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Studies on Effect of Aniline during Electrochemical Co-Polymerisation with 3,4-Ethylene dioxythiophene

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ABSTRACT

Co-polymer of polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) PEDOT films was electrochemically prepared by cyclic voltammetry onto Indium Tin Oxide (ITO) electrode in acetonitrile medium. The resulted co-polymer was highly electroactive and well-adhered polymeric film formation on electrode surface. The electrochemical nature of the co-polymer films was investigated through cyclic voltammetry. The effect of pH on the co-polymer films is discussed. The capacitance behaviour of the films is also studied.

1. Introduction

In recent years, poly (3,4-ethylenedioxythiophene) (PEDOT) has attracted significant attention due to its high electro chemical stability. During oxidative polymerization of the monomer EDOT, competition reactions at three and four positions are avoided due to the presence of ethylenedioxy substitute. Thus, EDOT is expected to yield high quality polymers having few defects and high electrochemical stability compared to the thiophene analogues. Several applications have been envisage for systems based on electrochromic devices, e.g. light and overheating protection windows [1-3], mirrors, glazing, smart sunglasses, temperature indicators, safeguarding systems, optical filters, and display panels [4].

Copolymerization is often used to prepare a new polymer with properties that differ from the constituent homopolymers. Generally, the physical and chemical properties of the co-polymer are intermediate between those of the respective homopolymers but significantly distinct from those of the composite and blend. The copolymerizations of EDOT [5-7] and other monomers such as 3-methylthiophene [8-11], 3-hexyl thiophene [12], 3-octyl thiophene [13], pyrrole [14-16] and N-substituted carbazole [17] have been widely reported because of their unique properties.

Among co-polymer modified electrodes, PEDOT-PANI has received a great deal of attention as an electrode material because it exhibits some very interesting properties. Joo-Hee kang et al. constructed an electrochemical device using PANI and PEDOT which showed an extremely fast response time and it is applicable as an optical device [18]. EI-Enany et al. prepared PEDOT-PANI co-polymer by electrochemical method onto a glassy carbon electrode which showed an electrochemical activity towards ascorbic acid oxidation [19]. PEDOT-PANI co-polymer was electrochemically polymerized by Gaber El-Elany which showed an improved capacitance stability [20]. Randriamahazaka et al. synthesize a polymer composite consisting of PEDOT and PANI which showed a good electrical properties [21].

In this study was attempted to synthesize the co-polymer of PEDOT-PANI by electrodeposition on ITO electrodes. The polymer electrodeposition was performed using cyclic voltammetry in aprotic acetonitrile medium. The resulting PEDOT-PANI polymer film was characterized by electrochemical methods.

2. Experimental Methods

2.1 Materials

The monomer 3,4-ethylenedioxythiophene (EDOT), aniline tetra butyl ammonium perchlorate (TBAP) and acetonitrile were purchased from Sigma Aldrich and buffer (pH 1.0 to pH 13.0) from Merck.

The electrochemical polymerization of these monomers was performed on the transparent conductive indium tin oxide (ITO) glass substrates (size 1x1 cm^2, thickness -2.1 mm, resistance-8 Ohm/square, Solaronix, Switzerland) from the monomer solutions. Prior to the polymerization the ITO electrodes were cleaned with acetone under ultrasonication followed by washing with distilled water and drying at 60-70 °C.

2.2 Electropolymerization

All electrochemical experiments were carried out using Electrochemical Workstation model 660C CH instruments. The electrochemical cell was a conventional three electrodes system with ITO plate as working electrode, a platinum mesh as the counter electrode and Ag/AgCl as the reference electrode. TBAP/ACN used as supporting electrolyte.

Poly (aniline-co-3,4-ethylenedioxythiophene) films were electrochemically synthesized in acetonitrile solution containing 0.01 M aniline, 0.01 M EDOT and TBAP/ACN on the ITO substrates by potentiodynamic method (Fig. 1).

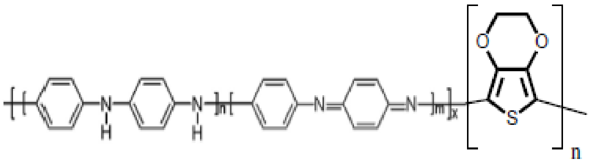

Fig. 1 General Structure of PANI-EDOT

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3. Results and Discussion

3.1 Electrochemical Polymerization of PANI-EDOT

Potentiodynamic electrolysis of aniline and 3,4-ethylenedioxythiophene in acetonitrile medium results in the deposition of a thin well adherent film. When transferred into supporting electrolyte solution the modified electrode shows its characteristic electrochemical activity. Fig. 2 represent the cyclic voltammograms recorded during the electropolymerization of PANI-PEDOT in the potential range from -600 to 1400 mV at scan rate of 50 mVs^{-1}. In the first potential scan an anodic peak appeared at E = 1.03 V, which indicates that aniline undergoes oxidation. The peak current value for this peak is much higher than for pure aniline. In the reverse scan one cathodic peak exhibited at E = 0.13 V. This indicates that subsequent to aniline oxidation, reaction with EDOT occurs. In the second potential scan two anodic peaks at E = 0.38 V and 1.1 V with corresponding cathodic peaks were observed.

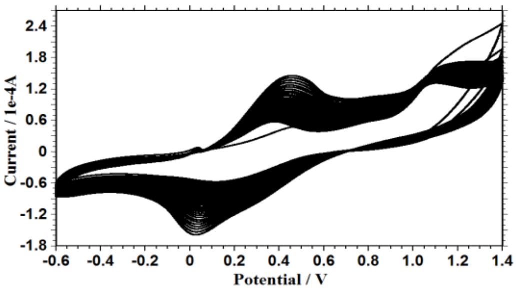

Fig. 2 Cyclic voltamogram of Poly (aniline -co-3,4-ethylenedioxythiophene) in the potential range from -0.6 V to 1.4 V at scan rate of 50 mVs^{-1}

From Fig. 2 all cycles shows redox peaks characteristic for the co-polymer formation and the current also increases with each consecutive cycling, which indicates an increase in the amount of deposited polymer on working electrode surface. At the same time homogeneous and adherent polymer films were deposited on the anode surface, which can be observed on electrode surface.

The anodic and cathodic peaks of this pair shift into positive and negative directions, respectively, with further potential scans. It is important to note that almost all anodic and cathodic peaks that appeared in the second cycle show a shift either to positive or negative potentials with subsequent cycling. Finally two redox pairs are observed. After electrolysis a light golden-brown deposit was observed on the electrode.

3.2 Electrochemical Behavior of Copolymer Films

Fig. 3 shows CVs, recorded in monomer free electrolyte solution, for the copolymer films modified electrodes at various scan rates.

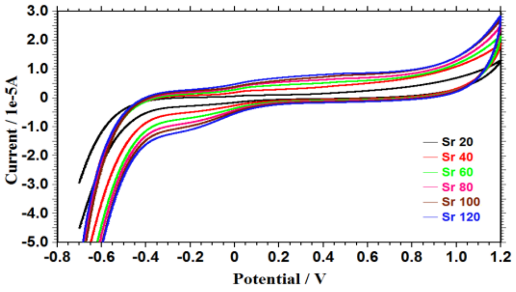

Fig. 3 Scan rate variation for copolymer PANI-EDOT in pH 7

Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. The peak current for a reversible couple is given by Randles and Sevcik equation. The current is directly proportional to concentration and increases with the square root of the scan rate. For these processes, it was assumed that the reactants and products are soluble in solution and the surface processes (adsorption of reactants and products) can be neglected. While studying the electrochemistry of a polymer, a monomer free system should be used. The polymer redox process is quasi-reversible and since the polymer is immobilized at the electrode surface, the redox process is not diffusion controlled. Thus, under these circumstances Randles and Sevcik equation is no longer valid. Instead, according to the theory of immobilized redox centers, the peak current is given by:

$$I_p = n^2F^2 \tau / 4RT$$

where τ is the total amount of reactant initially present at the electrode surface. According to this equation the current peak depends linearly on scan rate. Thus, investigation of peak current intensity with respect to scan rate will indicate the nature of electrochemical process being diffusion controlled or the polymer is well adhered to the electrode surface.

Polymer films prepared by sweeping the potentials from -0.6 V to 1.4 V were washed with electrolyte solution, and their redox switching in monomer-free electrolyte showed a single, well-defined redox process. The current response was directly proportional to the scan rate, indicating that the polymer film was electroactive and adhered well to the electrode. The scan rate dependence of the anodic peak currents shows a linear dependence as a function of the scan rate as expected. This demonstrates that the electrochemical processes are not diffusion limited and are reversible at high scan rates.

Fig. 4 shows plot of peak current vs. scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0 respectively. Fig. 5 shows plot of peak current vs. square root of scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0 respectively. Fig. 6 shows plot of log of peak current vs. log of scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0 respectively.

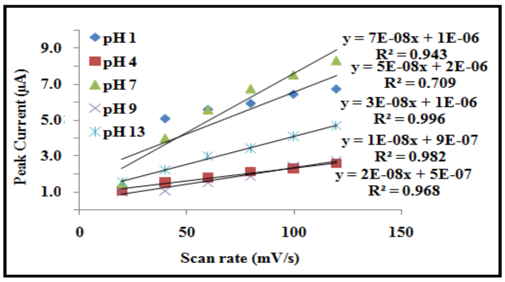

Fig. 4 Plot of peak current Vs scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0

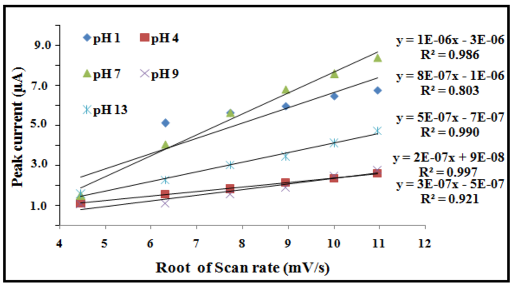

Fig. 5 Plot of log of peak current Vs square root of scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0

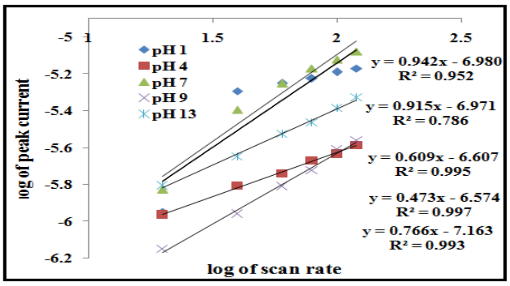

Fig. 6 Plot of log of peak current Vs log of scan rate in pH 1.0, 4.0, 7.0, 9.0 and 13.0

3.3 Effect of pH

The copolymer shows good electrochemical activity only in acidic and neutral medium and its redox activity is rapidly lost if the pH of the solution is increased. In case of the copolymer film the redox activity also decreased slowly when the pH of the solution was increased stepwise from 1.0 to 6.0. This indicates the slow decay in the electrochemical activity of poly (aniline-co-3,4-ethylenedioxythiophene) with increasing pH in the presently studied pH range (Fig. 7). According to the changes as a function of pH value the electrochemical activity of copolymer films decreases more quickly as the pH of the electrolyte solution is increased from 8.0 to 13.0.

On the basis of these results one can concluded very easily that electrolysis of a mixed solution aniline and 3,4-ethylenedioxythiophene resulted in copolymer. Moreover, copolymerization has not only increased the useful potential range of the redox activity of the polymer but also the resulting copolymer shows considerable redox activity at pH 1 and pH 7.

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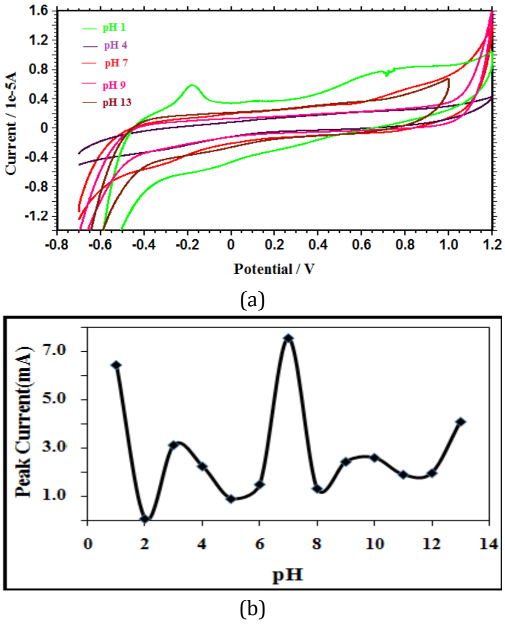

(a)

(b)

Fig. 7 Effect of pH on copolymer PANI-EDOT (a) current vs potential for pH 1.0,4.0,7.0,9.0 and 13.0. (b) Peak current vs pH ; scan rate 100 mV/s

3.4 Capacitance Studies

Capacitance properties of PANI-PEDOT co-polymer was investigated using electrochemical workstation in TBAP/ACN medium. The electrochemical measurements were recorded at room temperature where PANI-PEDOT coated ITO as working electrode pt as counter electrode and Ag/Ag$^+$ as reference electrode in pH 1 to 13. Cyclic voltammetry (CV) responses of PANI-PEDOT in TBAP/ACN as a function of scan rates 20,40,60,80,100 and 120 mV/s coated on ITO electrodes in pH 1 to 13.

The polymers were cycled between -0.8 V and 1.2 V. Generally, the rectangular shape of CV curves (no oxidative or reductive peak), explains the typical behaviour of the electrical double layer (EDL) capacitive behavior is shown in Fig. 8. The specific capacitance values of the supercapacitor have been estimated using CV-measurements and Table 1 shows the calculated value using Eq. (1),

$$C = i/s$$

where's' is the potential sweep rate and 'i' is the specific current. The typical behavior of capacitance as a function of scan rates can also be observed in Table 1. The CVs curves exhibit an identical double layer shape, indicating good charge propagation within the electrodes. When the scan rate increases from 20 to 120, the capacitance value decreases in all pH (1-13) solutions. At the same time the background current value increases when the scan rate value increases. This trend makes the possibility of PANI-PEDOT a good candidate for sensing platform.

Table 1 Capacitance value of PANI-PEDOT

	Capacitance (mF/cm^2)					
pH	Scan rate 20	Scan rate 40	Scan rate 60	Scan rate 80	Scan rate 100	Scan rate 120
1	0.15	0.15	0.13	0.1	0.1	0.1
2	0.15	0.15	0.13	0.112	0.1	0.1
3	0.06	0.0375	0.036	0.045	0.038	0.033
4	0.075	0.045	0.03	0.03	0.034	0.0316
5	0.035	0.02	0.0166	0.015	0.014	0.0133
6	0.04	0.025	0.025	0.0225	0.02	0.0217
7	0.07	0.0375	0.027	0.0225	0.02	0.0183
8	0.04	0.025	0.033	0.031	0.03	0.025
9	0.075	0.05	0.05	0.044	0.04	0.0375
10	0.075	0.05	0.033	0.031	0.03	0.033
11	0.075	0.045	0.033	0.031	0.03	0.029
12	0.05	0.05	0.0417	0.031	0.03	0.029
13	0.1	0.0625	0.05	0.05	0.05	0.05

Plot of capacitance vs. pH is shown in Fig. 9. From this graphs we know that when the pH value increases the capacitance value decreases. For all the scan rates (20, 40, 60, 80, 100 and 120) the capacitance values more or less same in pH 3 to 13 and the values are highest in pH 1 and 2.

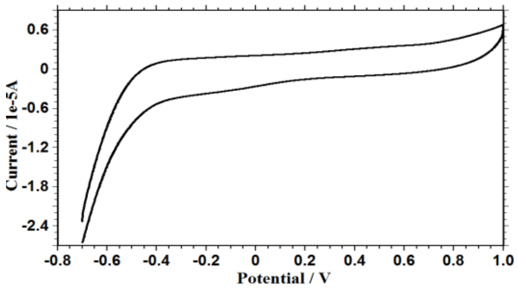

Fig. 8 Cyclic voltammetric behaviuor of PANI-EDOT on ITO at pH 13; scan rate 100 mVs^{-1}

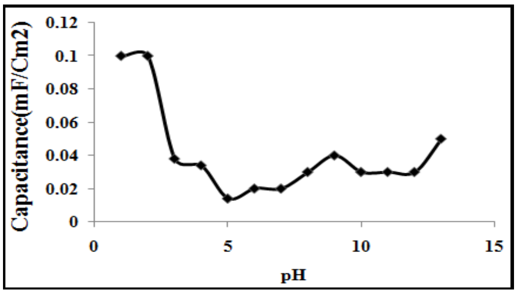

Fig. 9 Plot of capacitance Vs pH; Scan rate 100 mV/s

4. Conclusion

The co-polymer was electrochemically prepared from aniline and 3,4-ethylenedioxythiophene in acetonitrile medium on ITO plate. From cyclic voltammetric studies, good reversible redox behaviour was observed. The prepared co-polymer was tested for its electrochemical behaviour in various pH media. The copolymer film shows good electroactive nature, adherent and stability film on electrode surface. The capacitance behavior of copolymer film is exhibits good. The co-polymer is a good potential candidate as conductor and can be used as electrode material for sensors, capacitors and power sources.

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About the Conference…

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