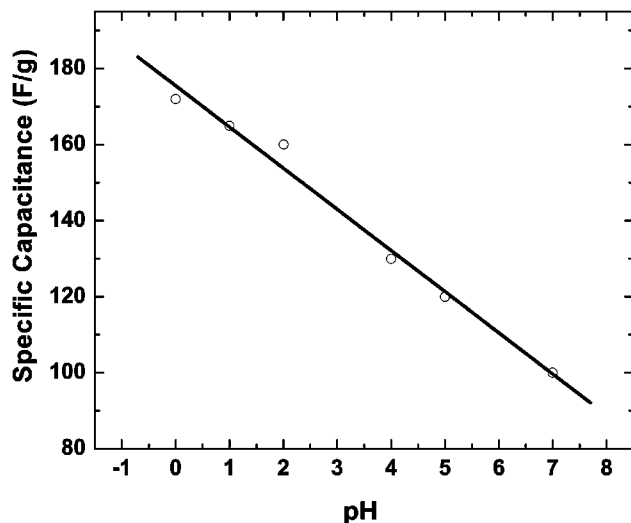




**Figure 8** SEM image of PEDOT/SS electrodes deposited in presence of (a) 0.01M and (b) 0.05M SDS at 0.9 V versus SCE.

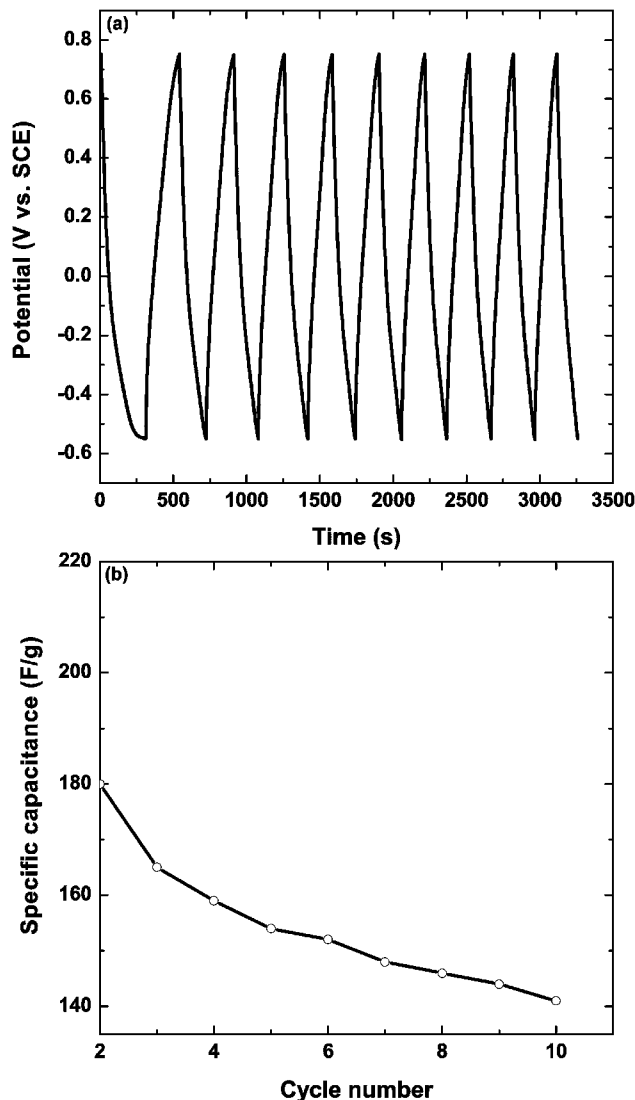
**Influence of concentrations during preparation of PEDOT**

It was intended to examine the influence of concentration of H<sub>2</sub>SO<sub>4</sub> and SDS used for preparation of PEDOT on SC. Several electrodes were prepared by



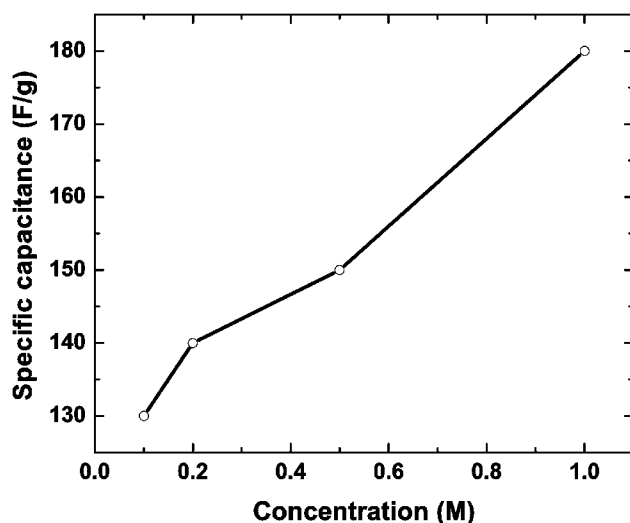
**Figure 9** Dependence of specific capacitance of PEDOT/SS electrode on pH of NaClO<sub>4</sub> electrolyte. The mass of the material was 0.6 mg/cm<sup>2</sup>. Charge-discharge current: 0.7 mA/cm<sup>2</sup> (1.17 A/g).

varying the concentration of H<sub>2</sub>SO<sub>4</sub> from 0.1 to 2M and keeping the concentration of SDS as 0.01M. For each electrode, the mass of the PEDOT was 0.6 mg/cm<sup>2</sup>. The electrodes were subjected to charge-discharge cycling in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> electrolyte, and the variation of SC with H<sub>2</sub>SO<sub>4</sub> concentration is shown in Figure 7(a). There is a steady decrease in SC from 175 F/g for the PEDOT/SS electrode prepared in 0.1M H<sub>2</sub>SO<sub>4</sub> to about 120 F/g for the electrode prepared in 2M H<sub>2</sub>SO<sub>4</sub>. Thus 0.1M H<sub>2</sub>SO<sub>4</sub> was used for preparing PEDOT/SS electrodes for rest of the studies. In a similar way, PEDOT/SS electrodes were prepared in 0.1M H<sub>2</sub>SO<sub>4</sub> by varying the concentration of SDS from 0.001 to 0.05M, and SC values were measured in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> mixed electrolyte. The variation of SC with



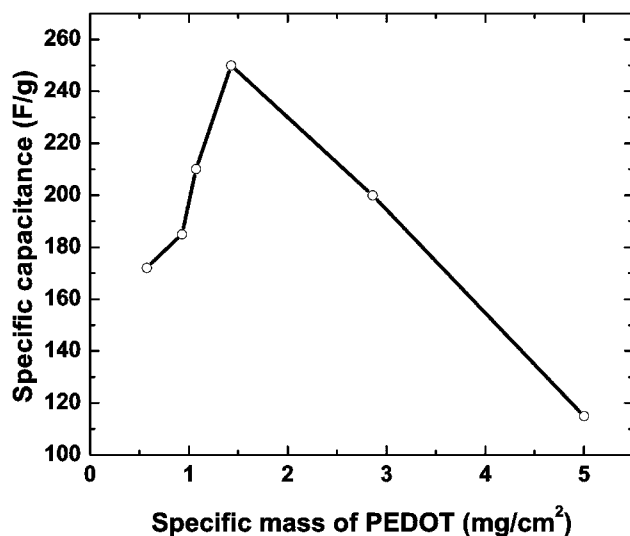
**Figure 10** (a) Galvanostatic charge-discharge curve at 0.7 mA/cm<sup>2</sup> of PEDOT/SS in 1M oxalic acid and (b) variation of SC during 10 charge-discharge cycles. Mass of the PEDOT was 0.6 mg/cm<sup>2</sup>.





**Figure 11** The effect of concentration of oxalic acid on the specific capacitance of PEDOT/SS electrode. The mass of the PEDOT was  $0.6 \text{ mg/cm}^2$ .

concentration of SDS is shown in Figure 7(b). A maximum SC of  $176 \text{ F/g}$  is obtained when SDS concentration is  $0.01 \text{ M}$ . There is a decrease in SC either by decreasing or increasing the concentration of SDS from  $0.01 \text{ M}$ . From SEM micrographs (Fig. 8), it is seen that there is a considerable change in morphology by increasing the concentration of SDS. The PEDOT/SS electrode prepared in  $0.1 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M SDS}$  has smooth surface [Fig. 8(b)] and the electrode prepared in  $0.1 \text{ M H}_2\text{SO}_4 + 0.01 \text{ M SDS}$  has globules indicating higher surface area [Fig. 8(a)]. Thus a decrease in porosity and surface area by increasing the concentration of SDS accounts for a decrease in SC of PEDOT/SS electrodes [Fig. 7(b)].



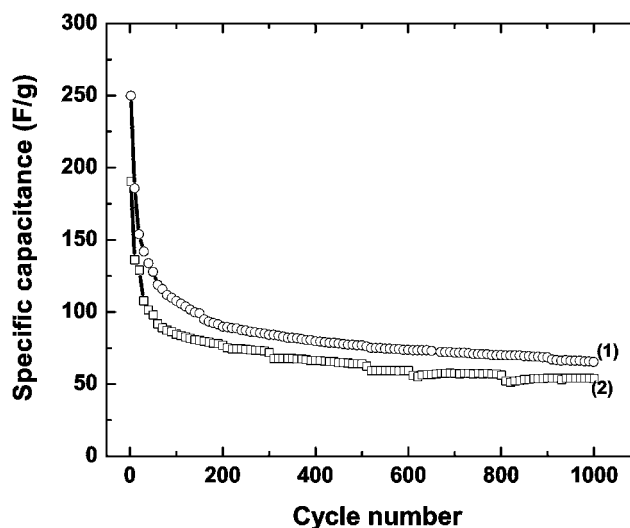
**Figure 12** Dependence of specific capacitance of PEDOT in  $1 \text{ M}$  oxalic acid on its specific mass.

### Influence of pH during capacitance studies

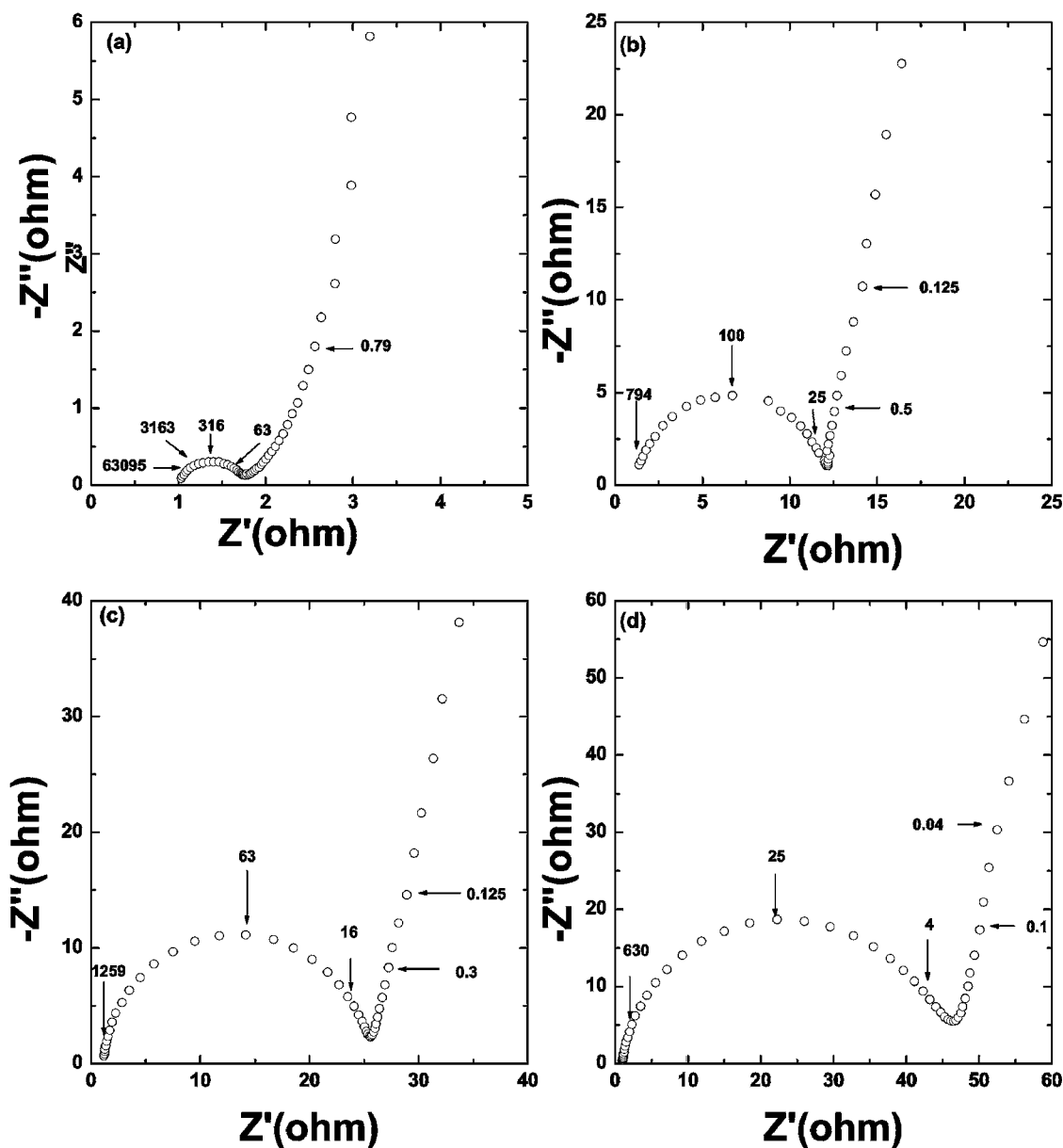
The influence of pH of  $\text{HClO}_4 + \text{NaClO}_4$  on SC was also examined. For this purpose  $0.1 \text{ M HClO}_4 + 0.3 \text{ M NaClO}_4$  was prepared and pH was adjusted to the required value by adding dilute NaOH. The variation of SC of a PEDOT/SS electrode with pH of the electrolyte is shown in Figure 9. There is a linear decrease in SC with pH of the electrolyte. This is due to the decrease in electronic conductivity of the polymer with increase in the supporting electrolyte.

### Capacitance studies in oxalic acid electrolytes

Subsequent to the earlier studies, it was intended to examine the effect of nature of the electrolyte on SC of PEDOT with an intention to obtain a maximum SC. Results of preliminary experiments on various supporting electrolytes suggested that an aqueous solution of oxalic acid produced has higher capacitance values than the  $0.1 \text{ M HClO}_4 + 0.3 \text{ M NaClO}_4$  mixed electrolyte. A broad voltammogram with a wide gap between the cathode and anodic parts, similar to the voltammogram recorded in  $0.1 \text{ M HClO}_4 + 0.3 \text{ M NaClO}_4$  [Fig. 6(a)] suggested that PEDOT exhibits capacitance behavior in  $1 \text{ M}$  oxalic acid solution also. The linearity of charge-discharge curves [Fig. 10(a)] without noticeable IR drop between  $-0.5$  and  $0.75 \text{ V}$  indicates suitability of  $1 \text{ M}$  oxalic acid medium for capacitor studies of PEDOT. However, the upper limit of potential in  $1 \text{ M}$  oxalic acid was only  $0.75 \text{ V}$  against  $0.9 \text{ V}$  in  $0.1 \text{ M HClO}_4 + 0.3 \text{ M NaClO}_4$  electrolytes. The charge-discharge curves deviated from the linearity



**Figure 13** Cycle-life data at  $0.7 \text{ mA/cm}^2$  of PEDOT/SS electrode prepared in presence (1) and in absence (2) of the surfactant. In both cases, the specific mass of the material was  $1.43 \text{ mg/cm}^2$ .

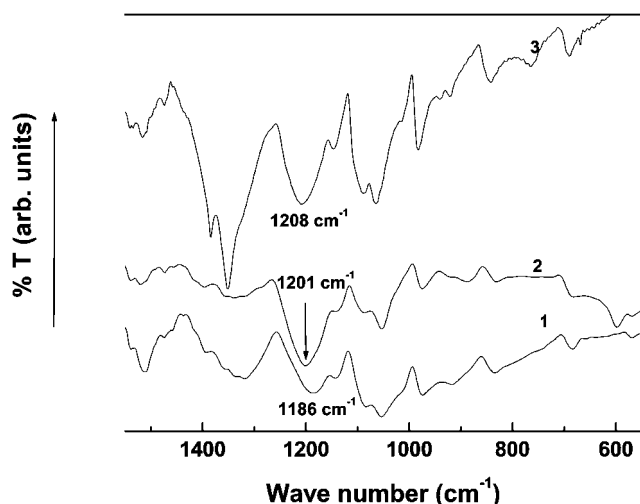


**Figure 14** Nyquist impedance spectra of PEDOT/SS electrode in 1M oxalic acid at 0.5 V (open circuit potential) after (a) 0, (b) 200, (c) 500, and (d) 1000 charge-discharge cycles [Fig. 13 curve (1)]. Frequency (Hz) values for some data points are indicated.

at potentials greater than 0.75 V in 1M oxalic acid, and therefore the upper potential limit was fixed at 0.75 V. It is likely that oxidation of oxalic acid occurs at >0.75 V thus causing deviation from linearity of potential-time data. From the second cycle of the data shown in Figure 10(a), a value of 180 F/g is obtained for SC of PEDOT/SS electrode. This value is nearly the same as the value of SC obtained in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> electrolyte in spite of the fact that the potential range is 1.25 V in 1M oxalic acid against 1.4 V in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> electrolyte. Nevertheless, the stability of SC on repeated charge-discharge cycling is slightly better in oxalic acid [Fig.

10(b)] than in 0.1M HClO<sub>4</sub> + 0.3M NaClO<sub>4</sub> [Fig. 6(c)]. Therefore, the rest of the studies were conducted in oxalic acid electrolytes.

In an attempt to optimize the concentration of oxalic acid for obtaining the highest possible SC, experiments were conducted in the concentration range from 0.1 to 1.0M. The value of SC increased with an increase in concentration of oxalic acid as shown in Figure 11. A maximum capacitance was obtained in 1.0M oxalic acid. As the solubility of oxalic acid in water is limited close to about 1.0M, experiments could not be carried out in oxalic acid solutions of higher concentrations.



**Figure 15** FT-IR spectrum of PEDOT (1) before cycling, (2) after 100 cycle, and (3) after 1000 cycle.

### Influence of thickness of PEDOT

Although the electrodeposited PEDOT films are found to have globular morphology (Fig. 4) the porosity does not exist throughout the thickness of the film. Consequently, the electrolyte cannot penetrate into the interior of the film. To examine the most appropriate thickness for obtaining a maximum possible efficiency, PEDOT/SS electrodes with varying mass of PEDOT were prepared and SC was measured in 1.0M oxalic acid solution (Fig. 12). The SC increases from about 180 F/g at 0.6 mg/cm<sup>2</sup> of PEDOT to about 250 F/g at 1.5 mg/cm<sup>2</sup>. By further increasing of specific mass, there is a decrease in SC to about 110 F/g at 5 mg/cm<sup>2</sup>, due to decrease in efficiency of utilization of active material. Thus, the appropriate specific mass of PEDOT is 1.5 mg/cm<sup>2</sup> to obtain a maximum value of SC under the present experimental conditions.

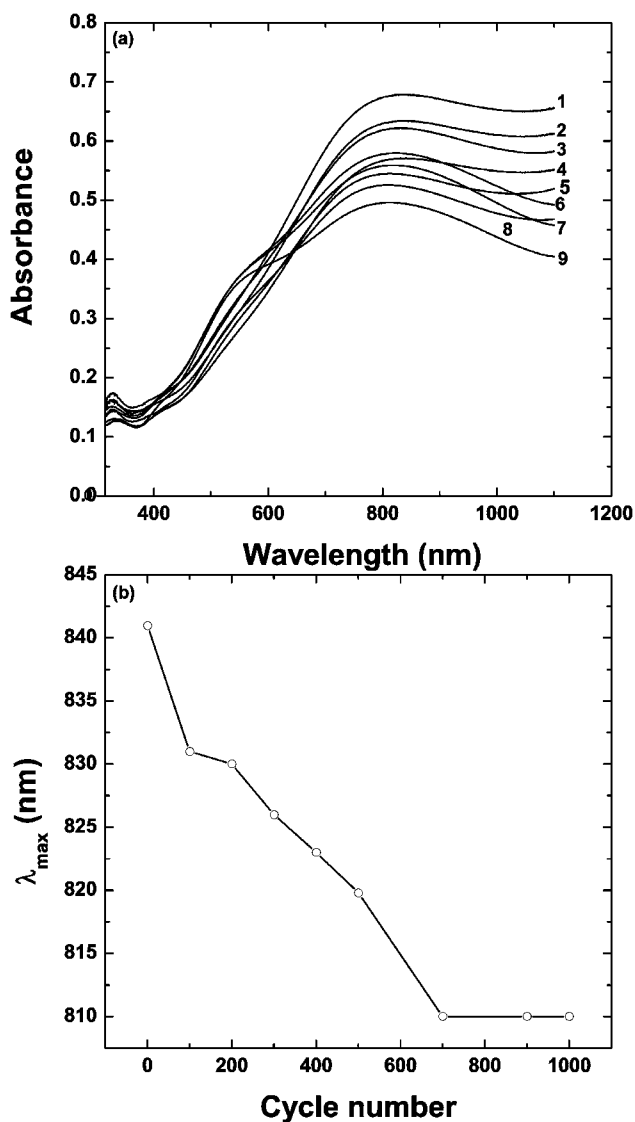
### Extended cycling and impedance measurements

PEDOT/SS electrodes were subjected to an extended charge-discharge cycling and the cycle-life data are shown in Figure 13. For the purpose of comparison, data obtained with a PEDOT/SS electrode prepared without SDS are also shown in Figure 13. Although the initial value of SC is as high as 250 F/g [curve (1) in Fig. 13], there is a steep fall in SC within about 50 charge-discharge cycles. Thereafter, the SC remains nearly constant at about 100 F/g. The SC of the electrode prepared without SDS [curve (2) in Fig. 13] is lower throughout the test.

During the extended cycle-life test [Fig. 13 curve (1)] electrochemical impedance of the PEDOT/SS electrode was measured at a few intervals of cycling. The Nyquist data of impedance recorded at 0, 200, 500, and 1000 cycles are shown in Figure 14. All plots

contain semicircles at high frequency region. The semicircle represents the resistance of the polymer and the linear spike corresponds to diffusion-limited Warburg or pseudocapacitance of the polymer.<sup>25</sup> The diameter of the semicircle, which is equal to the resistance of the polymer, increase from 0.75  $\Omega$  before cycling to 11  $\Omega$  after 200 cycles, 25  $\Omega$  after 500 cycles, and 46  $\Omega$  after 1000 cycles. Thus there is a rapid increase in resistance of PEDOT (nearly 60 times) on subjecting to 1000 charge-discharge cycles.

In a separate experiment, surface morphology of a PEDOT/SS electrode was examined after it was subjected to 500 charge-discharge cycles. The morphology of cycled electrode remained the same as an uncycled electrode, and it was similar to the SEM



**Figure 16** (a) The effect of cycling on UV-vis spectra of PEDOT/ITO glass of (1) before cycling, (2) after 100, (3) after 200, (4) after 300, (5) after 400, (6) after 500, (7) after 700, (8) after 900, and (9) after 1000 cycles and (b) shift of  $\lambda_{\max}$  with cycle number.

shown in Figure 4(a). Thus changes occurring in electrochemical properties of PEDOT film due to charge-discharge cycling are not related to its morphological changes.

### Spectroscopy

The FTIR spectra of PEDOT are shown in Figure 15 [curve (1)]. The bands around 1348 and 1514  $\text{cm}^{-1}$  are due to stretching of C—C and C=C in thiophene ring and stretching of thiophene ring, respectively.<sup>16</sup> Bands at around 1186, 1140, and 1053  $\text{cm}^{-1}$  are originated from stretching of C—O—C bond in the ethylene dioxy group. Vibrations of C—S bond in the thiophene ring are also seen 977, 833, and 682  $\text{cm}^{-1}$ . In Figure 15, the FTIR spectra after 100 cycles [curve (2)] and 1000 cycle [curve (3)] are also shown. With the increased cycling, there is shift of the 1186  $\text{cm}^{-1}$  to higher wave numbers, while there is no change in the rest of the main bands.

For the purpose of recording UV-vis spectra, a thin layer of PEDOT was deposited on an ITO coated glass plate and the electrode was subjected to charge-discharge cycling. The electrode was removed from the oxalic acid electrolyte, washed, dried, and spectra were recorded at periodic intervals of cycling. The spectra are shown in Figure 16(a). The band at 840 nm [curve (4) in Fig. 16(a)] corresponds to charge-carriers and the 300 nm peak to  $\pi$ - $\pi^*$  transition.<sup>26</sup> With an increase in cycling [curve (2–9) in Fig. 16(a)], there is a decrease in intensity of these two bands. Additionally, a new band at 500 nm appears and increases in intensity. Furthermore, there is a blue shift in the 840 nm band. Variation in wave number ( $\lambda_{\text{max}}$ ) of charge-carrier bands are shown in Figure 16(b).

The spectroscopic studies reflect the structural changes that occur in PEDOT as a result of electrochemical charge-discharge cycling. The shift in charge-carrier band suggests an increase in electronic resistance of the polymer on cycling, thus supporting the impedance data.

### CONCLUSIONS

The PEDOT/SS electrodes prepared in 0.1M  $\text{H}_2\text{SO}_4$  in presence of a surfactant, sodium dodecylsulphate (SDS), are found to yield higher specific capacitance (SC) than the electrodes prepared from neutral aqueous electrolyte. The influence of various experimental variables such as concentration of  $\text{H}_2\text{SO}_4$ , concentration of SDS, potential of deposition, and nature of supporting electrolytes used for capacitor studies are studied. Specific capacitance values as high as 250 F/g in 1M oxalic acid are obtained during initial stages

of cycling. However, there is a rapid decrease in SC on repeated charge-discharge cycling. Spectroscopic data reflect structural changes in PEDOT on an extended cycling, and also as increase in its electronic resistance.

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