Electrochemical polymerization and characterizations of polypyrrole in aqueous micellar medium

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ABSTRACT

Polypyrrole (PPy) was electrochemically deposited by cyclic voltammetry onto glassy carbon electrode from acidic micellar solution. The effect of acidic micellar solution on capacitive property were characterised using cyclic voltammetry. The specific capacitance of the PPy reached the value of 353.37 F g^{-1}after cycling in 0.5 M H_2SO_4 at 10 mVs^{-1}. Presence of sodium dodecyl sulphate (SDS) decrease the polymerization potential andaffect the microstructure of the obtained polymer and the pull of SDS anion, from the polymer backbone, during dedoping change the morphology of the obtained polymer, which enhanced the polymer specific capacitance. Also, the surface morphology of the resulting polymer films was characterised by scanning electron microscope.

Keywords: Conducting polymers; Pyrrole; Electron microscopy; Electrochemical properties; Supercapacitor.

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INTRODUCTION

Polypyrrole (PPy) is one of the first discovered and one of the most studied conducting polymers for application in energy storage (ES) and production systems[1-5].The interest in the application of PPY in ES is related to low cost and high conductivity of this material, which exhibits high specific capacitance in aqueous electrolytes [6,7]. The high specific capacitance of PPY is attributed to redox reactions, which allow charge storage in the bulk of the material. Many investigations have been conducted with the objective to utilize high theoretical specific capacitance [8] of PPY(620 F g^{-1}) in ES and avoid problems related to the slow diffusion of ions within the bulk of the electrode[2].In general, the resistance due to movement of ions through pores is less than the resistance due to redox conduction of electrons through the polymer layers. The role of morphology of the layer and the nature of charge carrying ions is important in defining the relative values of these two resistance values. Many studies highlighted the advantages of PPy films, deposited on high surface area current collectors and on composite material for improving the electrochemical performance of PPY supercapacitors [9-11]. The microstructure of PPy films is a most important factor affected the diffusion of ions within the bulk of the electrode. It is still surprisingly challenging to fabricate any desired nanostructure of PPy [12]. Most common approaches for the fabrication of diverse nanostructures of PPy include hard and soft templating methods. However, each of these categories has its own drawbacks. The hard template approach needs additional template removal treatments which can damage the original nanostructure whereassoft template methods involve the use of doping polyanions, surfactants etc. which raise environmental concerns [13,14]. The electropolymerization technique allows the pyrrole monomer, dissolved in a solvent, containing an anionic dopant, to be oxidized at the electrode surface by the applied anodic potential, forming a polymer film with anionic dopant incorporated into the polymer to ensure electrical neutrality of the resulting film. The effect of anionic dopant is one of the keys factors affecting the electrochemical performance of PPy.

Here we approach towards the control of conducting PPy microstructures through the use of larger dopants anions, such as anionic surfactant which added during the electrochemical polymerization. The use of sodium

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dodecylsulfate (SDS) as larger dopants anions create novel nanostructures for PPy film after depoing process and has been shown to exhibit unusual electrochemistry.

MATERIALS AND METHODS

2.1. Materials
The pyrrole monomer (99 %) was purchased from Aldrich, analytical grade H_2SO_4 (98%) and sodium dodecyl sulphate (SDS) were purchased from El-Nasr Pharmaceutical company, Egypt. Deionized water with resistivity of 18.2 MΩ cm was used to prepare all the solutions used in this work. The monomer was purified prior to use and all the other reactants were used as received.

2.2. Voltammetric Measurements
Cyclic voltammetric (CV) was made using a using VSP Potentiostat/galvanostat (BioLogic) connected to a computer with EC-Lab software. The electrochemical cell was a conventional three electrodes with a platinum mesh as the counter electrode, glassy carbon electrode as working electrode and SCE reference electrode. The electrolyte used in all the electrochemical experiments, was H_2SO_4. A thin film of conducting polypyrrole was grown under potentiodynamic conditions from a solution containing the 50mM pyrrole monomer in 0.5 M H_2SO_4 using 0.07M SDS and also without using SDS. The solution from which the film was generated was then replaced with a fresh electrolyte solution of 0.5M H_2SO_4, in which all cyclic voltammetry experiments were then performed. The potential window used for the polymerization and CV characterization studies was -0.8V to 0.9 V vs. SCE. Prior to use, the solution was purged with nitrogen gas for 20 min and maintained over during all the experiments.

The microstructures were examined with a high-resolution transmission electron microscope (HRTEM, FEI Philips Tecnai G2 S-Twin operated at 200 keV, Holland)

RESULT AND DISCUSSION

3.1. Electropolymerization of pyrrole using cyclic voltammetry.
3.1.1. Electropolymerization of pyrrole in presences of SDS.
Fig. 1 shows a multisweep cyclic voltammograms of GC electrode in 0.5 M H_2SO_4 and 50 mM pyrrole monomer in presence of 70 mM SDS as surfactant. The polymer films were deposited at a glassy carbon electrode using successive cycling between -0.8 to 0.9 V vs. SCE at 50 mV s^{-1}. From Fig.1a we can see that all CVs show redox peaks characteristic for the polymer formation and the current increases with each consecutive cycling, which indicates an increase in the amount of deposited polymer.

The polymerization current decrease with each consecutive cycling, which indicates a decrease in the rate of electrochemical polymerization due to increase of thickness of the obtained polymer film, where be more resistive, at the same time the total amount of formed polymer was increase.

The oxidation potential of pyrrole monomer was determined from the first cycles as 0.58 V vs. SCE, Fig. 1b, and start to increase in successive cycle, that indicate the obtained polymer film became more resistive and may be some sort of degradation was happened. Also as shown in Fig. 1bthe trace-crossings appear on the reverse sweeps of the first cycle in voltammograms and increase with cycle number. This interpreted as the additional anodic current observed in the reverse sweep results from slow follow-up reactions occurring in the diffusion layer in front of the electrode, that in case of E(CE)$_n$ reactions involve slow rate constants for chemical step [15],slow second-order coupling steps between dimmers and subsequent slow elimination of protons explain the observed trace-crossings. The electrocatalytic effect of SDS was characterized by a significant decrease of the pyrrole oxidation potential in the micellar medium relative to aqueous solutions. This behaviour might result from strong electrostatic interactions occurring between the formed radical cations and the dodecylsulfate anions during the polymerization process. The presence of the hydrophobic (micellar core) and hydrophilic interface in normal micellar solution may induce an orientation of reactants in micelles and on the working electrode surface, which in turn affects the regioselectivity of reaction and reaction kinetics [16]. Also, SDS lead to the reorientation of the growing polymer chains and make it more expended at the same time give chance to chains arrangement, that reflected on the surface morphologies of the as-prepared PPY-SDS film, Fig. 4a, where the sample was homogeneous with a cleavage surface and appear like a wrinkled paper in the structure. Also, SDS may be strongly bounded to formed polymer matrix and act as plasticizer for the obtained polymer, so smooth film were formed, and we conclude it formed from many stacking layers with very low porosity.

We suggested that under the influence of the electric filed the hydrophilic interface in micelles containing pyrrole will be attracted and oriented at the anode surface as is illustrated in Fig. 3. This facilitated the accumulation of

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pyrrole cation at the anode surface and hence decreasing polymerization potential as shown in Fig.1.On the other hand, the competitive adsorption of SDS anion on the electrode surface during oxidation decrease the area covered by monomer on the electrode surface which decrease the total polymerization charge from 73.83 mC in absence of SDS to 40.66 mC in presence of SDS. In the case of polymer-surfactant interactions, individual surfactant molecules and polymer chain interaction or polymer aggregate may occur. This leads to a complex formation between the polymer chain and micelles or pre-micellar aggregates.
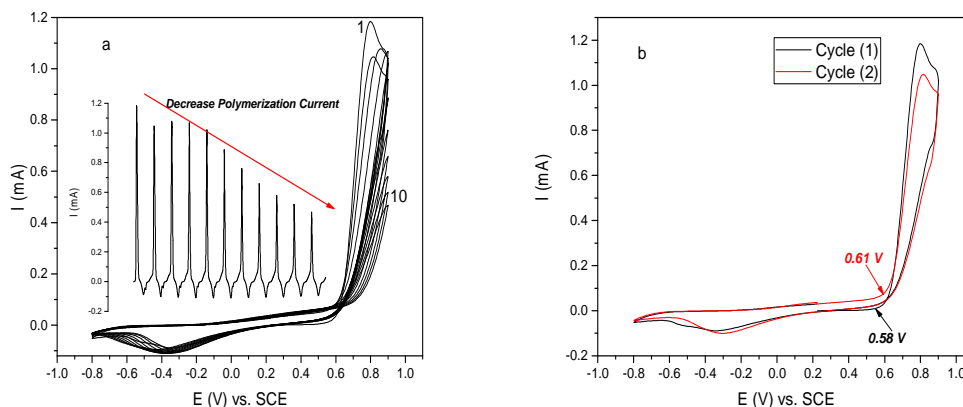

Figure 1.Cyclic voltamograms at 50 mV s^{-1} for GC electrode in 70 mM SDS and 0.5 M H$_2$SO$_4$ and containing 50mM Py (a) all cycles (b) first and second cycles

3.1.2. Electropolymerization of pyrrole without of SDS.

Fig. 2 shows a multisweep cyclic voltammograms of GC electrode in 0.5 M H$_2$SO$_4$ and 50 mM pyrrole monomer. The polymer films were deposited at a glassy carbon electrode using successive cycling between -0.8 to 0.9 V vs. SCE at 50 mV s^{-1}. From Fig.2 we can see that all CVs show redox peaks characteristic for the polymer formation and the current increases with each consecutive cycling, which indicates an increase in the amount of deposited polymer. The shape of the voltamogram different from that in case of polymerization in presence of SDS surfactant, where the polymerization potential was increase in the first cycle to 0.7 V vs. SCE, also the polymerization current increase in the first three cycle then start to decrease with successive cycling as shown in Fig.2 and there is no trace crossing noted during the polymerization. The surface morphologies of the as-prepared PPy films were evaluated by SEM measurement, Fig. 4c, the images reveal that, the surface morphology is more rough and consisting of different sizes of PPy clusters over the surface of the substrate which is responsible of porous structure of the electrode.

From the above mentioned results we can concluded that the presence of SDS decrease the polymerization potential via increasing the solubility of the monomer and facilitate the way for monomer to riches the anode surface via electrostatic attractions between its anionic head and positively charged anode. At the same time, SDS adsorbed on the anode and decrease the available surface for monomer oxidation so, the net polymerization charge calculated from the CVs were 42.17 mC and 73.84 mC in absence of SDS.
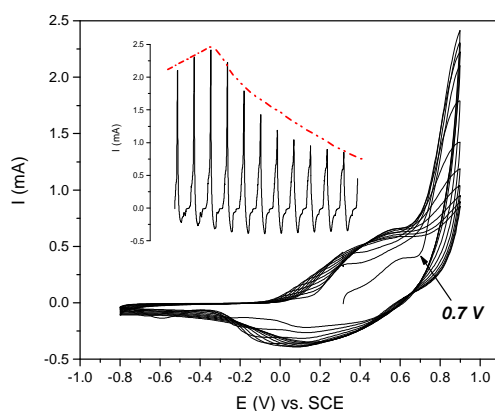

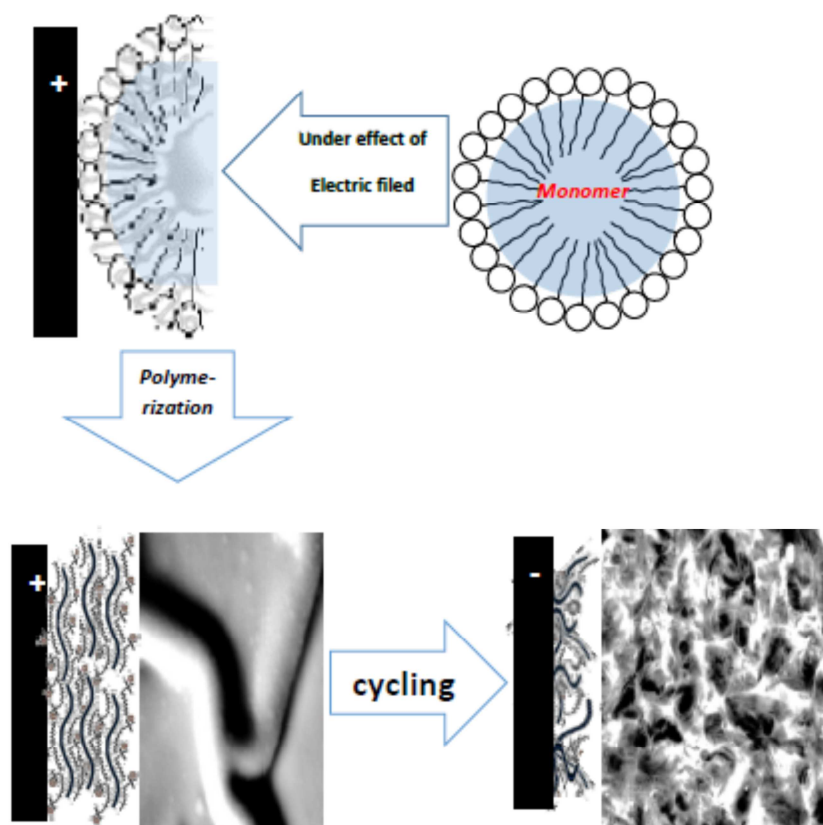**Figure 2. Cyclic voltamograms at 50 mV s^{-1} for GC electrode in 0.5 M H$_2$SO$_4$ and containing 50mM Py**

Figure 3.The hydrophilic interface in micelles containing Py will be attracted and oriented at the anode surface and the as prepared PPy-SDS and after cycling
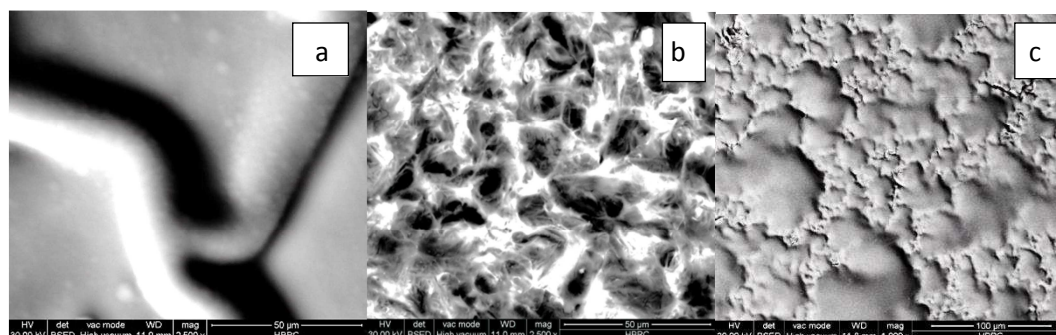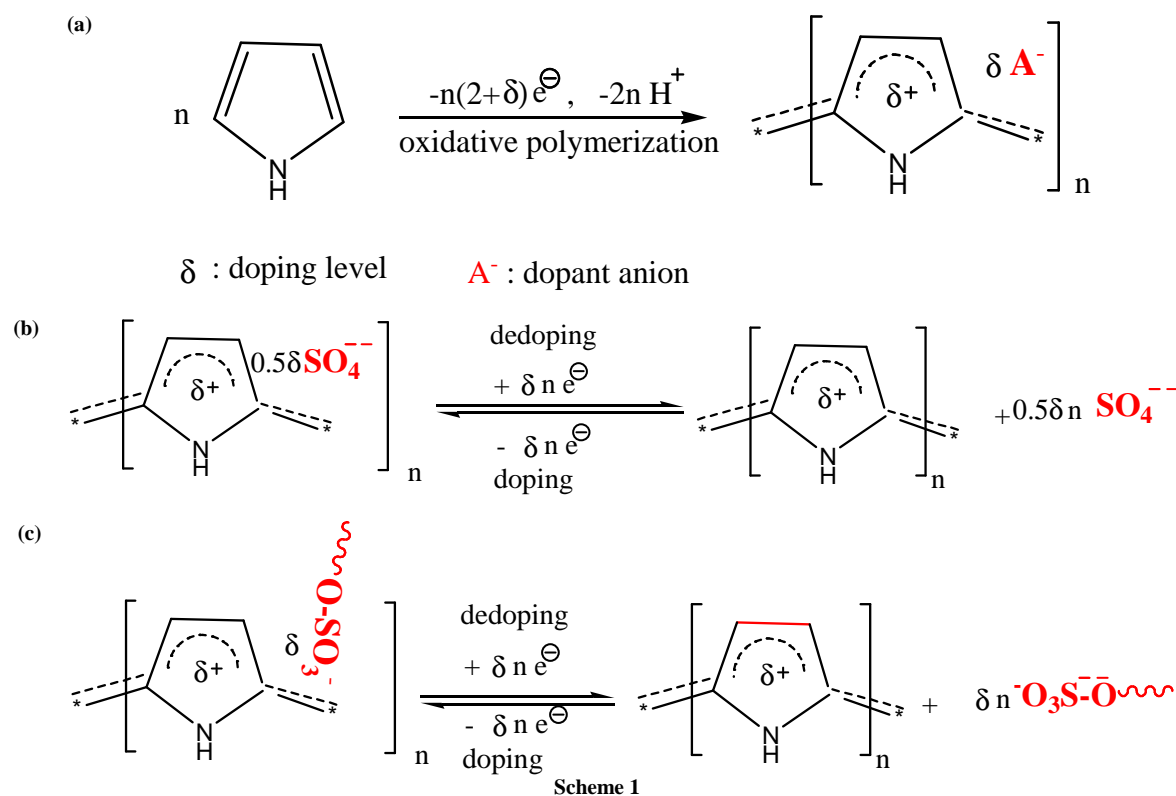

Figure 4.Scanning electron micrographs of (a) as prepared PPy-SDS (b) PPy-SDS after cycling and (c) PPy prepared from surfactant free solution

3.2. Electrochemical Characterizations.
Cyclic Voltammetry studies.

The effect of the counterion used during electropolymerisation on the properties of the polymer has been widely discussed in the literature [17-19], the as-formed polymers are molecular composites containing a cationic polymer backbone, with accompanying "dopant" anions for maintenance of charge neutrality, scheme 1(a-c). During electrochemical synthesis, as a result of simultaneous oxidation and polymerization of the pyrrole monomer, the conducting form of the polymer with a delocalized positive charge on the π-electron system is formed. Anions from the electrolyte solution in which the monomer has dissolved are incorporated into the polymer in order to achieve electroneutrality. In our case there are two anions present sulphate anion, scheme 1b, and dodecylsulfate anions, scheme 1c,much larger size, which dissolve pyrrole monomer with its hydrophobic chain and can be incorporated into PPy matrix as dopant subsequently [20].

(a)

$-n(2+\delta)\,e^{\ominus}$, $-2n\,H^{+}$

oxidative polymerization

$\delta\,A^{-}$

δ : doping level A^{-} : dopant anion

(b)

$0.5\delta\,SO_4^{--}$

dedoping
$+\,\delta\,n\,e^{\ominus}$
$-\,\delta\,n\,e^{\ominus}$
doping

$+0.5\delta\,n\ SO_4^{--}$

(c)

$\delta\ ^{-}O_3S\text{-}O$

dedoping
$+\,\delta\,n\,e^{\ominus}$
$-\,\delta\,n\,e^{\ominus}$
doping

$+\ \delta\,n\ ^{-}O_3S\text{-}\bar{O}$

Scheme 1

The electrochemical behavior of the PPy films deposited electrochemically from aqueous solution containing surfactants and without surfactant was studied in 0.5 M H_2SO_4 aqueous solution. Fig. 6a, represent the cycling of the PPy-SDS film in H_2SO_4 aqueous solution between -0.8 V to 0.9 V vs. SCE, as shown, there is no doping peak in the first cycle, Fig. 6a black line, that mean the oxidation of as formed PPy-SDS is difficult, that may attributed to high size of the surfactant alkyl chain, but also because of the presence of polar and apolar extremities of its molecule, the former being compatible with the charged(oxidized) form of the molecule, and the latter with the neutral backbone [21].The obtained polymer film doped with large amount from SDS anion which dissolved by its hydrophobic part in the polymer backbone at the same time make some sort of separation between positive charge along polymer backbone lead to more stabilization for the doping state of the obtained polymer, also, neutralized the positively charged polymer cation by its anionic part, which make the SDS anion highly bonded with the polymer. As a results, the ejection of SDS anion from the polymer matrix during the polymerization using cyclic voltammetry, is very difficult so there is no doping where noted for the as prepared polymer in the first cycle. The dedoping peaks of first cycle B1 and B2, Fig. 6a Blackline, has high charge, -6.21 mC, the dedoping peaks B1 may be attributed to pull of SDS anion from the obtained PPy-SDS composite and peak B2 with more negative potential attributed to an up-take of Na^+ cations [22-24],under the influence of the reduction process. The dedoping of a very large anion such as SDS anion, scheme 1c, in the first cycle, lead to convert the morphological structure of as prepared PPy-SDS from homogeneous with a cleavage surface, Fig. 4a, to flakes porous interconnected structures with fibre formation, Fig. 4b, which promote the efficient contact between the active material and the electrolyte, providing many active sites for electrochemical reactions. Structures with porosity and interconnectivity supply additional accessible space for ions, while maintaining sufficient conductivity for solid-state electronic transfer to improve the electrochemical capacity. This type of structure provides a short diffusion path length to both ions and electrons and, also sufficient porosity for electrolyte penetration to increase charge/discharge rates, so facelifted the doping-dedoping process using small anion such as SO_4^{--}, scheme 1b. At second cycle the very high doping process started, compared to the first cycle, the doping peak O where at 0.18 V vs SCE and the corresponding depoing R peak where at -0.2 V vs SCE. In case of PPY film obtained from electropolymerization at the same previous conduction except the presence of SDS as surfactant, the microstructure and surface morphologies of the as-prepared PPY films is more rough and consisting of different sizes of PPy clusters over the surface of the substrate which is responsible of porous structure of the electrode.

Fig. 6b shows the CV curve of PPY and PPy-SDS at the scan rate 30 mV s^{-1} the redox peaks can be observed for both PPY and PPy-SDS indicating the pseudocapacitive performance for both PPy and PPy-SDS. The couple peak (A/B), at 0.6/-0.02(V) and (O/R) at 0.18/-0.2 (V)for PPy and PPy-SDS, respectively, are attributed to the doping-dedoping process. Notably, the doping peak potential for PPy-SDS much less than that for PPy that indicate, the doping process in case of PPy-SDS much easier than in case of PPy. The specific capacitance generated by PPy-

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SDS sample, 353.37 Fg^{-1}, is much higher than that of the PPy sample, 188.50Fg^{-1} at scan rate 10 mVs^{-1}, that due to the expected high surface area and large pore volume of PPy-SDS results from the pull SDS anions in the first cycle as mentioned before.

Fig 6 (c, d) shows a typical CVs curves at different scan rates for the PPy-SDS and PPy, respectively. It is noteworthy that, the CV curves for both samples doesn't influenced with the increasing of the scan rates even at high scan rate, Moreover, the both samples having the fast current response due to the increasing of redox peaks current with the increasing of the scan rate. Also, with the increase of the scan rate in CV curves for PPy-SDS as shown in Fig. 6c, the cathodic and anodic peaks slightly shifted to the negatively and positively potentials simultaneously, in contrast to the PPy sample and can be attributed to the polarization of the PPy-SDS electrode at high scan rate.Fig7 shows the liner variation of doping peak current and scan rate for both PPy-SDS and PPy, indicating that the redox reaction occurred onto the electrode surface is kinetic-controlled.
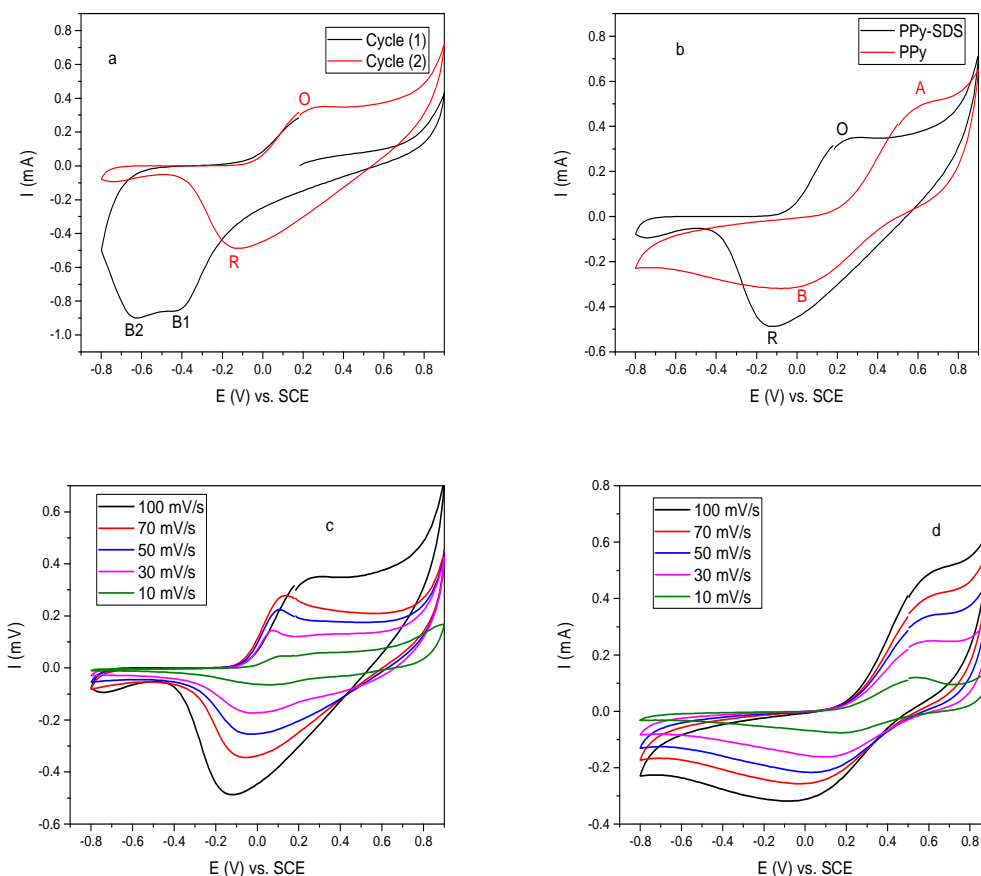

Figure 6. Cyclic voltammograms at 100 mVs^{-1} obtained for polymer films in 0.5 M H$_2$SO$_4$, (a) first and second cycles of PPy-SDS at 100 mVs^{-1}, (b) PPy-SDS and PPy at 100 mVs^{-1} (c) cycling of PPy-SDS at different scan rate and (d) cycling of PPy at different scan rate
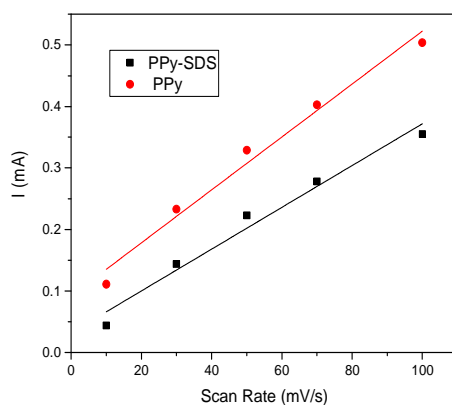

Figure 7.Linear variation of doping peek current and scan rate for both PPy-SDS and PPy

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CONCLUSION

Presence of sodium dodecyl sulphate (SDS) decrease the polymerization potential and affect the microstructure of the obtained polymer and the electro-reduction remove of SDS anion, from the polymer backbone, during dedoping change the morphology of the obtained polymer, which enhanced the polymer specific capacitance. The specific capacitance of PPy-SDS was 353.37 Fg^{-1}, is much higher than that of the PPy sample, 188.50 Fg^{-1} at scan rate 10 mVs^{-1}, that due to the expected high surface area and large pore volume of PPy-SDS results from the pull SDS anions in the first cycle as mentioned before.

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