



# Electrochemical Polymerization of Poly(3,4 ethylenedioxythiophene), Polyanthranilic acid and there co-polymer for Potential Use in detecting Cd(II) and Pb(II) in aqueous solutions

## KEYWORDS

Poly(3,4-ethylene dioxythiophen); Polyanthranilic acid; Cyclic Voltammetry, Electrochemical Polymerization; Cadmium; Lead; Stripping Voltammetry

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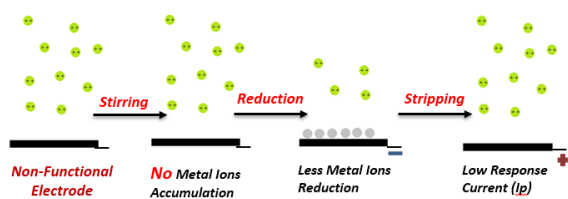
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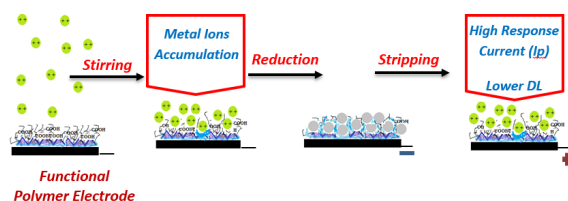
## ABSTRACT

*Poly (3,4ethylenedioxythiophene) (PEDOT), Polyanthranilic (PANA) acid and its co-polymer (PEDOT –ANA) modified electrodes have been prepared for the analysis of cadmium and lead metals cations in formulated samples using Anodic Stripping voltammetry (ASV) technique. The electrodeposition was performed using cyclic voltammetry from acidic solution containing appropriate monomer concentrations and sodium dodecyl sulphate (SDS) as a wetting agent. The structure and the surface morphology of the obtained polymers films were characterized using IR spectroscopy and a scanning electron microscope. In the electrochemical analysis of Pb (II), and Cd (II), very good responses have been observed for both metals with all modified electrodes employed. However, the poly(3,4ethylenedioxythiophene)-co-anthranilic acid modified electrode has resulted in very low detection limits. The Cd (II) detection limits for all the modified electrodes were 3.7  $\mu\text{M}$ , 0.7  $\mu\text{M}$  and 0.6  $\mu\text{M}$  and for Pb (II) were 1.25  $\mu\text{M}$ , 0.625  $\mu\text{M}$  and 0.125  $\mu\text{M}$  at PEDOT, PANA and PEDOT –ANA electrodes respectively.*

## Graphical Abstract



## Schematic representation of the accumulation on Non-Functional Polymer Electrode.



## Schematic representation of the accumulation on Functional Polymer Electrode.

### 1. Introduction

The problem of determination of heavy metal ions in multicomponent natural and industrial objects and new materials engineering remains actual. Highly-sensitive electroanalytical methods, such as stripping voltammetry, allow determining heavy metals at levels of sub  $\mu\text{gL}^{-1}$ . Every day there is an increasing need for the miniaturization of chemical sensors that are capable of operating outside the laboratory environment [1-3]. Electroanalytical approaches using conducting polymer modified electrodes (CPME) for the determination of trace metal ions have received considerable attention [4-6]. The functionalization of conduct-

ing polymers adsorbed on the electrode surface increases the scope of voltammetric analysis for metal ion determination. Various conducting polymer modified electrodes in their doped and undoped forms were used in the anodic stripping voltammetric determination of different heavy metal ions [7-8]. The utilization of newer conducting polymers or copolymers assumes importance in the electroanalytical trace analysis of heavy metals because of the increased surface area and conductivity and enhanced accumulation of the metal ions specifically on the pores of the electrode surface [9]. The conducting copolymers synthesized from polyaniline and EDOT with common pharmaceutical drugs such as dapsone and diclofenac in the absence and presence of surfactants were used already for trace analysis of organic compounds and they resulted in very good responses [10-11]. Thus it was thought of utilizing these newer conducting copolymer modified electrodes for the trace determination of heavy metal ions.

In our work the functionalization of conducting polymers is carried out using co-polymerization of monomers having covalently linked substituent such as carboxylic group to enhance the per-concentration of heavy metal ions on the electrode surface which facilitate the detection of trace metal ions.

### 2. Experimental

#### 2.1. Materials

The monomer 3,4-ethylenedioxythiophene EDOT was purchased from Bayer Company, and anthranilic acid from Aldrich. Sulphuric acid 98%, Sodium chloride, Sodium acetate and sodium dodecyl sulphate (SDS) were provided by El-Nasr Pharmaceutical Chemicals (ADWIC), Egypt. Deionized water (resistivity 18.0 M  $\Omega$  cm) was used for the preparation of all solutions. Metal standard solutions were prepared by diluting the standard stock solution of known concentrations with deionised water or supporting

electrolyte. The working electrode was made from a glassy carbon disk 3.0 mm diameter (SIGRADUR, Germany) by sealing 1.0 cm long x 3.0 mm diameter GC rod in glass tube and connected by copper wire using melted indium (Aldrich). Prior to each experiment the GC electrode was polished with alumina powder (1.0 and 0.5  $\mu\text{m}$ ) to a mirror finish, then sonicated in water to remove any residual alumina particles, dried in air and used immediately.

## 2.2. Electropolymerization and characterization of obtained films

All electrochemical experiments were carried out using VSP Potentiostat/galvanostat (BioLogic) connected to a computer with EC-Lab software. The electrochemical cell was a conventional three electrodes system with a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The aqueous solution used for the polymerization contained 0.5 M  $\text{H}_2\text{SO}_4$  as supporting electrolyte and 70 mM SDS as surfactant. The total monomers concentrations were 50 mM with different mole fraction from EDOT and ANA as shown in table 1 below.

**Table 1.** Solution molar ratios of EDOT and ANA used for the co-polymer electrodeposition.

Monomers	P1(PEDOT)	P2 (PANA)	P3 (PEDOT-ANA)
EDOT/ mM	50.0	0.0	25.0
ANA/ mM	0.0	50.0	25.0
$X_{\text{ANI}}$	1	1	0.5

Prior to each experiment the solution was purged with nitrogen gas for 20 min to remove any dissolved oxygen. Polymerization was carried out at GC electrodes by cycling in the potential range from  $-0.4$  to  $1.2$  V vs. SCE at scan rate of  $50 \text{ mV s}^{-1}$ .

The resulting polymer films were characterized by Infrared spectra in the range  $400\text{--}4000 \text{ cm}^{-1}$  using a Perkin-Elmer 1650 FTIR spectrophotometer. Scanning electron microscopy, SEM, (JEOL 6400) was used to study the film morphology.

## 2.3. Electrochemical measurements

The electrochemical cell was a conventional three electrodes system with a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrodes were PEDOT (P1), PANA (P2) and PEDOT-ANA (P3). A 20 ml of acetate buffer, pH 6, was used in presence of 10 ml NaCl 0.1M as supporting electrolyte. All solutions were purged with  $\text{N}_2$  for at least 3 min prior to analysis in order to remove dissolved  $\text{O}_2$ . Analysis for the dissolved metal ions involved the following steps. First, a negative potential was applied to deposit the contaminant metal on conducting polymer modified electrodes. This was performed for 300 s at a constant potential sufficiently negative of the  $E_0 = -1.2$  V vs. SCE while the solution was stirred. Voltammetry was then used for the positive-going or anodic scan to selectively oxidize each metal with scan rate  $20 \text{ mVs}^{-1}$ . Finally, a constant potential of 0.8 V vs. SCE was applied for 180 s while purging with  $\text{N}_2$  (for convection) after completion of the anodic sweep to ensure full oxidation of all metal deposits.

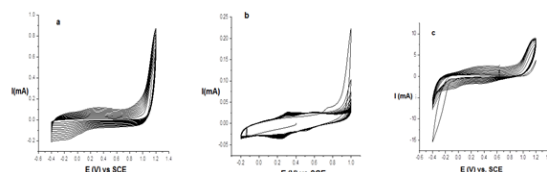
## 3. Results and discussion

### 3.1 Electropolymerization of EDOT and ANA mixed monomers using cyclic voltammetry.

Fig. 1 (a, b and c) shows the electrodeposition of PEDOT, PANA and PEDOT-ANA polymer and co-polymer films, respectively, at a glassy carbon electrode using successive cycling between  $-0.4$  to  $1.2$  V vs. SCE at  $50 \text{ mV s}^{-1}$ . The aqueous solution used for the polymerization contained 0.5 M  $\text{H}_2\text{SO}_4$  as supporting electrolyte 70 mM SDS as surfactant and 50 mM total monomers concentrations. Prior to each experiment the solution was purged with nitrogen gas for 20 min to remove any dissolved oxygen. In Fig.1 (a) CVs show redox peaks that are characteristic for the formation of PEDOT and the current increases with each consecutive cycling, which indicates an increase in the amount of deposited polymer with each cycle. At the same time homogeneous and adherent polymer films were deposited on the anode surface, which can be observed by the naked eye. During the first scan, the polymerization potential of PEDOT on GC is 0.82 V, while on following scans the onset of polymerization shifts significantly to less positive potentials and stabilizes at 0.75 V.

In Fig.1 (b) during the potentiodynamic cycling of the GC electrode in the ANA monomer solution, the cyclic voltammograms consisted of current peaks corresponding to the oxidation of anthranilic acid. However, there was no large increase in the cyclic voltammetric charge in contrast to an increasing charge during the growth of PEDOT in EDOT solution. Additionally, the surface of the GC electrode remained bright suggesting that there was no or very thin polymer film formed on it. But the electrolyte slowly changed to brown colour with continuation of electrolysis. The voltammogram Fig.1 (b) is characterized by a pair of broad current peaks in  $0.5\text{--}0.6$  V range, suggesting the electrochemical activity of PANA. During the first scan, the polymerization potential of ANA on GC is 0.65 V, while on following scans the onset of polymerization shifts significantly to higher positive potentials and stabilizes at 0.72 V which indicated that the PANA film formed is less conducting than the substrate and inhibit the formation of more PANA.

In the case of anthranilic acid and EDOT binary mixture in Fig. 1(c) we chose anthranilic acid to EDOT concentration ratio to be 1:1 (25 mM for each monomer) and cycle between  $-0.4$  and  $1.2$  V vs. SCE. From the CV in Fig. 1(c) the behavior is in between the polymerization of EDOT and that of ANA. However, there was increase in the cyclic voltammetric charge in contrast to an increasing charge during the growth of PEDOT or PANA.



**Figure 1.** Cyclic voltammograms recorded at  $50 \text{ mV s}^{-1}$  for (a) 50 mM EDOT, (b) 50 mM ANA and (c) 25 mM ANA + 25 mM EDOT, in 70 mM SDS and 0.5 M  $\text{H}_2\text{SO}_4$ .

### 3.2 Infrared Spectroscopic studies

The electrodeposited PEDOT, PANA and PEDOT-ANA co-polymers were examined by IR spectroscopy. Figure (2a) represents the IR spectrum of PANA which is in good agreement with previously reported spectrum for PANA [12]. Peak at  $1509 \text{ cm}^{-1}$  correspond to the  $\text{C}=\text{C}$  stretching deformation of quinoid and benzenoid rings respectively.

Peak at  $1689\text{ cm}^{-1}$  is due to stretching vibration of  $\text{C}=\text{O}$  of  $-\text{COOH}$  group. Peak at  $1383\text{ cm}^{-1}$  is assigned to the C-N stretching of the secondary aromatic amine group. Peak at  $1244\text{ cm}^{-1}$  is commonly attributed to the  $\text{C}-\text{N}^{+}$  stretching vibration in the polaron structure, indicating that the PANA is in the doped state [13-14]. The bands at  $758$  and  $530\text{ cm}^{-1}$  suggests the presence of C-H out of plane bending and confirms 1,4 disubstituted benzene ring. Figure 2.b shows the FTIR spectra obtained for a PEDOT film sample. Vibrations at  $1512$ ,  $1454$ ,  $1394$  and  $1370\text{ cm}^{-1}$  originates from the stretching of  $\text{C}=\text{C}$  and  $\text{C}-\text{C}$  in the thiophene ring. Further vibrations from the C-S bond in the thiophene ring can be seen at  $930$ ,  $830$ ,  $727$  and  $697\text{ cm}^{-1}$ [15-16]. Vibrations at  $1093$ - $1076$  and  $1052$ - $1047\text{ cm}^{-1}$  are assigned to stretching in the alkylendioxy group [17-18]. Based on this, it was concluded that PEDOT was the material sampled. In the case of the PEDOT-PANA co-polymer the IR spectrum in Fig. 2(c) shows the band at  $1056\text{ cm}^{-1}$  which is assigned to C-O-C ether bond of PEDOT and the absorption band at  $1689\text{ cm}^{-1}$  is due to stretching vibration of  $\text{C}=\text{O}$  of  $-\text{COOH}$  group in PANA. The existence of these two bands confirms the formation of PEDOT-PANA co-polymer.

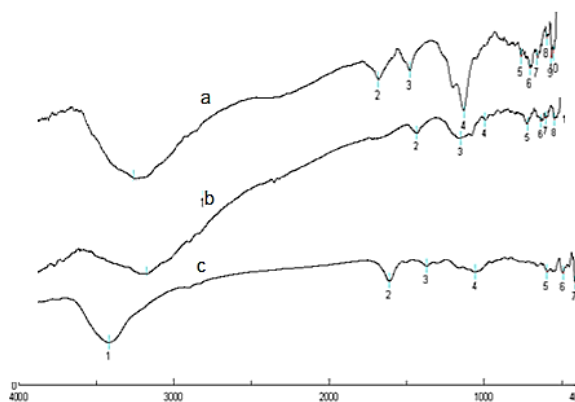


Figure 2. IR Spectrum of (a) PANA (b) PEDOT and (c) PEDOT-ANA

### 3.3 Scanning Electron Microscope

SEM is used as tool for examination the surface morphology for the prepared polymer films and to confirm the contribution of the two monomers in the copolymer composition when the electro-polymerization is carried out from binary monomer mixtures. The SEM images of (a) PEDOT; (b) PANA and (c) PEDOT-ANA films deposited using successive cycling between  $0.5$  to  $1.2\text{ V}$  vs. SCE at  $50\text{ mV s}^{-1}$  1500 time magnification are presented in Figure 3.

In addition to the backbone structure, the properties of conducting polymers are strongly dependent upon their morphologies [19]. Therefore, the surface morphologies of PEDOT films were characterized by SEM, Fig. 3a. The morphology of PEDOT film with SDS has spongy and cotton-like due to the presence of anionic tailing structure [20]. In the present work, the results shows a significant difference in morphology was observed for film prepared by electrochemical deposition of PEDOT on stainless steel in presence of surfactant (SDS). The SDS surface active agent helps in the rearrangements and influences the morphology of polymer chains as shown in the SEM picture of the film. SEM image of PANA, Fig. 3b, show that the material is glassy fibers with needle structure which facilitate the doping dedoping process. In case of PEDOT-ANA film, SEM image Fig 3c shows that the material looks like

wooden fibers which facilitate the doping dedoping process. As seen in Fig.3c the SEM images demonstrate how the copolymerization affect the morphology.

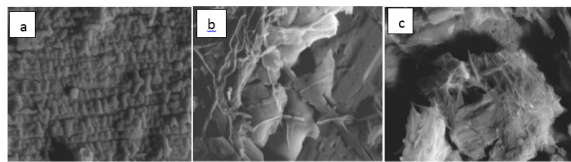
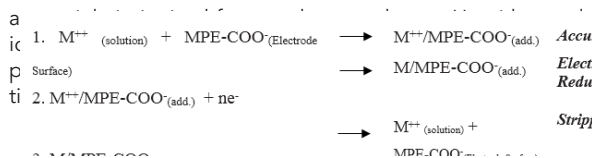


Figure 3. Scanning electron micrographs of (a) PEDOT; (b) PANA; (c) P (25mM EDOT-co-25mM ANA) ;films deposited using successive cycling between  $-0.5$  to  $1.2\text{ V}$  vs. SCE at  $50\text{ mV s}^{-1}$  1500time magnification

### 3.4 Analytical characteristics

The influence of concentration under optimum experimental conditions was studied by increasing the concentration of the metal ions and measuring the stripping current. Standard solutions of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were used to evaluate the ASV responses of PEDOT, PANA and PEDOT-ANA modified polymer electrodes (MPE). The same conditions were used for deposition and stripping at each electrode enabling the direct comparison of at least some of the detection figures of merit for each. All experiment were carried out in accumulating media of  $\text{pH}=6$  where the voltammetric response of electrodes and anodic peaks current were increased as the pH is changed from  $3.0$  to  $6.0$ , reaching a maximum at  $\text{pH } 5$  [21-22]. Since the ionization of functional groups depends on the accumulating solvents and its pH, at  $\text{pH} > \text{pK}_a$ , most of these functional groups

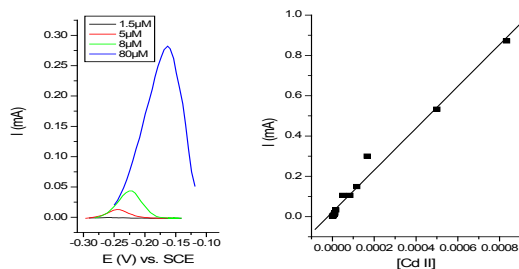


The expected pre-concentration mechanisms in case of PEDOT-electrode may be due to the attraction force between  $\text{M}^{++}$  and the n-doped PEDOT in negative potential and its acidic character in the positive potential [23].

### 3.4.1 ASV responses of $\text{Cd}^{2+}$ on PEDOT, PANA and PEDOT-PANA modified electrodes

Fig. 4, 5 and 6 shows overlaid stripping voltammetric  $i-E$  curves for the  $\text{Cd}^{2+}$  on modified polymer electrodes and its calibration plot from ASV experiment. The deposition of  $\text{Cd}^{2+}$  was carried out at  $-1.2\text{ V}$  under stirring for a defined period of time, followed by a  $15\text{ s}$  rest period. The stripping voltammograms were recorded between  $-1.2$  and  $0.8\text{ V}$ , and the electrode was then cleaned of residual metal at  $0.3\text{ V}$  for  $30\text{ s}$  without stirring. All measurements were carried out in  $0.1\text{ mol L}^{-1}$  acetate buffer ( $\text{pH } 6$ ) plus  $50\text{ mmol L}^{-1}$  NaCl solution.

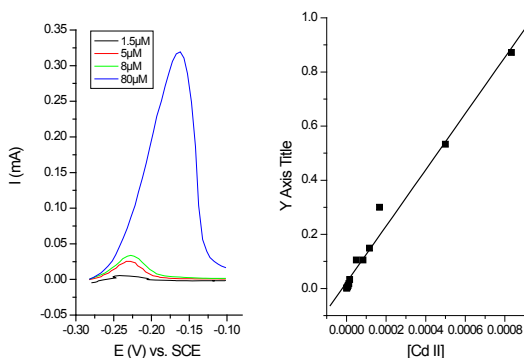
Figure 4 illustrates the results obtained with a solution containing different concentration of  $\text{Cd}^{2+}$  ( $1.5 - 80\text{ }\mu\text{mol L}^{-1}$ ) using PEDOT electrode. the liner fit equation for anodic peak current and  $[\text{Cd}^{2+}]$  shown in Fig. 4 and reported in Table (1),  $i_p = 0.0128 + 1245 [\text{Cd}^{2+}]$  where,  $i_p$  (mA) and concentration in mole  $\text{L}^{-1}$ .



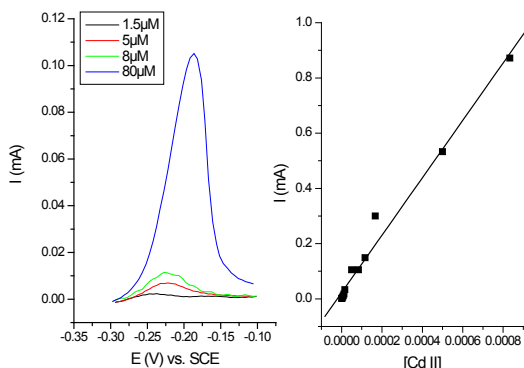
**Figure 4.** Overlaid individual stripping voltammetric  $i$ - $E$  curves for  $\text{Cd}^{2+}$  solutions on acetate buffer pH 6 at PEDOT modified electrode. The electrolyte solution also contained 0.1 M NaCl.

Under the same conditions as in case of PEDOT electrode, the stripping voltammograms were recorded using PANT electrode as shown in Fig. 5 and reported in Table 2. The liner fit equation for anodic peak current was  $i_p = 0.0093 + 2562 [\text{Cd II}]$ .

The slope of  $I - [\text{Cd}^{++}]$  line in case of PANT modified electrode, as shown in Table 2, 2562  $\text{mA.L.mol}^{-1}$ , was very high compared to in cases of both PEDOT and PEDOT-ANT electrodes, 1245 and 1039  $\text{mA.L.mol}^{-1}$  respectively. These results indicated the high voltammetric response and anodic peak current of PANT-electrode and also the sensitivity of the electrode was increased, where small change in the concentration gives high change in the anodic peak current.



**Figure 5.** Overlaid individual stripping voltammetric  $i$ - $E$  curves for  $\text{Cd}^{2+}$  solutions on acetate buffer pH 6 at PANT modified electrode. The electrolyte solution also contained 0.1 M NaCl.



**Figure 6.** Overlaid individual stripping voltammetric  $i$ - $E$  curves for  $\text{Cd}^{2+}$  solutions on acetate buffer pH 6 at

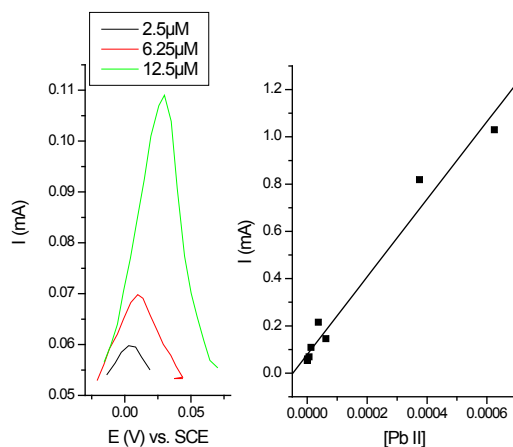
**PEDOT-PANT modified electrode** The electrolyte solution also contained 0.1 M NaCl.

Fig. 6 illustrates the results obtained under the same stripping conditions using PEDOT-PANT-electrode as co-polymer modified electrode. The liner fit equation for anodic peak current was  $i_p = 0.022 + 1039 [\text{Cd II}]$ . The incorporation of a complexing function groups to the conducting polymer as a modifier has also been used to accumulate metal ions chemically, so the detection limit of electrodes coating  $-\text{COOH}$  group is much less than that in case of PEDOT electrode. The detection limits for all the modified electrodes were 3.7  $\mu\text{M}$ , 0.7  $\mu\text{M}$  and 0.6  $\mu\text{M}$  for PEDOT, PANT and PEDOT -PANT respectively.

### 3.4.2. ASV responses of $\text{Pb}^{2+}$ on PEDOT, PANA and PEDOT-PANA modified electrodes

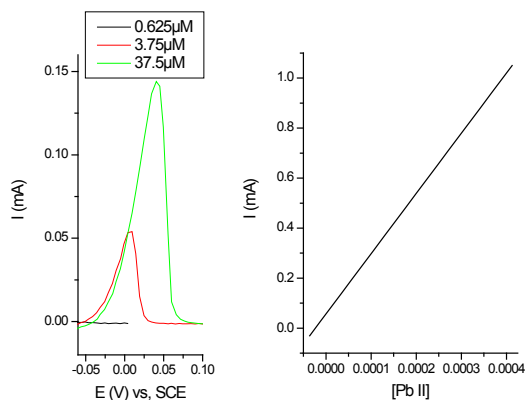
Fig. 7, 8 and 9 shows stripping voltammetric  $i$ - $E$  curves for the  $\text{Pb}^{2+}$  on modified polymer electrodes and its calibration plot from ASV experiment. The accumulation voltage was  $-1.2 \text{ V vs. SCE}$ . The stripping voltammograms were recorded between  $-1.2$  and  $0.8 \text{ V}$ , all measurements were carried out in  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH 6) plus  $50 \text{ mmol L}^{-1}$  NaCl solution.

Fig. 6 illustrates the results obtained using different concentration of  $\text{Pb}^{2+}$  ( $2.5 - 12.5 \mu\text{M}$ ) with PEDOT electrode. The liner fit equation for anodic peak current, as shown in Fig. 7 and Table 1, was  $i_p = 0.022 + 1039 [\text{Cd II}]$  and the detection limit was  $0.625 \mu\text{mol.L}^{-1}$ .



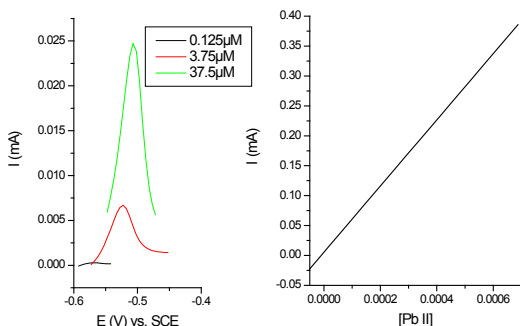
**Figure 7.** Overlaid individual stripping voltammetric  $i$ - $E$  curves for  $\text{Pb}^{2+}$  solutions on acetate buffer pH 6 at PEDOT-PANT modified electrode, the electrolyte solution also contained 0.1 M NaCl.

Figure 8 and table 1, shows the results obtained using different concentration of  $\text{Pb}^{2+}$  ( $2.5 - 12.5 \mu\text{M}$ ) with PANT electrode. The liner fit equation for anodic peak current, as shown in Fig. 7 and Table 1, was  $i_p = 0.056 + 2410 [\text{Pb II}]$  and the detection limit was  $1.25 \mu\text{mol.L}^{-1}$ . As in case  $\text{Cd}^{++}$ , the slope of  $I - [\text{Pb}^{++}]$  line in case of PANT modified electrode, as shown in table 3.1, 2410  $\text{mA.L.mol}^{-1}$ , was very high compared to in cases of both PEDOT and PEDOT-PANT electrodes, 1640 and 553.2  $\text{mA.L.mol}^{-1}$  respectively. This indicated high anodic peak current and sensitivity of PANT-electrode.



**Figure 8.** Overlaid individual stripping voltammetric *i*-*E* curves for  $Pb^{2+}$  solutions on acetate buffer pH 6 at PANT modified electrode The electrolyte solution also contained 0.1 M NaCl.

Figure 8 and table 1, shows the results obtained using different concentration of  $Pb^{2+}$  (0.625 – 37.5  $\mu M$ ) with PEDOT-PANT electrode. The liner fit equation for anodic peak current, as shown in Fig. 7 and Table 1, was  $i_p = 0.005 + 553.2 [Pb (II)]$  and the detection limit was 0.125  $\mu mol.L^{-1}$ . the detection limit is much less than in case of PANT electrode where, The detection limits for all the modified electrodes were 0.125  $\mu M$ , 0.625  $\mu M$  and 1.25  $\mu M$  for PEDOT-co-PANT, PANT and PEDOT respectively. That indicates the large synergetic effect between PEDOT and PANTA in case of detection of  $Pb^{++}$ .



**Figure 9.** Overlaid individual stripping voltammetric *i*-*E* curves for  $Pb^{2+}$  solutions on acetate buffer pH 6 at PEDOT-PANT modified electrode The electrolyte solution also contained 0.1 M NaCl.

**Table 2.** Experimental conditions and ASV experimental data for the individual metal ion determination.

Analyte	Modified Electrode Materials	pH	Dis-solution Potential ( $\mu M$ )	De-tection Limits ( $\mu M$ )	Linear interpolation equation parameters	
					$I_p = A + B [M II]$	
					A (mA)	B (mA. L. Mole <sup>-1</sup> )
Cd (II)	PEDOT	6.00	~ -0.2	3.7	0.0128	1245
	PANT	6.00	~ -0.2	0.7	0.0093	2562
	P(EDOT-co-ANT)	6.00	~ -0.2	0.6	0.022	1039

Analyte	Modified Electrode Materials	pH	Dis-solution Potential ( $\mu M$ )	De-tection Limits ( $\mu M$ )	Linear interpolation equation parameters	
					$I_p = A + B [M II]$	
					A (mA)	B (mA. L. Mole <sup>-1</sup> )
Pb (II)	PEDOT	6.00	~ -0.01	0.625	0.079	1640
	PANT	6.00	~ -0.01	1.25	0.056	2410
	P(EDOT-co-ANT)	6.00	~ -0.5	0.125	0.005	553.2

**Conclusion**

The prepared three polymers modified electrodes were used for detection of cadmium and lead metals in formulated samples by stripping voltammetry technique. Very good responses have been observed for both metals with all modified electrodes employed. However, the poly(3,4ethylenedioxythiophene)-co-anthranilic acid modified electrode has lower detection limits than both homopolymer, that reflect the synergistic effect between EDOT and ANA in the obtained copolymer. The presence of carboxylic groups in the main chain of polymer enhance the accumulations of metal cations through the ionic interaction and complexation, which increase response current ( $I_p$ ) and enhance the detection limits. The work shows the development of a sensors for the sensitive determination of cadmium and lead with detection limit of 3.7  $\mu M$ , 0.7  $\mu M$  and 0.6 for Cd (II) and 1.25  $\mu M$ , 0.625  $\mu M$  and 0.125  $\mu M$  for Pb (II) at PEDOT, PANT and PEDOT-PANT electrodes respectively. This technique does not use mercury and, therefore, has a positive environmental benefit.

## REFERENCE

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