

MODIFIED ELECTRODES OBTAINED BY ELECTROCHEMICAL CODEPOSITION OF SOME CONDUCTING POLYMERS ON METALLIC SUBSTRATE

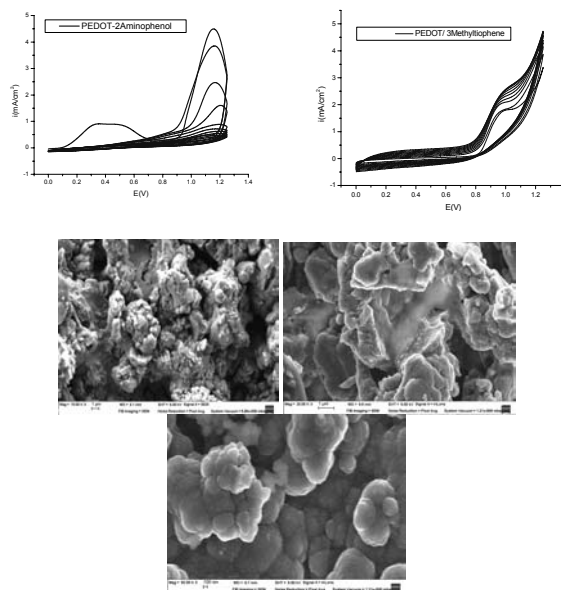
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Electropolymerization and characterization of poly (3, 4-ethylenedioxythiophene) (PEDOT) /3-methylthiophene and 3,4 ethylenedioxythiophene/2 aminophenol were studied. They were fabricated by a simple oxidative electropolymerization method. The nanocomposite coatings have been prepared by using electrochemical methods from aqueous solutions, such that the components were deposited simultaneously onto platinum electrode substrate. The morphology of composite films was analyzed by scanning electron microscopy (SEM). The electrochemical and physical properties of the resulting composites were evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) techniques in 0.1M LiClO₄ aqueous solutions. The synthetic, morphological and electrical properties of the obtained nanocomposite films were compared. The value of specific electrochemical capacitance of the composite films is considerably higher than for pure polymer films, and PEDOT/3-methylthiophene composite films have high specific capacitance than PEDOT/2 aminophenol. The improved properties of the electrodes were obtained by using these composite films. All of the composite films constituted a very promising electrode material for application in a supercapacitor.



INTRODUCTION

Conducting polymers are also intriguing molecular structures because their ability to dramatically change properties when stimulated by an electric signal. These materials offer exciting prospects for a wide range of new devices as membranes, artificial muscles, solar cells, batteries, capacitors, corrosion protection coatings

or sensor applications.¹⁻⁵ Often practical applications of conductive polymers are hindered by the limited mechanical strength or the low conductivity of the material. Conducting polymers exhibit oxidation-reduction properties and also have high specific surface area and better accessibility of the ions to the electrochemically active surface. Conducting polymers (CP) with good electrical conductivity and large pseudo

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capacitance have aroused wide interests as the electrode material in supercapacitors which are unique for provision of pulsed high power.³⁻⁷ A special attention has been paid to the following CPs: polyaniline (PANI), polypyrrole (PPY), polythiophene (PTh) and their derivatives have been considered as promising electrode materials for supercapacitor.^{8-15,16-21} The numerous materials devised, development of the polythiophene derivative, polyethylenedioxythiophene (PEDOT), 3-methylthiophene has shown significant promise for the challenge at hand. Poly (3, 4-ethylenedioxythiophene) (PEDOT) is one of the most successful polythiophene derivative because of its interesting properties: high conductivity, unusual electroactivity and a relative environmental stability.¹⁹⁻²⁴ PEDOT proved a better aqueous stability and biocompatibility than polypyrrole and polyaniline and therefore it is considered a promising polymer appropriate for continuous sensing and even *in vivo* implantation.²⁵⁻²⁷ It can be produced electrochemically in a variety of solvents. It has been shown that the electrochemical and physical properties of polymers are greatly influenced by the nature of dopant and electrolyte during the polymeric process.²⁸⁻³⁰

In this paper we have studied electrochemical synthesis of nanocomposite film from poly (3, 4 – ethylenedioxythiophene)/3-methylthiophene and 3,4 ethylenedioxythiophene/2 aminophenol such that the components were deposited simultaneously onto platinum electrode substrate and electrochemical characterisation of these composite by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy (SEM), have been presented in this paper.

EXPERIMENTAL

The electrochemical synthesis and measurements were carried out by using a single –compartment cell with the conventional three electrode set up at room temperature. The cell was connected to a VoltaLab potentiostat coupled to a PC running VoltaMaster software. A saturated calomel electrode (SCE) was employed as the reference electrode and a platinum sheet as an auxiliary electrode. The working electrode was a platinum disk with a surface area 0.5 cm^2 . All chemicals were reagent grade and used as received without further purification. In this paper were used 3,4-ethylenedioxy thiophene (EDOT) 3-methylthiophene and 2 aminophenol (99.5% Aldrich), LiClO_4 (Merck), All the solutions were prepared with double distilled water.

Preparation of modified electrode

Before each electrochemical measurement the surface of the working electrode was mechanically polished with 0.3 and $0.05 \mu\text{m}$ alumina powders and rinsed in double distilled water and ethanol. The prepared electrodes were dried and used for modification.

Nanocomposite films of 3,4 ethylenedioxythiophene/2-aminophenol and 3,4 ethylene-dioxythiophene/3-methylthiophene have been prepared by electrochemical polymerization from a solution containing the corresponding monomer (PEDOT), 2-aminophenol and 3-methylthiophene.

Thus, PEDOT/ composite films were obtained from an aqueous solution containing 0.025 mol/L of 3,4 ethylenedioxythiophene + 0.025 mol/L 2-aminophenol and 0.025 mol/L of 3,4 ethylenedioxythiophene + 0.025 mol/L 3-methylthiophene in 0.1 M of LiClO_4 by cyclic voltammetry in the potential scanning range of 0 mV to $+1250 \text{ mV}$ at a scan rate of 10 mV/s and for a cycles number of 10.

Characterization of the modified electrodes

The electrochemical properties of the composite films were evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The electrochemical characterization of the PEDOT/2-aminophenol and PEDOT/3-methylthiophene was carried out in 0.1 M LiClO_4 cycling aqueous solutions for comparison and because the dopant anion of the polymeric films is the same with the anion of the cycling solution. Twenty consecutive potential scans were performed for modified electrodes and they were cycled in the potential range of 0 mV to $+1250 \text{ mV}$ with a scan rate of 50 mV/s . The impedance measurements were carried using a VoltaLab 40 potentiostat/galvanostat in the frequency range of 100 kHz to 1 mHz with an AC wave of 5 mV (peak-to-peak) overlaid on a DC bias potential and the impedance data were obtained at a rate of 10 points per decade change in frequency.

RESULTS AND DISCUSSION

Composite films of poly (3, 4-ethylenedioxythiophene)/2-aminophenol were fabricated by a simple oxidative electropolymerization method. These films were electrodeposited on a platinum working electrode using a classical system with three electrodes. The PEDOT /poly-2-aminophenol film was obtained on the platinum substrate in a synthesis solution of 0.025 mol/L 3,4 ethylenedioxythiophene + 0.025 mol/L 2-aminophenol + 0.1 M LiClO_4 by cyclic voltammetry in the scanning potential range of 0 to $+1250 \text{ mV}$ at a scan rate of 10 mV/s and for 10 cycles.

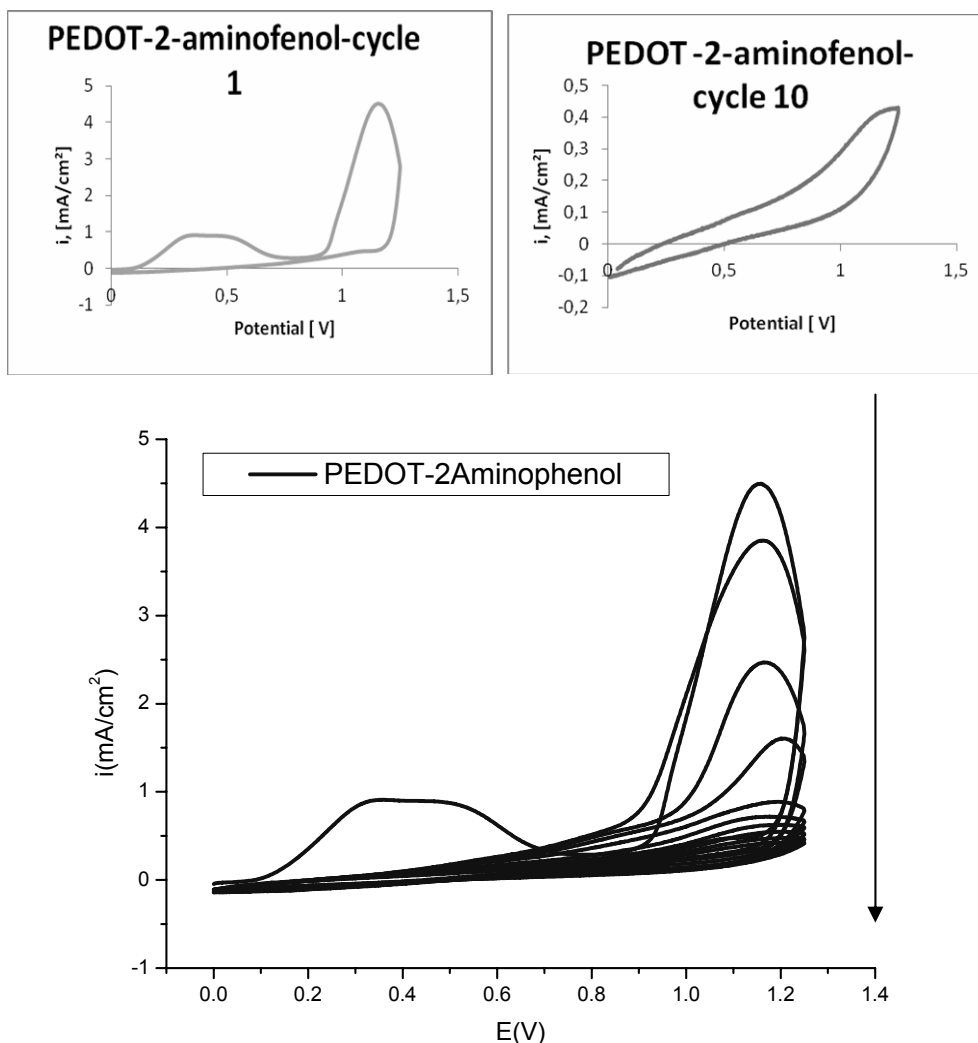


Fig. 1 – Polymerization cyclic voltammograms of 3,4 ethylenedioxythiophene + 2-aminophenol in 0.1M LiClO₄ aqueous. Solution. Inset 1st Cycle (a) and 10th Cycle (b).

Fig. 1 shows the cyclic voltammograms of the electropolymerization of PEDOT and 2-aminophenol monomers. From Fig. 1 it can be seen that at the increasing anodic potential sweep, on the anodic branch two anodic oxidation peaks appear while, at the reverse potential sweep on the cathodic branch the reduction peak doesn't appear. The absence of a reverse cathodic peak can be assigned to a fast result chemical reaction following the oxidation of the amino group. In general, cations radicals obtained from aromatic amine derivatives couple quickly to give dimers, which are more easily oxidizable than basis monomer. The broad peak on the first cycle between 0.2 and 0.6V is due to the oxidation of the hydroxyl group and amino group of aminophenol which leads to the polymerization of the monomer. A second oxidation peak appears in the first cycle

between 1.05 and 1.25V which reveals the formation of the radical cations and that the EDOT radical cations start to electropolymerize onto the platinum electrode. During the first potential scan, the polymerization potential of PEDOT/2-aminophenol on Pt is around 1 V, while the onset of polymerization shifts significantly on following scans to more positive potentials and stabilizes at 1.2-1.25 V. After the first cycles 1-5, the anodic peak at 1.1V was found to decrease as the number of scans increased and it is observed that the current response of the polymerization PEDOT/2-aminophenol films decreases from 4.5 mA/cm² to 0.45 mA/cm² with continuous cycling in the potential range as seen in Fig. 1. When cycling occurs the current density decreases with each cycle and finally reaches stable value.

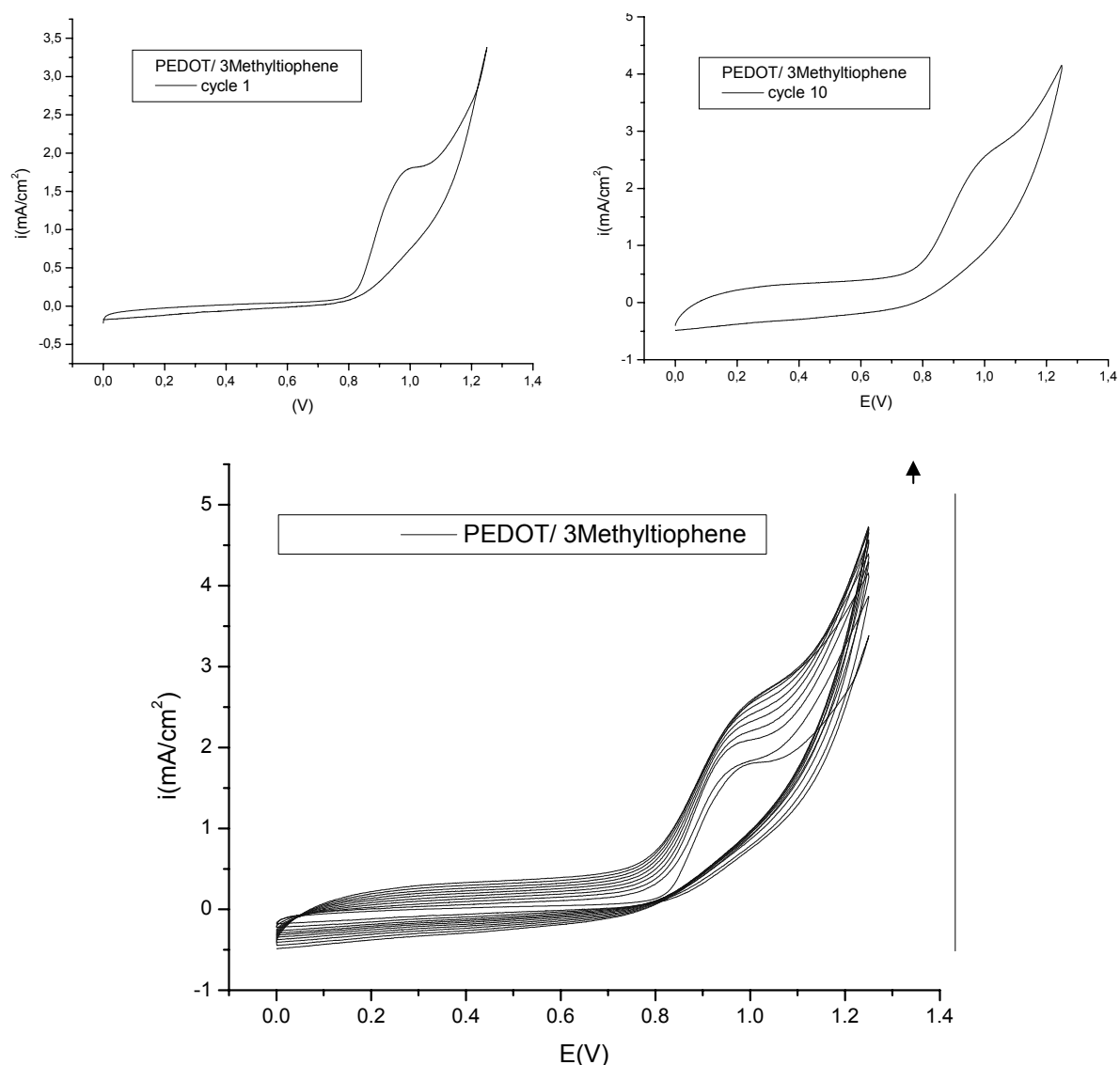


Fig. 2 – Polymerization cyclic voltammograms of 3,4 ethylenedioxythiophene + 3-methylthiophene in 0.1M LiClO₄ aqueous. Solution. Inset 1st Cycle (a) and 10th Cycle (b).

Composite films of poly (3, 4-ethylenedioxythiophene) and 3-methylthiophene were fabricated by a simple oxidative electropolymerization method where it can be observed in Fig. 2. The PEDOT/P3MT film was obtained on the platinum substrate in a synthesis solution of 0.025 mol/L 3,4 ethylenedioxythiophene + 0.025 mol/L 3-methylthiophene + 0.1M LiClO₄ by cyclic voltammetry in the scanning potential range of 0 to +1250 mV at a scan rate of 10 mV/s and for 10 cycles.

It is can be seen from Fig. 2 that, the reaction current increases sharply when the applied potential is larger than 0.88 V, which reveals the formation of the radical cations. The increased current implies that the EDOT and 3MT radical cations start to electropolymerize onto the platinum

electrode. During the first potential scan, the polymerization potential of PEDOT/ P3MT on Pt is around 0.94 V, while the onset of polymerization shifts significantly on following scans to more positive potentials and stabilizes at 1.25 V.

After the first cycles 1-5, the anodic peak at 1.18 V was found to increase as the number of scans increased and it is observed that the current response of the polymerization PEDOT/ P3MT films increases from 1.8 mA/cm² to 3.5 mA/cm² with continuous cycling in the potential range as seen in Fig. 2 and these proposes that the electroactive products were deposited onto the electrode surface. This fact can be explained taking into account that the conductivity of PEDOT/3-methylthiophene's composite film increases.

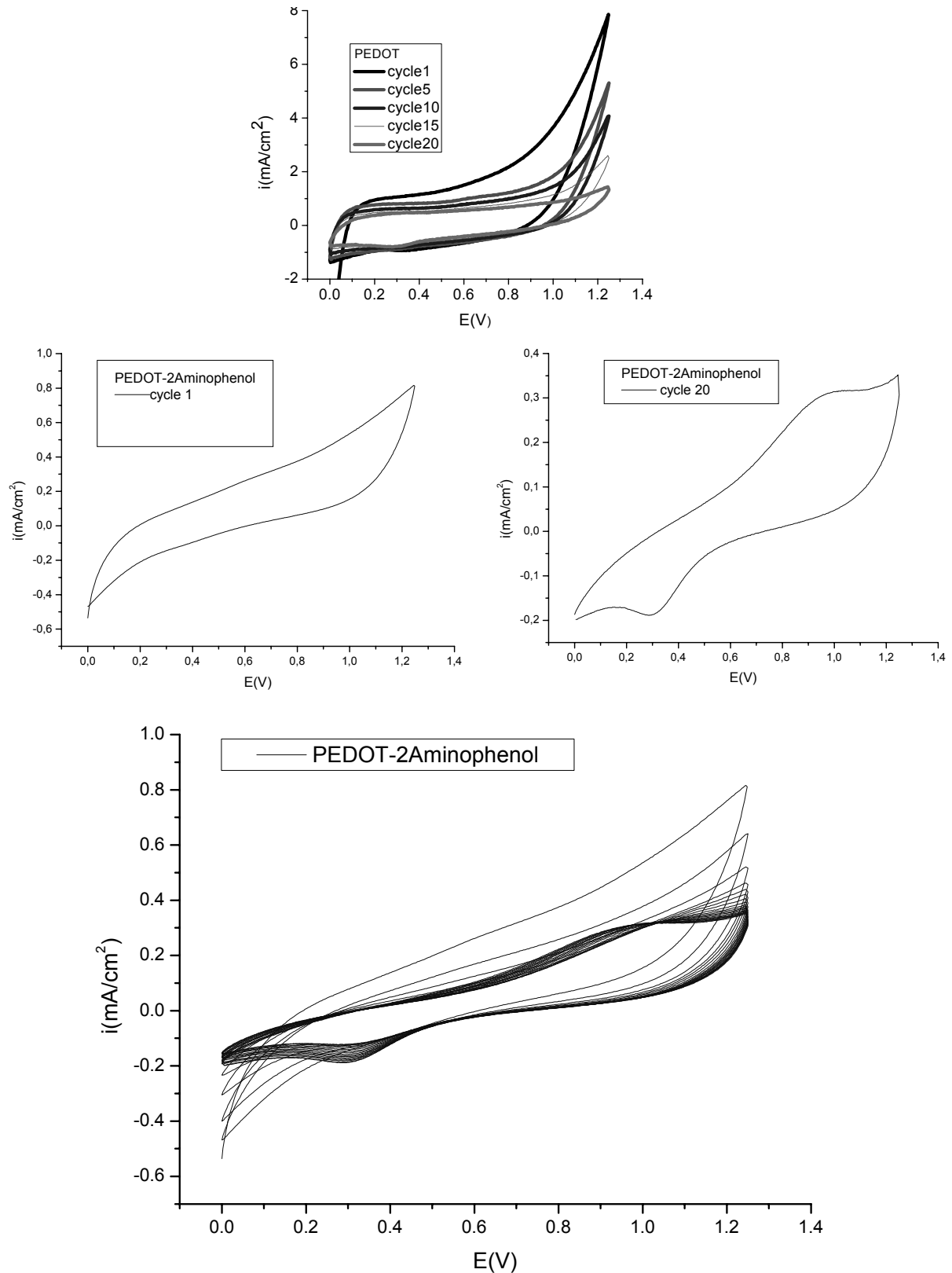


Fig. 3 – Cyclic voltammograms of PEDOT/ poly-2-aminophenol film in cycling solution (monomer free) of 0.1M LiClO₄. Inset 1st Cycle and 20th Cycle; and PEDOT film.

After the 10th cycle of the cyclic voltammograms of PEDOT/3MT shows an

increase in current, showing that the films have become thicker. These results propose that the

electroactive PEDOT/3MT composite films polymerized on platinum electrodes successfully.

Thus, the PEDOT/3MT composites exhibit slightly higher currents than PEDOT/2-aminophenol composite films, which can be translated into larger capacitance. This is an indication of faster kinetics in the PEDOT/3MT composite, which can be attributed to the higher electronic conductivity. This means that the redox processes which take place in PEDOT/3MT composite film are more intense than those in the pure PEDOT film and PEDOT/2-aminophenol composite film.

The electrochemical properties of the obtained modified electrode type PEDOT/2-aminophenol and PEDOT/3-methylthiophene films were investigated by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

The electrochemical behaviour of the PEDOT, PEDOT/2-aminophenol and PEDOT/3-methylthiophene films deposited electrochemically from aqueous solution was characterized further using cyclic voltammetry. The electrochemical characteristics of obtained PEDOT/2-aminophenol and PEDOT/3-methylthiophene composites film was studied in the cycling solutions, an aqueous solution of 0.1M LiClO₄ (see Figs. 3-4).

Fig. 3 reports the cyclic voltammograms of PEDOT/2-aminophenol recorded in aqueous solution of 0.1M LiClO₄ in wide potential range to explore all possible electrochemical properties of this film in aqueous electrolyte. The modified electrode type PEDOT/PEDOT/2-aminophenol/Pt was cycled on the potential range from 0 up to 1250 mV with a sweep rate of 50 mV/s and for a cycles number of 20, see Fig. 3.

It can be observed that, with the increase of the cycle's number, the shape of cyclovoltammograms considerably changes. Analyzing Fig. 3 one can see that, together with the increase of the cycle number takes place an accentuated decrease of the peak heights, a lowering of the peaks number and a movement of them towards more electropositive value, for anodic peaks. A counter-ion insertion could explain this peak system. The ClO₄⁻ anion inserted in the polymer matrix would interact with the oxidized sites of the polymer chain. This would change of the redox potential of the polymer by the formation of the mixed chain. These films can be cycled repeatedly between the conducting and insulating state without significant decomposition

of the material, which is consistent with the results reported in the literature.³⁰ As can be seen from Fig. 3, the curves of these composite films have nearly rectangular shape, which is typical of the pure capacitive behavior of the tested object.³¹⁻³⁵

The electrochemical characteristics of obtained PEDOT/P3MT film were studied in the cycling solutions, an aqueous solution of 0.1M LiClO₄. The electrode potential was cycled on the potential range from 0 up to 1250 mV with a sweep rate of 50mV/s and for a cycles number of 20.

By comparing the cyclic voltammograms for PEDOT/2-aminophenol and PEDOT/3-methylthiophene composites film it can be seen that the shape of voltammograms is similar, but the PEDOT/3-methylthiophene composites presents higher currents than the PEDOT/2-aminophenol films ones, which can be translated into larger capacitance of the composites.

The significance of this is that the 3-methylthiophene films becoming neutral and the negative charge of ClO₄⁻ being balanced by the cations with small size from the supporting electrolyte solution, these ClO₄⁻ anions are immobilized and hence exhibit a permanent electrostatic repulsion to the electron on the polymer chain.

The difference in current between PEDOT/2-aminophenol and PEDOT/3-methylthiophene composites film can be explained by the latter having a certain structure for ion transport as well as higher and potential-independent electronic conductivity through the adsorbed film.

The shape of the cyclic voltammograms curve in all the cases is close to rectangular (see Figs. 3-4). The best electrochemical behavior is presented by PEDOT/3-methylthiophene/Pt composites film.

Moreover, the composite films were studied by electrochemical impedance spectroscopy (EIS) at open circuit potential, in an aqueous solution of 0.1M LiClO₄ at 25°C. Electrochemical impedance spectroscopy has been used in a field of electroactive polymer coated electrodes. EIS is a more reliable technique than cyclic voltammetry for measuring the capacitance with the minimal effect from noncapacitive faradaic contributions. The resulting Nyquist plots and Bode plots for PEDOT/2-aminophenol and PEDOT/3-methylthiophene composite films are shown in Figs. 5-6. The impedance plot is composed of a semicircle at high frequencies for composite

PEDOT/ 2aminophenol (see Figs. 5-a) and a capacitive slope at low and middle frequencies for composite PEDOT/ 2aminophenol and PEDOT/3-methylthiophene composite films (see Fig. 5). The semicircle appeared at high frequencies is considered to owe to the charge transfer resistance, which originates from the interface structure between the electrode surface and the electrolyte.³⁴⁻³⁷ At low frequencies, the impedance plot becomes a near vertical line. The Nyquist plots for PEDOT/2-aminophenol and PEDOT/3-methylthiophene composite films are featured by a

vertical trend at low frequencies, indicating a capacitive behaviour according to the equivalent circuit theory.³⁷⁻⁴⁰ In conclusion, at PEDOT/3-methylthiophene and PEDOT/2-aminophenol composite films, all the imaginary part of the impedance at low frequencies were almost perpendicular to the real part, which verified a good capacitance behaviour of the system. Bode diagrams point out also the capacitive behaviour in concordance with Nyquist plots (see in comparison Figs. 5a-5b and Figs. 6a-6b).

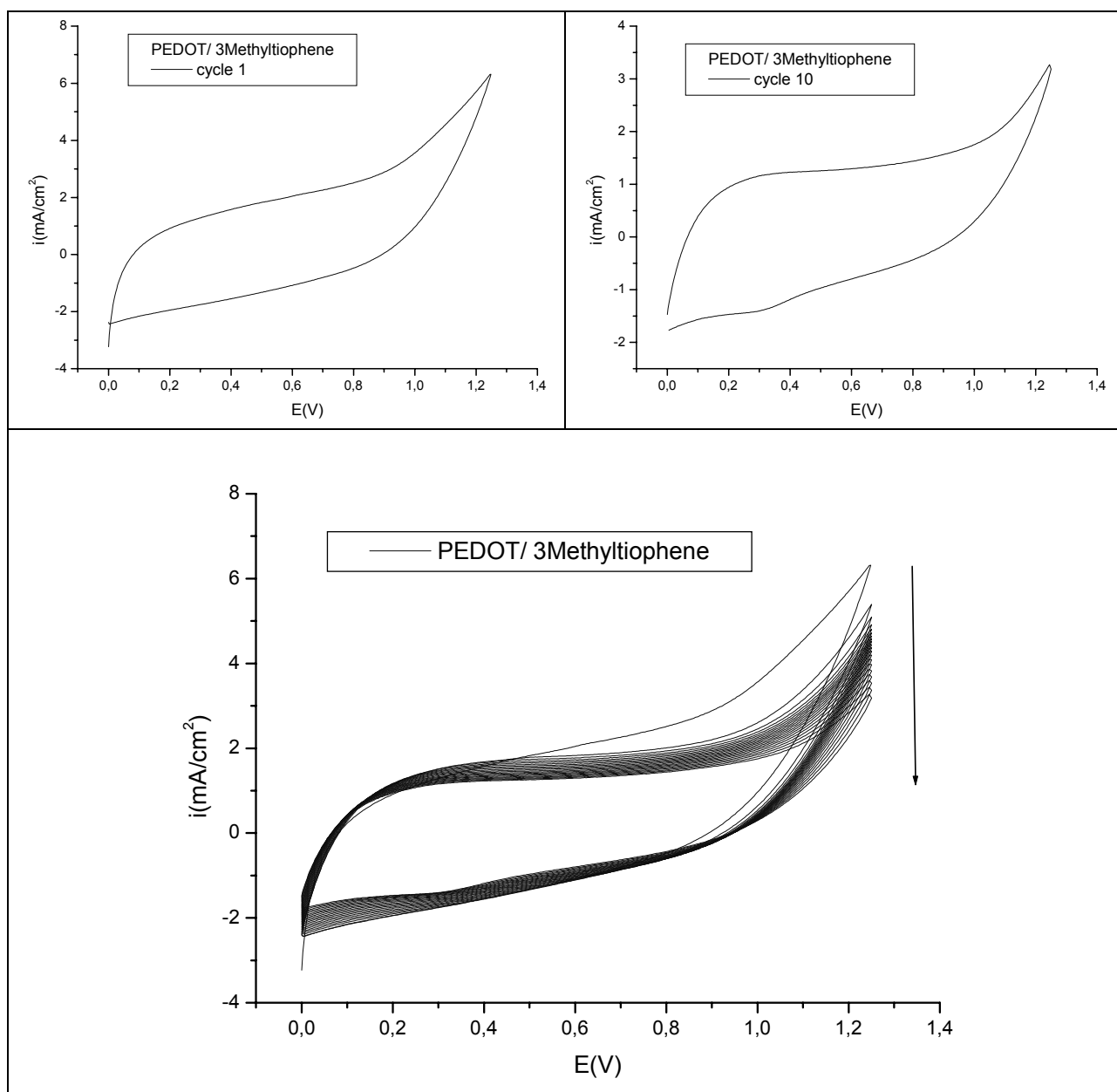


Fig. 4 – Cyclic voltammograms of PEDOT/ P3MT film in cycling solution (monomer free) of 0.1M LiClO₄. Inset 1st Cycle and 20th Cycle.

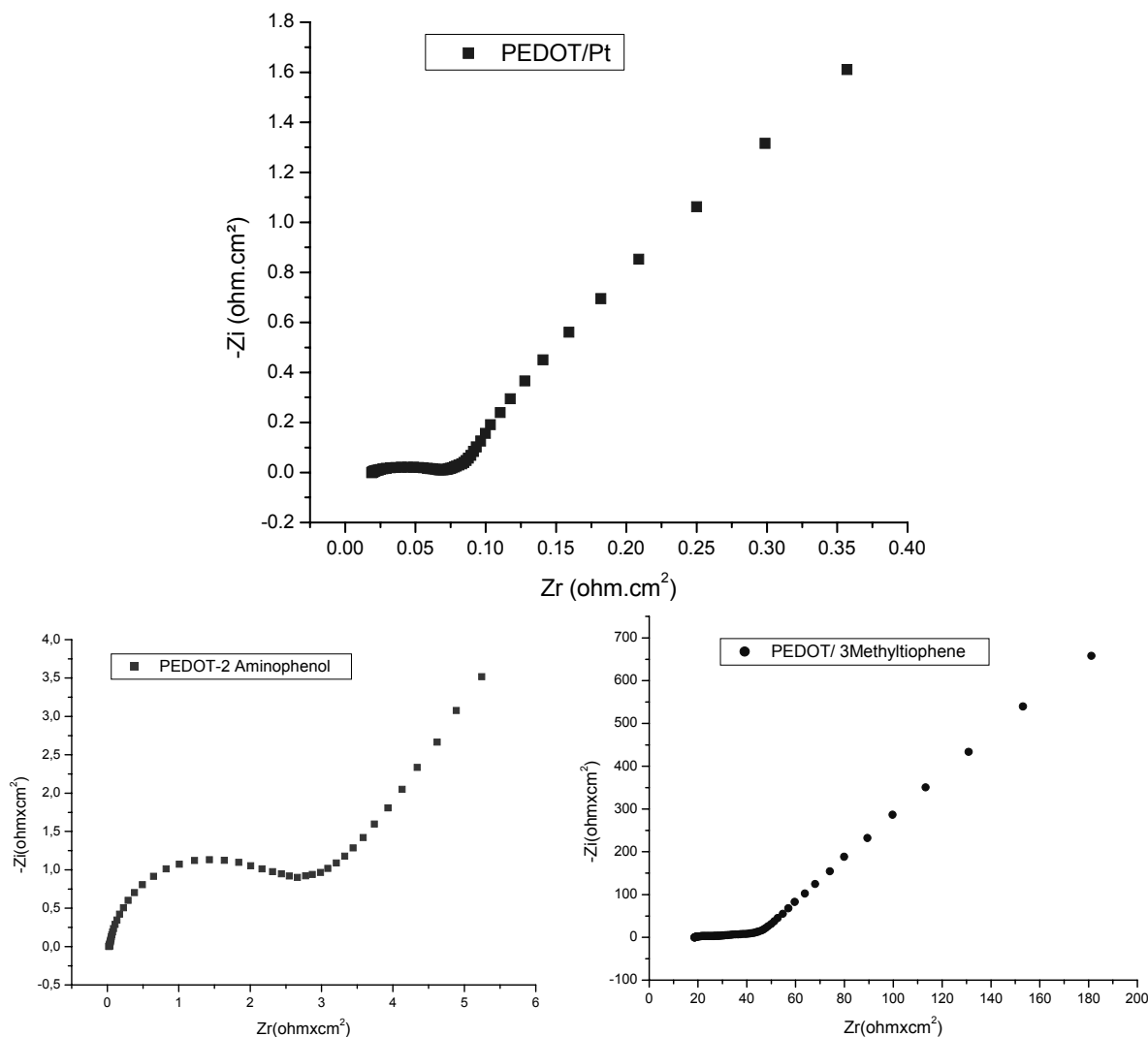


Fig. 5 – The Nyquist diagrams for modified electrodes (a) PEDOT/Pt, (b) PEDOT/ 2-aminophenol/Pt and (c) PEDOT/3-methylthiophene/Pt at open circuit potential in an aqueous solution of 0.1 M LiClO₄.

The capacitances of the electrode materials were calculated according to the equation:

$$C = -1/(2\pi f Z_{im}).$$

(f = frequency; Z_{im} = imaginary impedance), from the slope of the linear correlation between the imaginary impedance and the reciprocal of the frequency at low frequencies.

From these Figs. 5-8 and Table 1, one can observe higher capacitance one order of magnitude value for PEDOT/3-methylthiophene film in respect with PEDOT/2-aminophenol composite film and PEDOT pure polymeric films. As mentioned, the PEDOT/3-methylthiophene composite films is good electrode material for supercapacitor applications.

We can conclude that the capacitance of PEDOT/3-methylthiophene is larger than that of the pure polymeric PEDOT films and PEDOT/ 2-aminophenol composite film because the structure of PEDOT/3-methylthiophene composite films makes

the doping ions (ClO₄⁻) enter into/eject from PEDOT/3-methylthiophene composite films more easily.

The combined resistance of the electrolyte and the film including electronic as well as ionic contributions is indicated by the real impedance at low frequencies where the capacitive behaviour predominates. The values of the real impedance at 0.01Hz are given also in Table 1. It can be seen that the PEDOT/3-methylthiophene films were significantly lower in resistance than PEDOT films and PEDOT/2-aminophenol composite films. In comparison with the PEDOT film and PEDOT/2-aminophenol composite films, it can be observed that PEDOT/3-methylthiophene offered much higher overall conductivity. As mentioned before, the real impedance of an electrode material, in general, decreases as the material's structure increases due to improved ionic accessibility.^{36-40, 41-44}

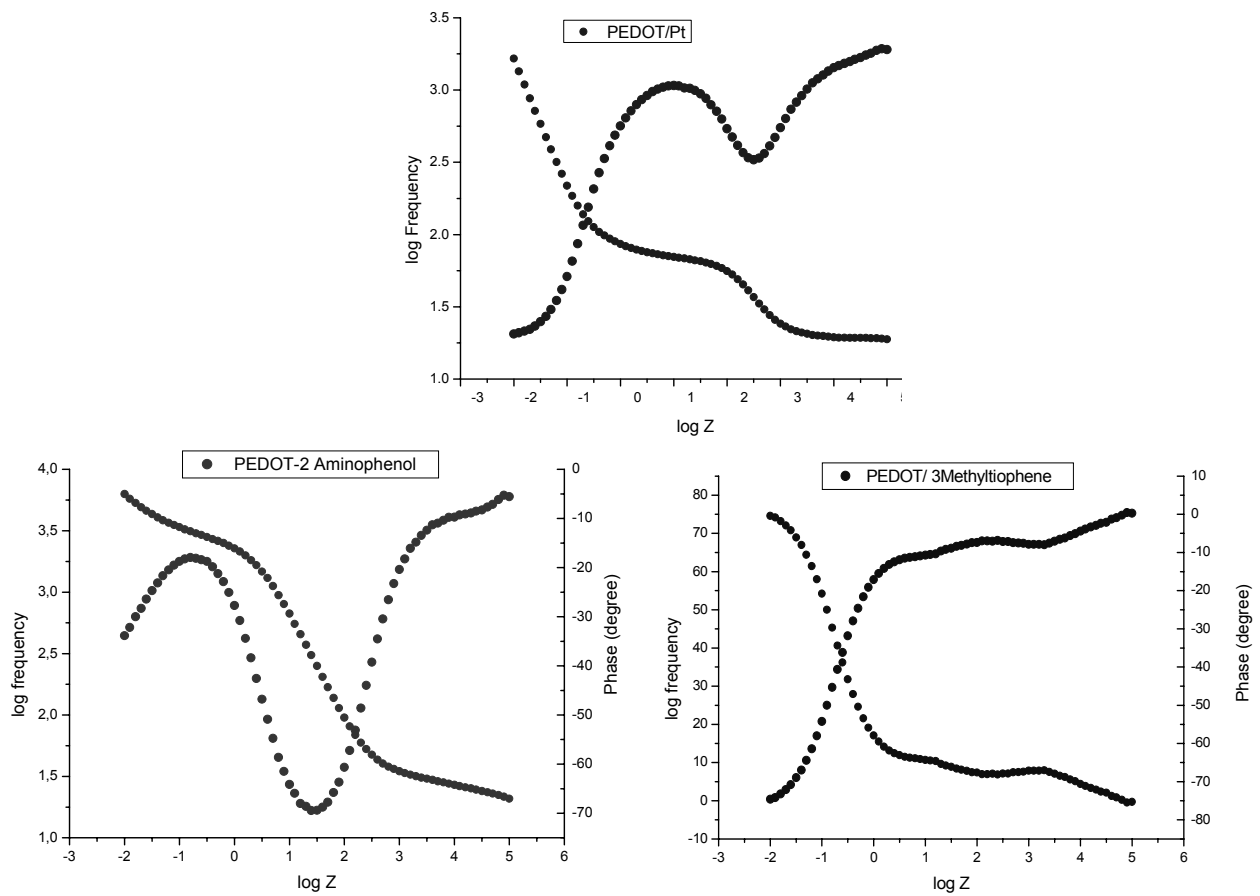


Fig. 6 – The Bode diagrams for modified (a) PEDOT/Pt, (b) PEDOT/ 2aminophenol/Pt and (c) PEDOT/3-methylthiophene/Pt at open circuit potential in an aqueous solution of 0.1M LiClO₄.

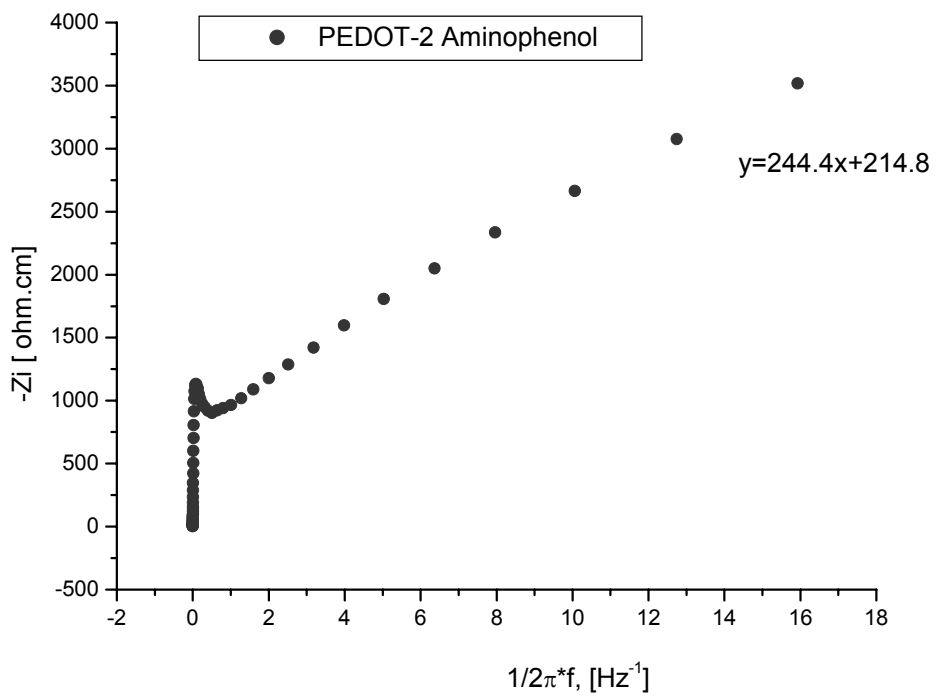


Fig. 7 – Capacitance evaluation for PEDOT/ poly-2-aminophenol modified electrode.

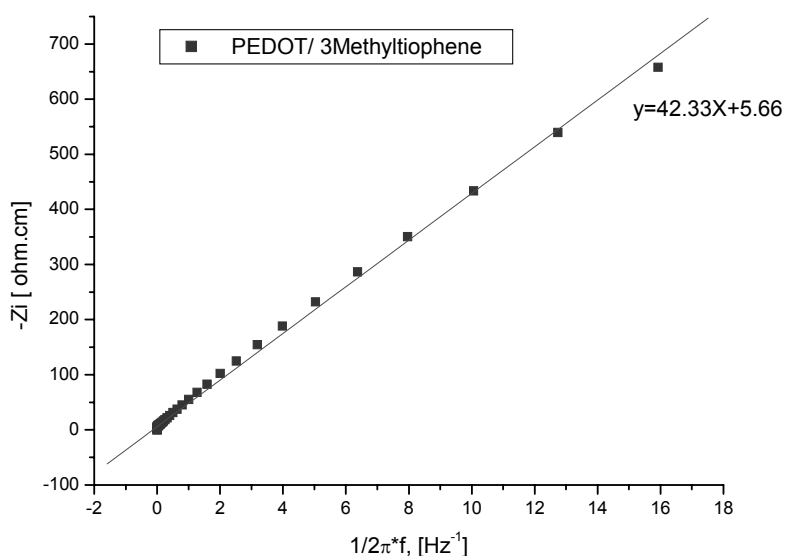


Fig. 8 – Capacitance evaluation for PEDOT/3-methylthiophene modified electrode.

Table 1

Real impedance and capacitance values of pure PEDOT film, PEDOT/ poly-2-aminophenol and PEDOT/ poly3-methylthiophene nanocomposite film obtained by co-polymerization using the cyclic voltammetry (CV) at 0.01Hz

Polymeric film	Slope values obtained from graph $-Z'' = f(1/2\pi f)$	C [F/cm ²]	Z _r (Ωcm ²) at 0.01Hz
PEDOT	103	0.009	357
PEDOT/ 2-aminophenol	244.4	0.004	5243
PEDOT/3-methylthiophene	42.33	0.024	182

Fig. 9 shows the SEM images of the PEDOT/Pt, PEDOT/2aminophenol/Pt and PEDOT/3-methylthiophene/Pt composite film. In Fig. 9a a nodular accumulating structure is evidenced. The size of the nodules ranged a few hundred nanometers in diameter and they aggregate to form gobbets. In figure 10b, the morphology of PEDOT/2aminophenol film can be observed: globular and lamellar structure with almost vertical orientation to the substrate.

It can be observed that copolymers change the morphology of PEDOT film into a smaller porous structure with a great interface area. This is in accord with the SEM results presented below that illustrated a smaller porosity in the PEDOT film than in the case of the composite film (see Fig. 10 b-c). The porous structures in the PEDOT film and composite films should also facilitate ionic and solvent motion. The SEM images showed that the composite films, PEDOT/3-methylthiophene were more porous than PEDOT films (see Fig. 10c). The microstructural variation has profound influence on the capacitive behavior of the composite.

CONCLUSIONS

We obtained nanocomposite films type PEDOT/2-aminophenol and PEDOT/3-methylthiophene by cyclic voltammetry method from a synthesis solution;

The electrochemical activity PEDOT/2-aminophenol/Pt and PEDOT/3-methylthiophene modified electrode in 0.1M LiClO₄ cycling solution is much higher than of PEDOT/Pt modified electrode in the same cycling solution;

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) demonstrated that these composite films had similar electrochemical response rates to pure polymeric films but a higher electronic conductivity;

The best electrochemical behavior is presented by PEDOT/poly3-methylthiophene/Pt modified electrode;

Nearly rectangular shaped cyclic voltammograms are obtained for all composite films suggesting that the charge and the discharge reversibly occur at the electrode/electrolyte interface;

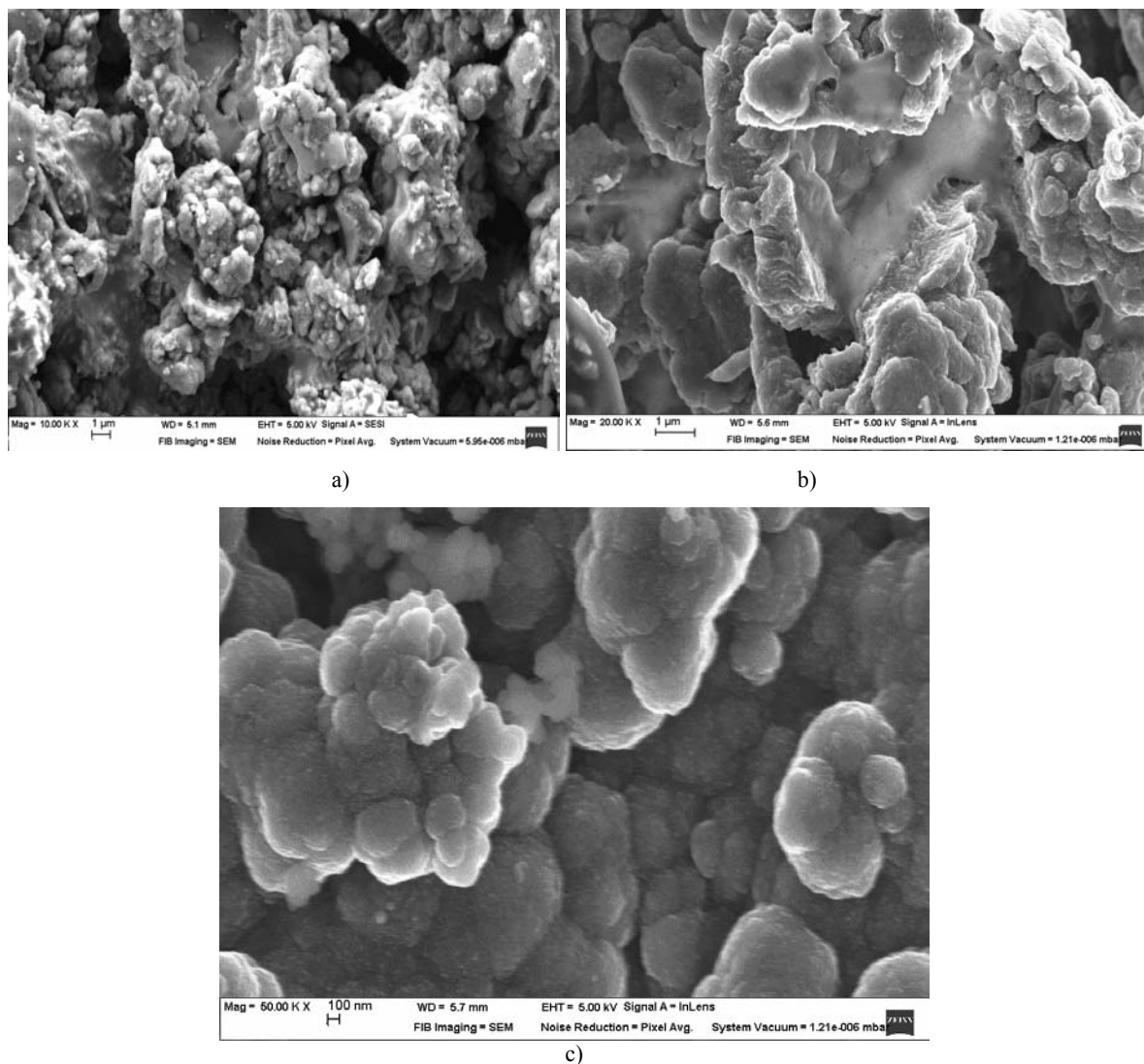


Fig. 9 – SEM images of the film surface of a) PEDOT, b) PEDOT/2-aminophenol and c) PEDOT/3-methylthiophene composite film formation by cyclic voltammetry (0 to 1250mV at a scan rate of 10 mV/s).

The Nyquist plots for both PEDOT and composite films PEDOT/2-aminophenol, PEDOT/poly3-methylthiophene are featured by a vertical trend at low frequencies, indicating a capacitive behaviour according to the equivalent circuit theory;

The PEDOT/3-methylthiophene composite films have high specific capacitance, very quick charging/discharging ability and very low charge transfer resistance;

The SEM micrograph of the composite film (PEDOT/poly3-methylthiophene and PEDOT/2-aminophenol) shows a more porous morphology than PEDOT polymer film surface;

The PEDOT/2-aminophenol and PEDOT/poly3-methylthiophene composites were a very promising electrode material for application in supercapacitor.

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