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A New Approach for Electrodeposition of poly (3, 4-ethylenedioxythiophene)/polyaniline (PEDOT/PANI)Copolymer

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In this study, poly (3, 4-ethylenedioxythiophene)(PEDOT) and polyaniline (PANI) based copolymer was synthesized by electrochemical oxidative polymerization using chronoamperometry technique. A new approach was used to perform the copolymerization process. The copolymer film was prepared at a potential obtained from the intercept point in the LSV of the both monomers. The electrodeposition was performed in solution containing 10 mM of concentrations of each monomer and 0.1 M lithium perchlorate ($LiClO_4$). The resulting conducting polymer films were characterized using scanning electron microscope (SEM), Raman spectroscopy and Fourier transform infrared (FTIR) to study the surface morphology, chemical properties and the presence of the functional groups of the conducting polymer films. The FTIR and Raman spectra proved the successful formation of the conductive polymers and copolymer onto the ITO glass. The electrochemical properties of the resultant polymer films were further analyzed using the cyclic voltammetry and electrical impedance spectroscopy.

Keywords: Conducting polymer; poly (3, 4-ethylenedioxythiophene); copolymer; electrodeposition; polyaniline

1. INTRODUCTION

Since the discovery in 1977, conducting polymers (CPs) has become most demanding subjects of the research in the field of electrochemistry for its unique and captivating properties and application possibilities in various fields. CPs are widely being used as sensors, actuators, organic solar cells organic light emitting diodes (OLED), and field effect transistors (FETs) [1-7]. For the most of the CPs based application, the preferences are given to their properties. Thus, several approaches and investigations have been made on CPs to improve and understand the properties *i.e*. processibility, conductivity, stability and morphology. Amongst the CPs have been studied so far, special attention has been given to poly (3, 4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI).

PEDOT become the potential candidate of the polythiophene derivative for the commercial application developments since it exhibits some good properties including high electrical conductivity, narrow band gap, excellent thermal, environmental and chemical stability in doped formed [8, 9]. Moreover, substitution of ethylenedioxythiophene group at the position 3- and 4- of the thiophene ring favors the polymerization occur at the 2,5 position in the thiophene ring resulting a stable linear chain with less defects compared to the other thiophene analogous [9, 10]. In addition, the presence of the substituent containing electron donating oxygen stabilizes the positive charges on the polymer backbone and lowers the oxidation potential of the monomer [11, 12]. However, surprisingly PEDOT was found to be partially soluble conducting polymer which limited its application potentials [13].

On the other hand, PANI gained the attention of the numerous researchers for its three different oxidation states, namely leucoemeraldine, emeraldine and perningraniline. Emeraldine is the conducting form of the PANI, obtained from the doping of the emeraldine salt [14]. PANI owns several advantages, namely good environmental stability, good electrical conductivity and thermal stability. Like other CPs, PANI also having difficulties in processing due to its poor solubility and fusibility [15].

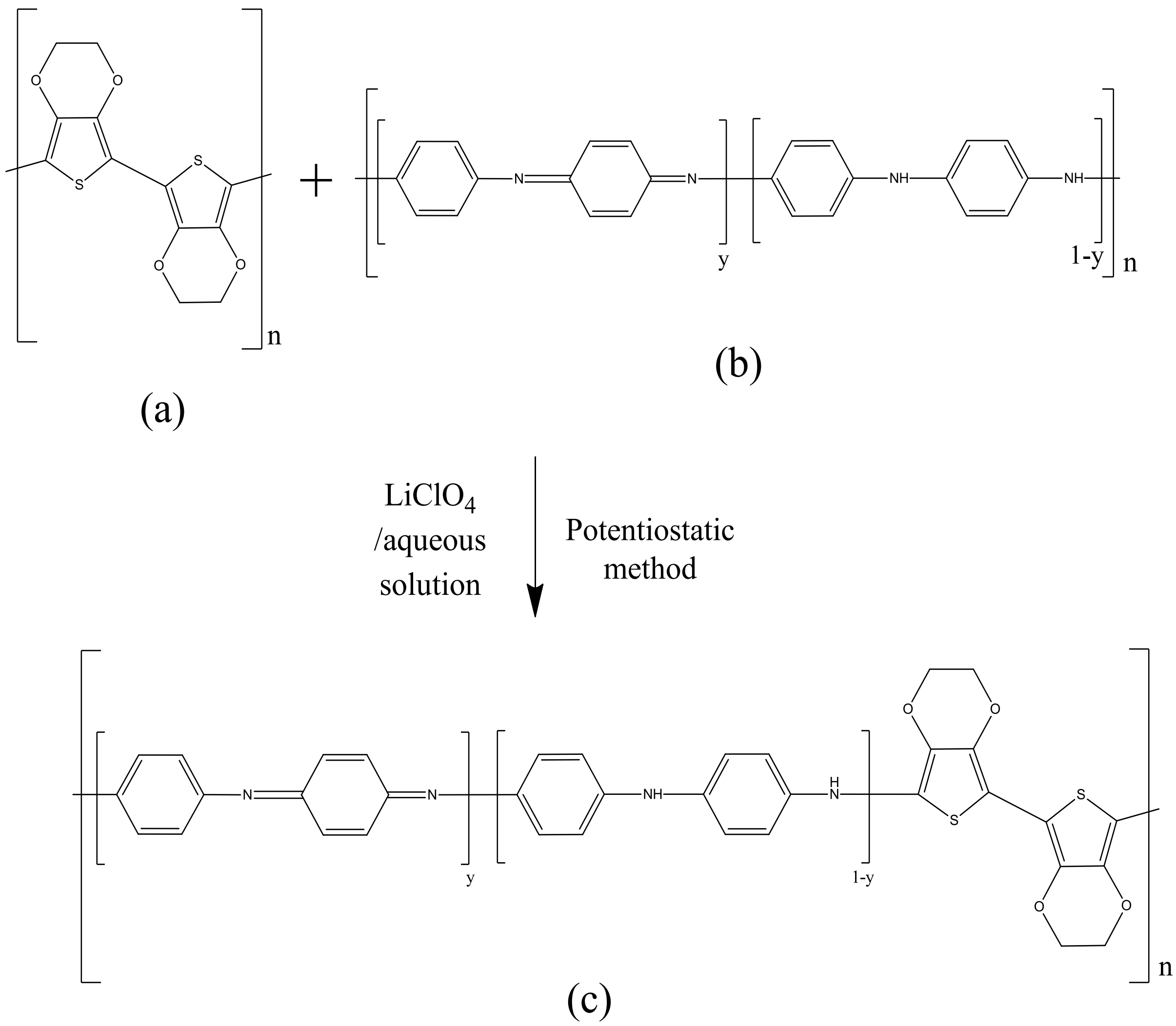
Generally, the properties of the CPs depend on the method of the synthesis. Polymerizations of PEDOT and PANI have been succeesfully prepared by both chemical oxidative and electrochemical polymerization methods in aqueous or non aqueous solution [13, 16-18]. Indeed, electropolymerization method is more preferable method since the thickness and conductivity of the polymers could be tuned by altering the potential, current density, concentration, and dopant.

Many of the advantages and uses for the CPs remained undiscovered and still in the foreground of the investigations because of the certain restriction in CPs that needs to be overcome. In order to produce CPs with outstanding properties, blending, composite and copolymerization approaches were adapted. Recently, more attentions have been given on the copolymerization with the intention to produce new conductive copolymers with appealing properties which overcome the shortcomings and limitation of the corresponding monomers. The resultant new copolymer appeared in combination of the positive properties of both homopolymers [19].

Owning to the great properties of the EDOT and ANI, the copolymerization of these monomers may lead to a new copolymer with great properties. The investigation of the properties and structure of the PEDOT based copolymers as well PANI based copolymers were reported [20-23]. However, far less attention has been paid on the copolymerization of PEDOT/PANI monomers since both individual polymers grown in two different electrolyte conditions; PANI required to be prepared in acidic medium. Randriamahazaka, H. et. al., (2005) [24] have reported that copolymer composite of PANI and PEDOT can be prepared in the same electrolyte condition in the absence of the acids. Their studies demonstrated that oxidized PEDOT act as Lewis acid, allowing the PEDOT/PANI based composite to form.

Herein in the present study, PEDOT and PANI were copolymerized successfully by electrochemical polymerization of the mixture of corresponding monomers as shown in Scheme 1. In this study, a new approach in preparing the copolymer was used. It would be interesting to prepare a copolymer that combines the properties of both individual polymers. Apart from it, greater knowledge of the relation between the structure and properties of PEDOT, PANI, and conducting copolymer prepare in aqueous solution without the addition of acid could be obtained.

In addition, to the best of our knowledge, there have been no works reported on the electrochemical copolymerization based on the intercept point of the monomers from the linear sweep voltammetry (LSV). In contrast, most of the reported literature, copolymerization of the material was based on the feed ratio of the two monomers and the oxidation potential of the dominating monomer has been chosen as the applied potential [25-27]. The resultant polymers and copolymer were analysed by scanning electron microscope (SEM), energy-dispersive X-ray analysis (EDX), Raman spectroscopy and Fourier transform infrared (FTIR). The electrochemical characteristics of the prepared polymer films were investigated in detail using electrochemical impedance spectroscopy (EIS).



Scheme 1. The electrochemical copolymerization reaction between (a) PEDOT and (b) PANI yields copolymer (c) (PEDOT/PANI)[28]

2. EXPERIMENTAL

2.1 Materials

3, 4-Ethylenedioxythiophene (EDOT, 97.0 %) and supporting electrolyte (lithium perchlorate, $LiClO_4$, 95.0 %) were purchased from Sigma-Aldrich. EDOT was used without further purification while aniline obtained from Fisher Scientific was freshly distilled. The deionized water (resistivity ~ 18.2 MΩ) was used as a solvent to prepare all the aqueous solutions. Indium tin oxide coated glass (ITO, 7 $\Omega\ sq^{-1}$) was purchased from Xin Yan Technology Limited.

2.2 Equipments

All the electrochemical measurements were performed using a potentiostat /galvanostat (Autolab 101) equipped with NOVA software at room temperature. Perkin Elmer's Fourier transform infrared (FTIR) spectrometer designed with Universal Attenuated Total Reflectance (UATR) accessory was used to study the composition of the films. The Raman spectra of the films were recorded on Alpha300 R microscopic confocal Raman spectrometer (WITec GmbH) equipped with a 633 nm laser line. Surface morphology of the polymer films were determined via scanning electron microscope JEOL JSM 6400 and Leo 1455 VP-SEM model.

2.3 Preparation of polymer films

All the electropolymerizations were performed in one compartment, three-electrode electrochemical system and placed in a Faraday cage. The ITO glass (1 cm^2), platinum wire and Ag/AgCl (3.0 M NaCl) were served as a working electrode, counter electrode and reference electrode, respectively. Prior to each experiment, the working electrodes were cleaned ultrasonically for 15 minutes in acetone followed with ethanol and finally rinsed with distilled water.

2.3.1 Electrodeposition of Poly (3, 4 ethylenedioxythiophene) (PEDOT) and Polyaniline (PANI) films

The polymer films were grown potentiostatically from the solution containing 10 mM monomer, either EDOT or ANI in the presence of supporting electrolyte, 0.1 M $LiClO_4$. PEDOT (and PANI) films were deposited onto the ITO substrate at 1.0 V for 300 seconds.

2.3.2 Preparation of PEDOT/PAni copolymer films

The electrochemical copolymerization of EDOT and ANI was made by applying potential of 1.07 V with a concentration ratio of 1:1 in 0.1 M $LiClO_4$. The oxidation potential used was obtained from the intercept point of both monomers in the linear sweep voltammetry measurement.

2.4 Electrochemical Properties

The electrochemical performances of the films were explored by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), in a compartment of three electrode cell. The polymer coated ITO electrode was used as a working electrode and the platinum wire as a counter electrode. All the reported potentials were referenced to the Ag/AgCl (3.0 M NaCl). The voltammograms of the polymers were recorded in 0.1 M KCl in the potential ranging from -0.5 V to 0.5 V with a scan rate of 100 mV/s. The EIS measurements were conducted in the solution consisting of 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl as supporting electrolyte with an alternating current (ac) perturbation signal of 10 mV at frequency ranging from 10 kHz to 0.01 Hz ; sine wave as excitation signal. The direct current (dc) potential was applied at open circuit potential (OCP). The impedance spectra were further analyzed using the frequency response analysis (FRA) fitting program in NOVA software (version 1.10.1.9., Metrohm Autolab B.V.).

3. RESULTS AND DISCUSSION

3.1 Electrochemical Polymerization

Applied potential is a crucial parameter in the preparation of the polymers in the electropolymerization process. The oxidation potential of each monomer differs with each other. Therefore, it is important to choose the appropriate potential value for the electropolymerization,. In addition, the applied potential value also determined the structure and conductivity of the polymers. The PEDOT and PANI films were prepared at a constant potential of 1.0 V vs. Ag/AgCl using potentiometric technique.

The linear sweep voltammetric response of a solution containing 10 mM EDOT in 0.1 M $LiClO_4$ aqueous solution and a solution containing 10 mM ANI in 0.1 M $LiClO_4$ aqueous solution is shown in Fig. 1. The voltammograms were scanned between 0 V and 1.2 V vs. Ag/AgCl at the sweep rate of 100 mV/s. It can be noticed from the voltammograms that, onset potential ($E_{op)}$ values are approximately + 1.0 V and + 0.7 V (vs Ag/AgCl) for EDOT and ANI, respectively.

It has commonly known that the differences of the E_{op} determined the possibility of the copolymerization process by producing copolymer with alternating monomer units [25, 26]. The differences between the E_{op} values of the monomer ANI and monomer EDOT is 0.3 V. Thus, this result implies that the copolymerization process between the ANI and EDOT monomers are hard to achieve. Furthermore, the E_{op} of the EDOT monomer is higher compared to ANI monomer, indicating the polymerization of PEDOT is slower than polymerization of PANI. As a result, it is expected the content of the PANI in the electropolymerized copolymer to be higher than the content of the PEDOT in the copolymer.

Therefore, a new approach on copolymerization of the monomers was attempted. As mentioned earlier, the intercept point of the both monomers in the LSV is used as the applied potential for the copolymerization process. In reviewing the literature, no attempts have been made so far on the copolymerization based on the intercept point of the monomers in the LSV. The intercept value (potential value) lies between the onset potential and highest potential of the corresponding monomers implying that it is significant to produce the copolymer with a combination of the properties of both polymers. As pointed by an arrow in Fig. 1, the value for copolymerization is 1.07 V (vs. Ag/AgCl).

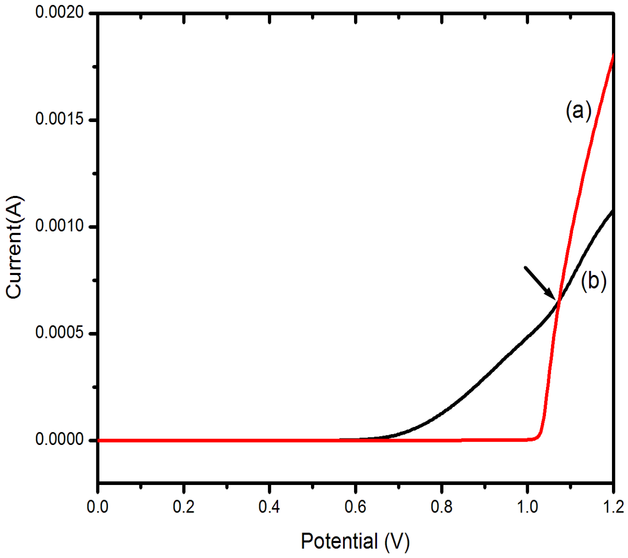


Figure 1. Linear sweep voltammogram recorded on the ITO in the presence of (a) 10 mM EDOT and (b) 10 mM ANI in aqueous solution containing in 0.1 M $LiClO_4$ between potential ranges 0 V to 1.2 V. Arrow indicated the intercept point (potential) for the copolymerization of PEDOT/PANI.

3.2 Structural Characterization

3.2.1 Infrared spectroscopy of polymers

IR spectroscopy is an extremely effective method to identify the presence of a broad range of functional groups in a substance. In this study, the FTIR spectra of the PEDOT and PANI polymers were measured via FTIR-ATR and used to determine the existence of main functional groups in the polymers and their copolymer. FTIR-ATR spectra of the PEDOT, PANI and their copolymer are depicted in the Fig. 2. Comparison between the spectra of the PEDOT, PANI and their copolymer, PEDOT/PANI shows the incorporation of both monomers in the copolymer.

The PEDOT spectrum shows typical characteristic bands at 618 cm^{-1}, which attributed to the symmetric C-S, and the peak at 1083 cm^{-1} is refer to the stretching of C-O-C in ethylenedioxy group [29, 30]. The stretching vibration of C-C is appeared at 1364 cm^{-1} and 1418 cm^{-1}. Additionally, the stretching of C=C of thiophene ring is related to the peak around 1478 cm^{-1} to 1823 cm^{-1} [27, 30-32]. The spectrum of PANI shows characteristic bands of the partially oxidized (emeraldine form) PANI positioned at the 1600 -1450 cm^{-1}, 1320 cm^{-1}, 1205 cm^{-1}, 1096 cm^{-1} and 833 cm^{-1}. The bands at the 1550 cm^{-1} and 1447 cm^{-1} responsible for the quinoid and benzoic form of the PANI. The appearance of these bands indicates the partial oxidized state of PANI [33, 34]. The band at the 1320 cm^{-1} results from the stretching of the C=N in the quinoid rings [35]. Whereas, the bands at 1205 cm^{-1} and 1096 cm^{-1} are attributed to the C-N stretch vibration of semiquinoid form [34] and a band at 840 cm^{-1} is referred to C-H out of plane. The above bands signifying the polymer chain consists of para disubstituted benzene rings [33, 36].

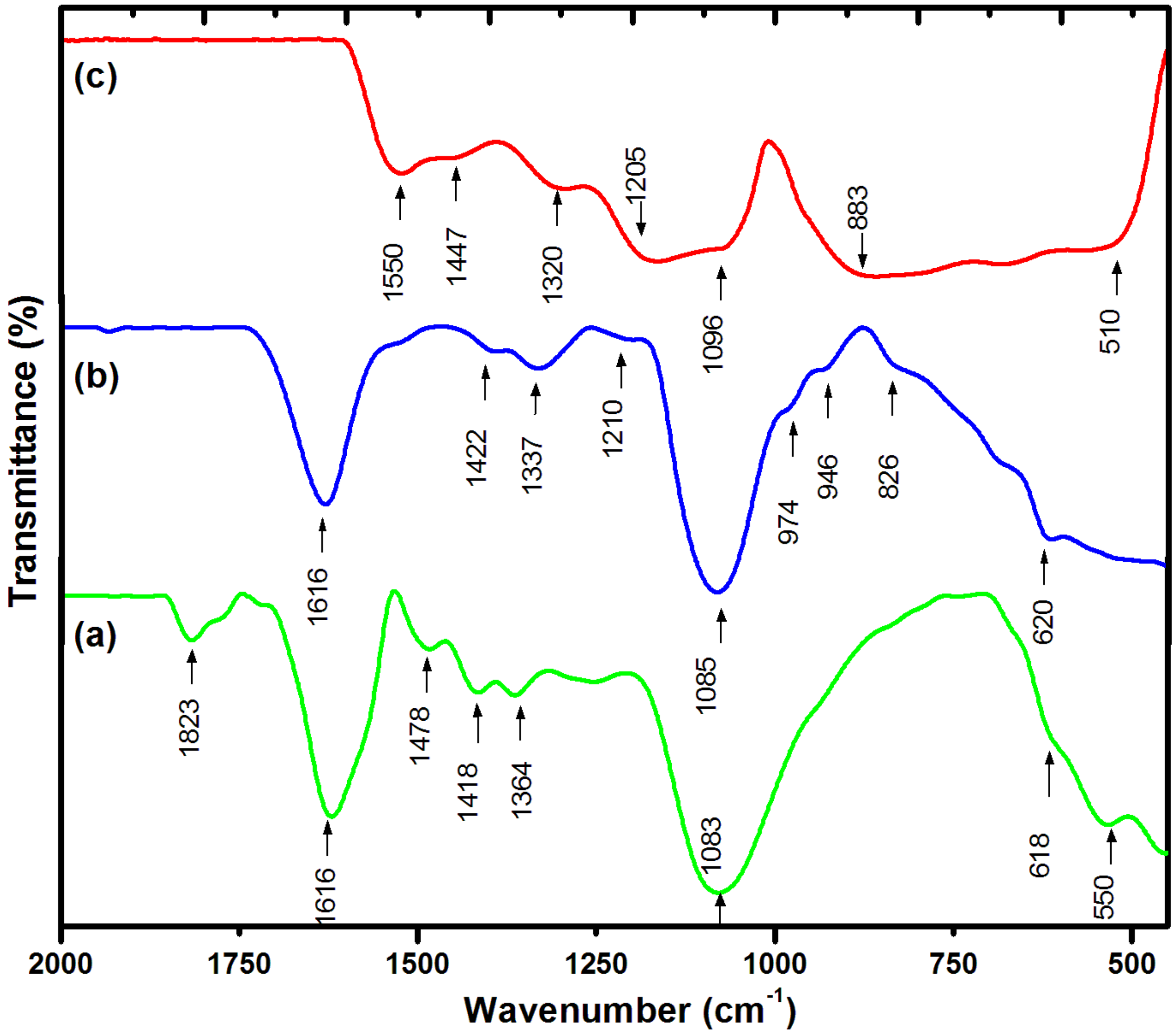


Figure 2. FTIR-ATR spectra of (a) PEDOT, (b) copolymer (PEDOT/ PANI) and (c) (PANI). Growth conditions: PEDOT and PANI is electropolymerized potentiostatically at 1.0 V on ITO containing 10 mM monomer/0.1 M $LiClO_4$. Copolymer PEDOT/PANI is electropolymerized potentiostatically at 1.07 V on a ITO from 10 mM EDOT/10 mM ANI /0.1 M $LiClO_4$

The PEDOT/PANI copolymer yields the characteristic bands of homopolymer. The vibration for C-S and C-O-C functional groups in PEDOT polymer were observed in the copolymer spectrum at position 620 cm^{-1} and 1085 cm^{-1} respectively, while the bands at 1337 cm^{-1} and 1425 cm^{-1} signifying the presence of C=N and C-N functional group vibrations, respectively. A band located at 1616 cm^{-1} is noticed in the copolymer spectrum that assigned to C=C of thiophene ring. On the other hand, the peak which responsible for C=N stretching (1320 cm^{-1}) in PANI spectrum shifted to higher frequency (1337 cm^{-1}) in the PEDOT/PANI copolymer spectrum. The band at 1418 cm^{-1} in PEDOT spectrum is observed at the position of 1422 cm^{-1} in the copolymer spectrum. The shifted peaks indicate the interaction between monomer ANI and monomer EDOT. Thus, these observations confirm that there are some PEDOT-PANI linkage apart from PEDOT-PEDOT and PANI-PANI linkage.

The resemblance of the spectra of PEDOT, PANI and copolymer show the incorporation of both monomers inside the copolymer. Furthermore, these results indicate that PEDOT/PANI copolymer has been been successfully prepared via the potentiostatic polymerization of mixture EDOT and ANI using the new approach of copolymerization.

3.2.2Raman spectra of the polymer

The information on the structure of deposited PEDOT and PANI polymer films and copolymer (EDOT/ANI) film was further analyzed by using Raman spectrocopy (Fig. 3).

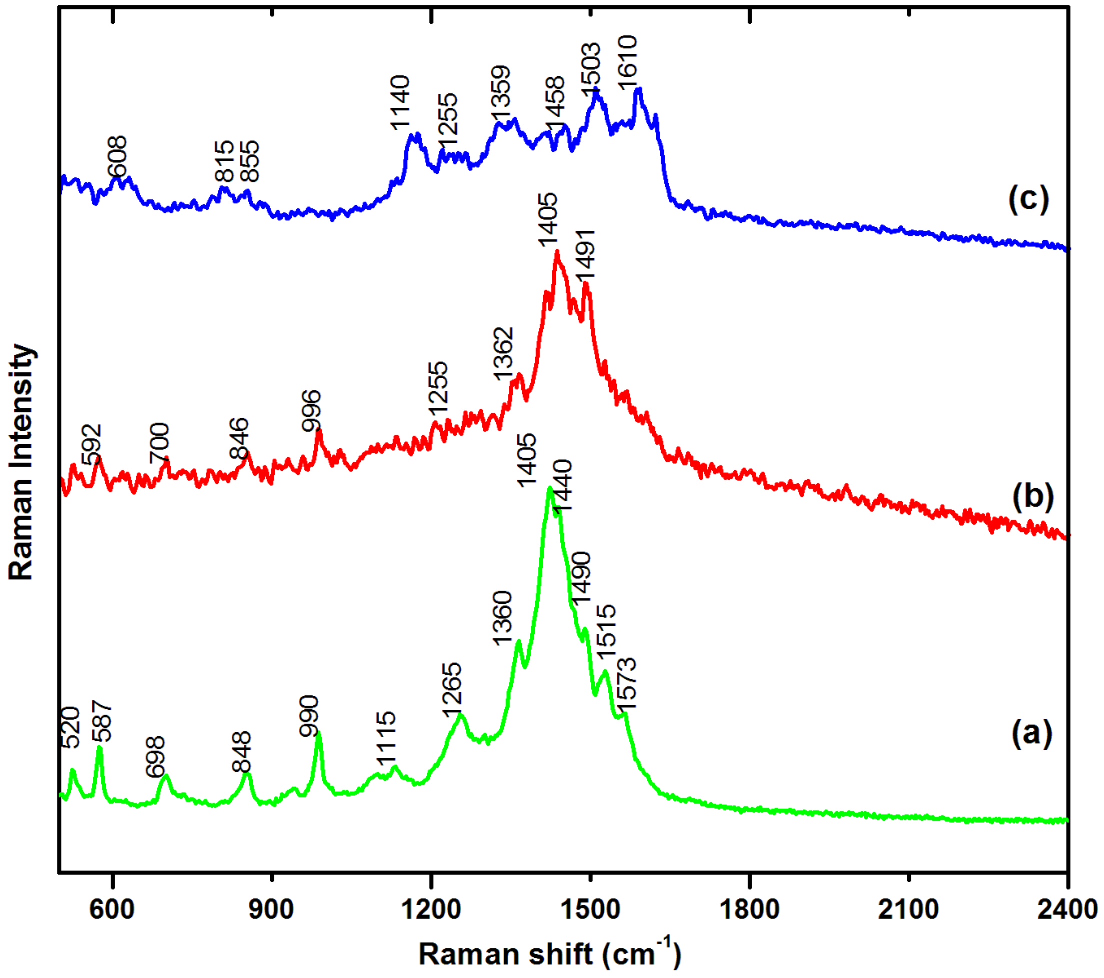


Figure 3. Raman spectra of (a) PEDOT, (b) copolymer (PEDOT/ PANI)and (c) (PANI). Growth conditions: PEDOT and PANI is electropolymerized potentiostatically at 1.0 V on ITO containing 10 mM monomer/0.1 M $LiClO_4$. Copolymer PEDOT/PANI is electropolymerized potentiostatically at 1.07 V on an ITO from 10 mM EDOT/10 mM ANI/0.1 M $LiClO_4$

Fig. 3a presents the Raman spectrum of the PEDOT polymer. The spectrum shows typical bands of the polymer at the 520 cm^{-1} to 990 cm^{-1}, 1115 cm^{-1}, 1265 cm^{-1}, 1360 cm^{-1}, 1405 cm^{-1} to 1440 cm^{-1}, 1515 cm^{-1} and 1573 cm^{-1},respectively [37]. PEDOT spectrum exhibits most prominent peak located in the range of 1405 cm^{-1} to 1490 cm^{-1} refer to symmetrical $C_α=C_β$ (stretch) mode. Peaks in the range of 1515 cm^{-1} to 1573 cm^{-1},belong to asymmetrical $C_α=C_β$ stretching vibration mode. Additionally, 1115 cm^{-1} (C-O-C ring deformation), 1265 cm^{-1} ($C_α$-$C_{α'}$ inter ring stretching) and 1360 cm^{-1} ($C_β$-$C_{β'}$ stretching) are observed. Also, other peaks in the region of 520 cm^{-1} to 990 cm^{-1} are denoted to oxyethylene ring deformation.

There are three main frequency regions which determining the characteristics of the PANI polymer (Fig. 3c) as reported by the Mažeikienė et al., (2013) [38]. The same trend is also observed in this work. In the region between 1100 cm^{-1} to 1300 cm^{-1}, C-H bending vibrations in the emeraldine salt and stretching of C-N in amine form were noticed. Within the region of 1300 to 1510 cm^{-1}, $C\sim N^+$ (polarons) stretching in semiquinone form and C=N stretching in quinoid form are seen [38-41]. Whereas, C-C stretch in the benzene aromatic ring is appeared in the range of 1510 cm^{-1} to 1620 cm^{-1}.

Comparison with the homopolymer spectra, the PEDOT/PANI copolymer exhibits similar peak patterns of the both polymer PEDOT and PANI which indicate the combination of the mixture EDOT and ANI monomers in the copolymer. As can be seen clearly from the copolymer spectrum (Fig. 3b), all the vibration modes are shifted to higher frequency, which expected as a result of the interaction of both monomers. The vibrational assignments from the Raman spectra of PEDOT and PANI support the wavenumber assignments interpreted from the FTIR of the PEDOT and PANI. Both analyses prove the existence of PEDOT/PANI and the obtained results support the successfulness of the new approach in preparing the copolymer.

3.3 Morphology

SEM is used to examine the morphology of the formed polymers. The morphology and structures of the films are very important to determine the properties of the formed polymers.

The PEDOT (Fig. 4a) films revealed globular surface morphology. It was reported that PEDOT prepared in organic solution, acetonitrile in the presence of $LiClO_4$ exhibits loose spongy network[42]. On the other hand, PEDOT in the ionic liquids exhibit porous structure[43]. While in our study, the PEDOT film prepared in the aqueous solution was in the compact and densely packed. The porous morphology is barely can be seen. Whereas, the micrograph of PANI (Fig. 4c) reveals two different surface morphologies. It is interesting to observe film with network structure (fibrillar morphology) with non uniformity on the surface (arrow (b)) and smooth surface as indicated by the arrow (a). The appearance of these two different morphologies could be due to the absence of the acid medium during the electrodeposition. In contrast, the PANI prepared in the acidic medium reveals nanocrystalline granular structure as observed by Kim et al., (2012) [44].

With regard to copolymer of PEDOT with PANI (Fig. 4b), the film has a homogenous distribution of densely accumulated globules referring to EDOT. Likewise, the surface of copolymer appeared to be rougher with some granules onto the surface. This is expected due to incorporation of the ANI monomer into the copolymer. These observations indicate that the formation of the copolymer is derived from the electropolymerization in the presence of ANI and EDOT monomers mixture.

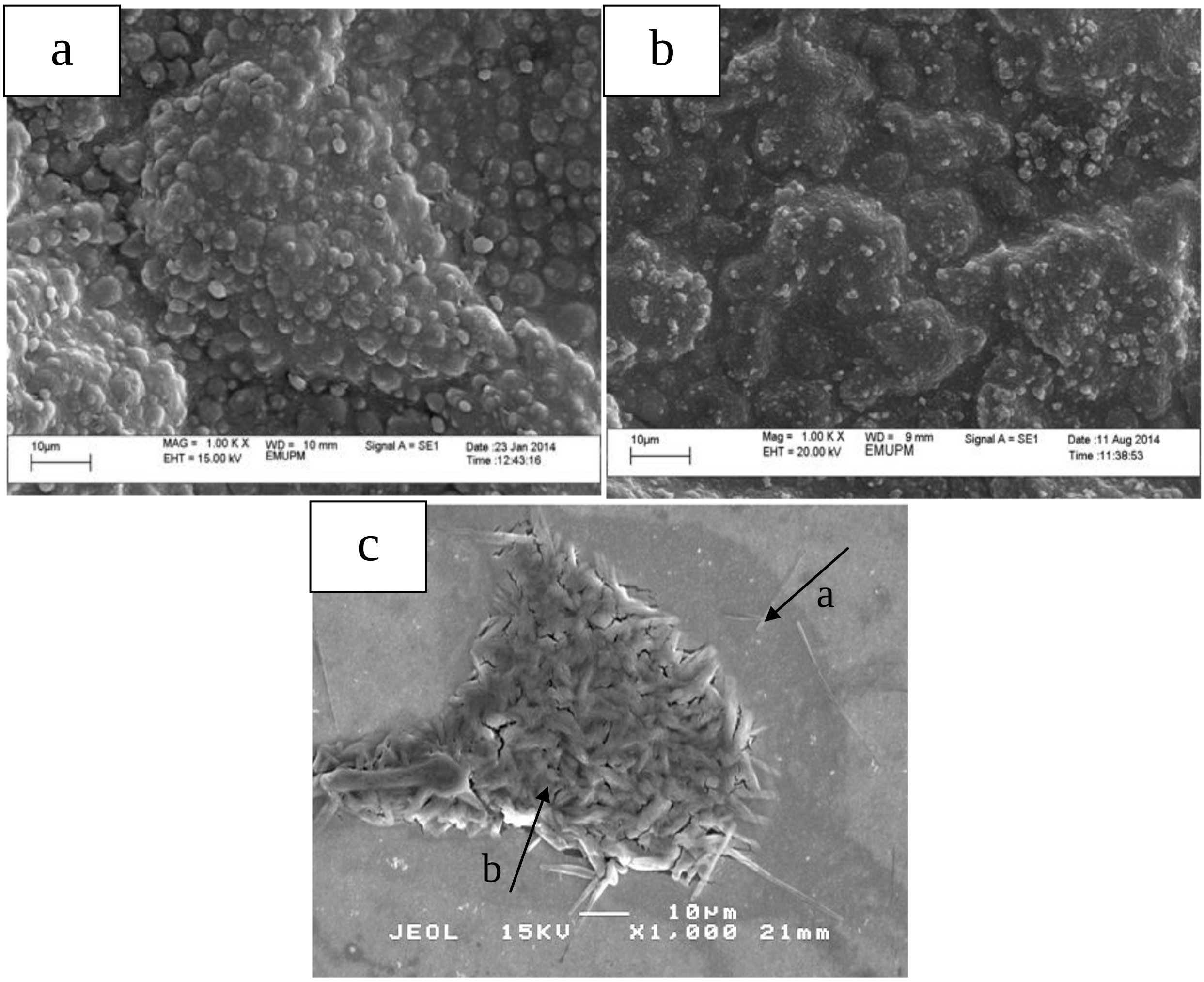


Figure 4. SEM micrographs of (a) PEDOT, (b) copolymer (PEDOT/ PANI) and (c) (PANI). Growth conditions: PEDOT and PANI is electropolymerized potentiostatically at 1.0 V on ITO containing 10 mM monomer/0.1 M $LiClO_4$/aqueous solution. Copolymer PEDOT/PANI is electropolymerized potentiostatically at 1.07 V on an ITO from 10 mM EDOT/10 mM ANI /0.1 M $LiClO_4$.

3.4 Electrochemical Properties

The CV curves of PEDOT (curve a), PEDOT/PANI copolymer (curve b) and PANI (curve c) in 0.1 M KCl solution with a scanning rate of 100 mV/cm^1 are displayed in the Fig. 5. The polymers were cycled between -0.5 V and 0.5 V. Generally, the rectangular shape of CV curves (no oxidative or reductive peak), explains the typical behaviour of the electrical double layer (EDL) capacitive behaviour [45]. As can be seen in the Fig. 5, the curves of the polymers in the current study exhibit oblique and narrow CV loops. This behaviour attributed due to the poor electrolyte/electrode interfacial contact[46, 47].

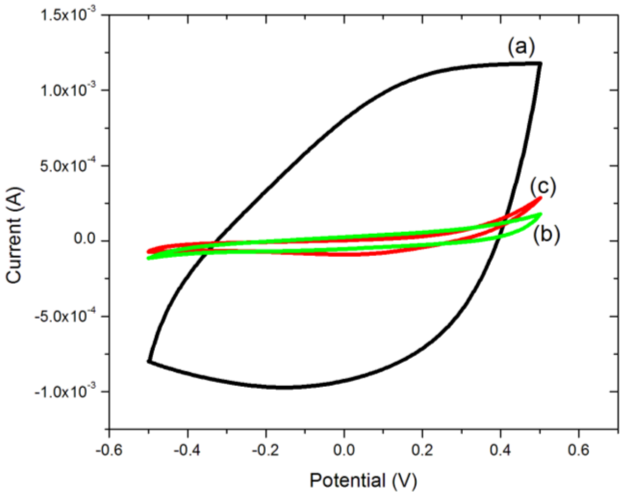


Figure 5. Cyclic voltammogram of (a) PEDOT, (b) copolymer (PEDOT/PANI) and (c) (PANI) in 0.1 M KCl solution. Growth conditions: PEDOT and PANI is electropolymerized potentiostatically at 1.0 V on ITO containing 10 mM monomer/0.1 M $LiClO_4$/aqueous solution. Copolymer PEDOT/PANI is electropolymerized potentiostatically at 1.07 V on an ITO from 10 mM EDOT/10 mM ANI /0.1 M $LiClO_4$.

However, the closed CV loop of the PANI and copolymer are very small signifying low capacitance value due to the deficient of electroactive sites on the surface[46]. Whereas, the PEDOT illustrates larger closed CV loop compared with PANI and copolymer revealing higher EDL capacitance values. The explanation agreed with the calculated capacitance value of the polymers from the CV measurement. The capacitance values for PEDOT, PEDOT/PANI copolymer and PANI are tabulated in Table 1. The capacitance of the PANI and PEDOT/PANI show almost similar capacitance value indicating the incorporation of EDOT monomer into the ANI monomer does not affect the activity of the ANI and pre-dominating the activity of the ANI in aqueous solution. This feature also makes the possibility of PEDOT/PANI a good candidate for sensing platform.

The capacitance value of the polymers was calculated based on the equation given below:

$$C= \frac{S}{\Delta U\times \upsilon\times a}$$

where C is capacitance, *S* is the enclosed area in the CV curve, ΔU is potential window, υ is the scan rate and *a* is the area of the electrode.

The electrical impedance spectroscopy (EIS) is a useful and powerful method that widely used to provide data on the electrochemical characteristics, for instance, double layer capacitance, charge transfer resistance, diffusion impedance and solution resistance [48, 49]. The values of the electrical impedance are determined over a wide range of the frequencies of the applied alternative current (AC) signal [49, 50]. Impedance is composed of the real component and the imaginary component and they are measured as a function of the frequency. Generally, a small amplitude AC potential (sinusoidal form) is introduced to the system and measured the response, current.

Table 1. Electrochemical parameters obtained from CV and fitting data to the model in Fig. 7.

Polymer	R_{ct} (Ω)	Capacitance (mF cm^{-2})	χ^2 (10^{-3})
PEDOT	20.3	12.80	13.61
PANI	11850.0	0.67	8.85
PEDOT/PANI	2079.7	0.62	36.46

In the present study, electrochemical properties of the PEDOT, PANI and copolymer (PEDOT/PANI) are investigated by performing the EIS measurements. Fig. 6 shows a typical Nyquist plot of the PEDOT, PANI and copolymer (PEDOT/PANI) recorded at open circuit potential. As shown in the Fig. 6A, Nyquist plot of PEDOT consists of a small semi circle arc at high frequency range (inset picture) and a straight line indicates to the real part of the plot. Theoretically, in the low frequency region, the vertical line parallel to the imaginary part (y-axis) of the Nyquist plot (90^o slope) is attributed to the pure capacitor behaviour [51]. In the case of PEDOT, the line more inclined towards real part of the plot, close to 45^o slop indicating diffusion controlled process [52] at polymer-electrolyte interface. This process is indicated as the Warburg diffusion region [53].

Whereas, the Nyquist plot of the PANI (Fig. 6c) and PEDOT/PANI copolymer (Fig. 6b) are different with the Nyquist plot of the PEDOT. The Nyquist plot of the PANI and copolymer shows two semi circle arc, one in the higher frequency range (inset picture) which later deviate to form another semicircle at the lower frequency range. The two semicircles on PANI plot is expected might due to two different morphologies of PANI film (Fig. 4c).

It worth to note, the semicircle seen in the high frequency section represents to the double layer charging and discharging process at the electrode surface (polymer) – electrolyte interface [54]. The interface structure is characteristic of the charge- transfer resistance, R_{ct} [51]. Furthermore, the nonfaradaic process occurred at the bulk solution was described by the impedance response at the low frequency region [55]. The R_{CT} value can be depicted from the diameter of the semicircle. The R_{CT} value for PANI (Table 1) is much larger than PEDOT and copolymer value. A lower R_{CT} value for copolymer compared to PANI indicates the conducting nature of the PEDOT. This behaviour explaining the incorporation of the EDOT in ANI makes the interfacial resistance of the copolymer to be lower than PANI.

In order to explain the impedance characteristics of the resultant polymers, two electrical circuits are proposed as presented in the Fig. 7. It is composed of the solution resistance (R_s), charge transfer resistance (R_{ct}), constant phase element (CPE) and the ‘‘classical’’ finite-length Warburg diffusion element (Z_W). Considering the non homogenous and irregular geometry (Fig. 4), the CPE is included into the circuit. CPE is the expression for the double layer capacitance and faradaic pseudocapacitance [56].

The accuracy of the fitted data quality is determined based on the chi square (χ^2) test. The lower the value of χ^2, the more accurate the proposed electrical equivalent circuits used to fit the data [57]. The values of the χ^2 of our current work are in the range of 10^{-3} to 10^{-4} (Table 1).

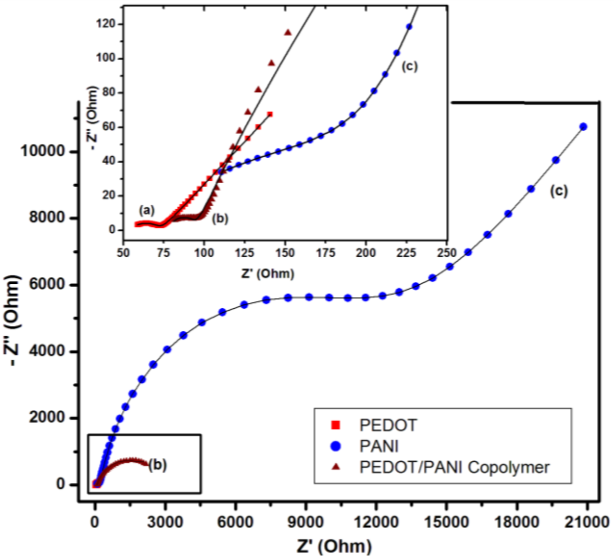


Figure 6. Nyquist plot of PEDOT, copolymer (PEDOT/PANI) and (PANI) deposited on the ITO glass in solution consisting 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl. Frequency range = 10 kHz to 0.01 Hz. E_{dc}= at OCP and E_{ac}=10 mV. Inset: Magnified representation of the Nyquist plot at the high frequency. The solid lines represent the best fitting results in accordance to the equivalent circuits represented in Fig. 7.

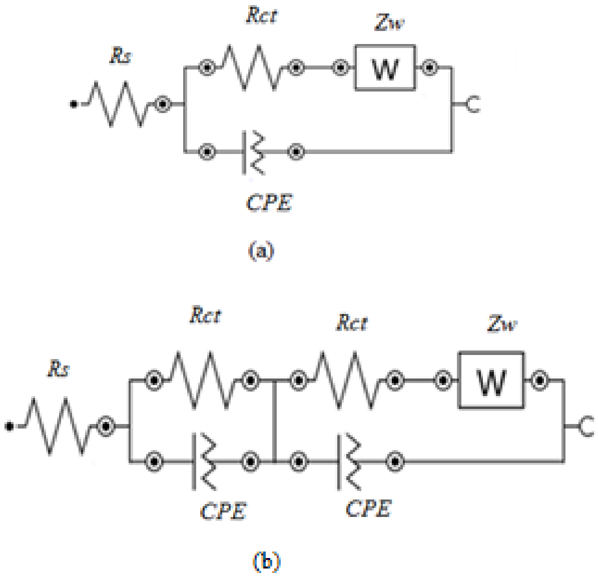


Figure 7. Equivalent circuits used for the fitting of the measured (a) PEDOT and (b) PANI and PEDOT/PANI copolymer

4. CONCLUSION

The electrochemical synthesis of a copolymer from the monomers, EDOT and ANI was successfully achieved via a new approach of copolymerization. The applied potential for the copolymerization was taken from the intercept point of the monomers on the LSV which is a new attempt in the preparation of the copolymer. The formation of the PEDOT/PANI copolymer was confirmed by the FTIR, Raman spectroscopy analyses and the copolymer was further analyzed by CV and EIS studies.

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