

The Effect of Applied Voltages and Coating Thickness on the Capacitance of Electrode Coated With Poly (Potassium Tetrakis-2-Thienyl Borate)

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Abstract:
In this study, PT2TB was polymerized electrochemically in 0.1M tetrabutylhexafluorophosphate (Bu_4PF_6)-Polycarbonate (PC) at range of 0-1.7V and scan rate of 50 mV/s and obtained electrode coated with poly (T-2-TB) was investigated in the way of impedance and capacitance. As a result, it was found that impedance values changed and its capacitive property decreased with increasing of coating thickness. So, specific capacitances (C_{spe}) were 0.31mF/cm^2 and 0.064 mF/cm^2 at 2 cycle and 8 cycle, respectively. On the other way, as applied voltage was increased, capacitive feature of polymer was decreased, due to that the structure of polymer was damaged. It was determined that the voltage must be 0V or 0.2V. In morphological investigation, the particles were observed on the polymer surface, which was estimated due to potassium, probably. Nevertheless, cauliflower structure accepted as a typical for Polythiophene was observed on the surface.
Key words: Potassium tetrakis-2-thienyl borate, electropolymerization, electrochemical impedance spectroscopy, capacitance.

1. Introduction

Conducting polymers (CPs) include delocalized π-bonded electrons over the polymeric backbone. Thus, CPs having this structure show the properties such as low ionization potentials, and high electron affinities, electric, electronic, magnetic and optical properties inherent to metals or semiconductors and are named as “synthetic metals” because of that. The CPs have been widely used in the areas of bioanalytical science [1] due to their inherent charge transport properties and biocompatibility [2, 3], conducting polymers have been reviewed by many scientists especially in biosensors evaluations [4, 5]. Some CPs are doped and/or covalently and physically modified by bionano-materials [6-9], especially proteins [10], neurotransmitters [11] and nucleic acids [12, 13], which exhibit unique catalytic [14] properties that can be easily employed in the design of biosensors [15]. To obtain super capacitors having high power density and to develop the mechanic and the electrochemical properties of conducting polymer, the researchers modified the electrodes with conducting polymers, electrochemically [16-17]. The sensitivity and selectivity of CP based biosensors are determined by the difference in specific properties before and after exposure to a test target molecule [18]. The test target molecule can change the number and mobility of charge carriers, which results in the overall change in conductivity, current, impedance data etc.

Impedance is a totally complex resistance encountered when a current flows through a circuit made of resistors, capacitors, or inductors, or any combination of these [19]. Depending on how the electronic components are configured both the magnitude and the phase shift of an ac can be determined. For this aim, researchers used the Electrochemical Impedance Spectroscopy (EIS) to obtain impedance data and to investigate the charge transfer, ion diffusion and capacitive property of electrodes coated with conducting polymer [20-21]. EIS method was able to use as the readout of Poly (Cz) coated electrode as a biosensor for the determination of epinephrine (EP) [22].

Potassium tetrakis-2-thienyl borate (PT2TB) is a monomer having thienyl and Boron (B) and exists in form tetrakis-2-borat anion in solution. Since its discovery by Witting et. al. [23], sodium tetraphenylborate has been extensively studied as an analytical reagent for various cations, including potassium and certain heavy metals [24]. Its electrochemical oxidation has been the subject of several investigations, both in organic and aqueous solutions [25]. Two irreversible voltammetric peaks were observed. First includes the cleavage of the carbon-boron bond to yield biphenyl and biphenyl borinic acid and as a result the formation of a film are observed onto the working electrode. Tetrakis(2-thienyl)borate as its phenyl analogue were studied [26-29]. Polythiophene including B is obtained at chain when it was polymerized electrochemically [26]. But its impedance and capacitance properties were not studied in detail. So, we were investigated the impedance and capacitance properties of poly(tetrakis-2-thienyl borate, Poly(T-2-TB)) and that how these properties were affected from applied voltage on the poly(T-2-TB) coated electrode and the coating thickness of the electrode.

2. Material and Methods:

Potassium tetrakis-2-thienyl borate was purchased (471941) from Sigma-Aldrich, which was salt form. It was used as received. Solutions were prepared as 0.01 M PT-2-TB in the 5 ml of 0.1M tetrabutylhexafluorophosphate (Bu_4PF_6)-Polycarbonate (PC). All solutions were degassed with nitrogen gas and all experiments were carried out in room temperature (20 ±2°C).

2.1. Linear Sweep Voltammogram (LSV) and Cyclic Voltammetry (CV):

Firstly, polymerization conditions were determined. Cyclic voltammetry (CV) experiments, spectroelectrochemistry and electropolymerization were performed with a Princeton Applied research potentiostat model 2263 potentiostat/galvanostat interfaced to a PC computer and controlled PowerSuit software package in a three-electrode setup employing a Polyethylene terephthalate film, ITO coated (ITOPET) as working electrode and Platinum wire (Pt) as counter electrode and silver wire (Ag) as reference electrode (pseudo). Applied scan rate was 50 mV/s. To avoid over oxidation linear sweep voltammograms (LSV) were obtained in different potential ranges (0-1,3; 1.5; 1.7V). The potential range was determined by forming of the coating on ITOPET. Obtained LSVs were illustrated in Fig.1.

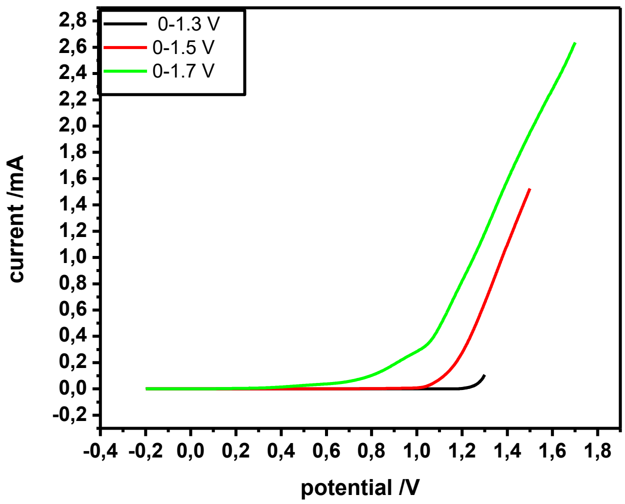


Figure 1. LSV curves of PT-2-TB (0.01M PT-2-TB; scan rate: 50mV/s; working electrode ITOPET; different potential range)

As seen in the fig. the monomer was oxidized about at 1.2 V, but the coating was not observed on ITOPET in 0-1,3V case, as well as in 0-1,5V case. Differently, in case 0-1.7 V, it was oxidized about at 0.9V and the coating was seen on the ITOPET. So, voltage range was determined as 0-1.7 V to be used in other experiments.

To determine the proper scan rate LSVs was carried out at 0-1.7V potential range by using 0.01M PT-2-TB included 5 ml in 0.1M tetrabutylhexafluorophosphate (Bu_4PF_6)-Polycarbonate (PC) solution by applying various scan rates (20, 50, 75 and 100 mV/s). The obtained data was illustrated in Fig.2 as LSV.

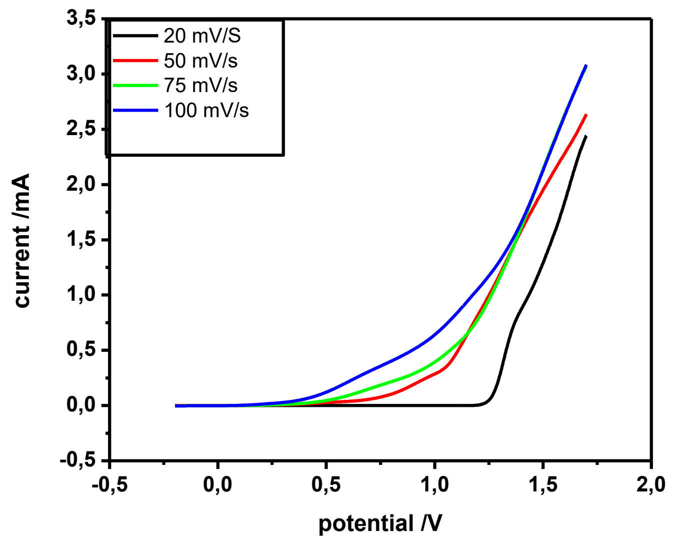


Figure 2. LSV curves of Poly(T-2-TB). (0.01M PT-2-TB; working electrode ITOPET; different scan rate

Depending on the figure, as scan rate was increased, oxidized potential was decreased. Higher scan rate was not suitable for this polymerization. So, a 50 mV/s of scan rate was determined as scan rate. Thus, PT-2-TB was polymerized electrochemically in 0.1M tetrabutylhexafluorophosphate (Bu_4PF_6)-Polycarbonate (PC) at range of 0-1.7V and scan rate of 50 mV/s. Obtained Cyclic Voltammogram was given in Fig.3.

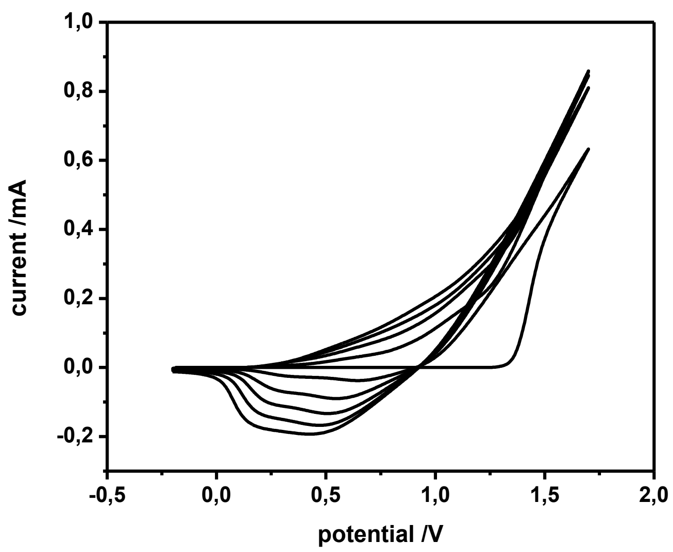


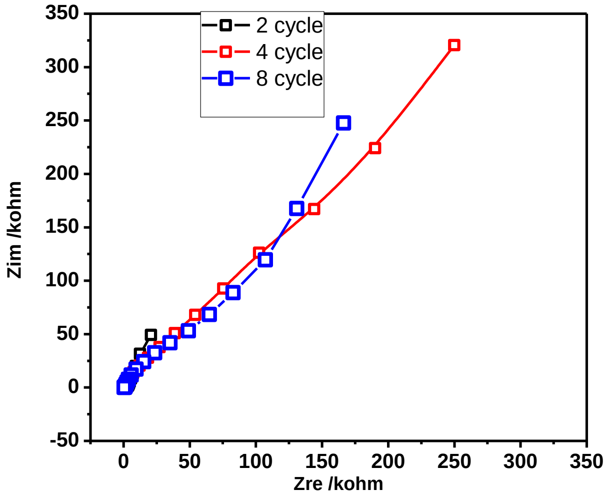
Figure 3. The polymer growth graph of Poly(T-2-TB). (0.01M PT-2-TB; scan rate: 50mV/s; working electrode: ITOPET)

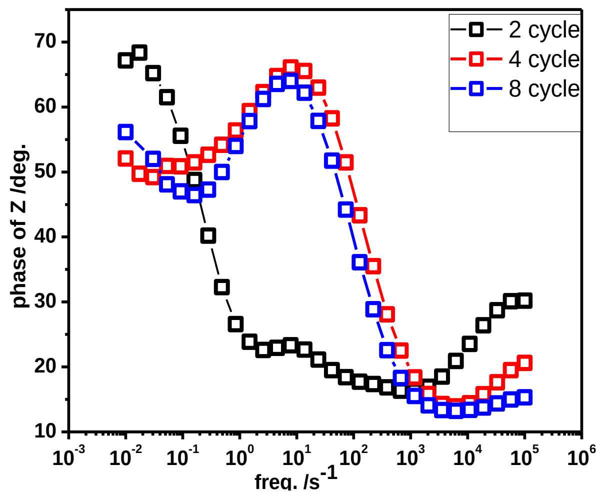
According to the graph, the monomer was oxidized at about 1.3V in these experimental conditions. The conditions were given in the graph. In these conditions the coating formation was observed on the surface of ITOPET, poly(T-2-TB).

2.2. Electrochemical Impedance Spectroscopy (EIS):

To describe electrochemical reaction at electrode/electrolyte interface requires impedance measurements made over a broad frequency range at various potentials and determination of all the electrical characteristics of the interface Obtained electrode coated with poly (T-2-TB) was investigated in the way of impedance and capacitance. Impedance experimentals were carried out in tetrabutylhexafluorophosphate (Bu_4PF_6)-Polycarbonate monomer free solvent system. Electrochemical impedance spectroscopy analyzes the changes in interfacial properties of coated electrode, resulting from the recognition process taking place at the surface. Interfacial interaction between the conjugated polymer and the electrolyte at the conductive or semiconductive interface results in changes in electrical properties, such as capacitance or resistance.

Different from resistance obtained DC measurements (using ohm law), impedance is not limited by the properties of the ideal resistor. The expression Z is composed of a real (Z_{re}) and an imaginary part (Z_{im}). The standard impedance plot used to characterize a conducting polymer is the Nyquist plot on which the real part is plotted on the X-axis and the imaginary part on the Y-axis of a graph. To investigate the effect of thickness coating on impedance and capacitance values, firstly polymerization was carried out at different cycle (2, 4 and 8 cycles). Obtained impedance graphs were given in Fig 4, which were Nyguist , Bode-Phase and Bode-Magnitude.





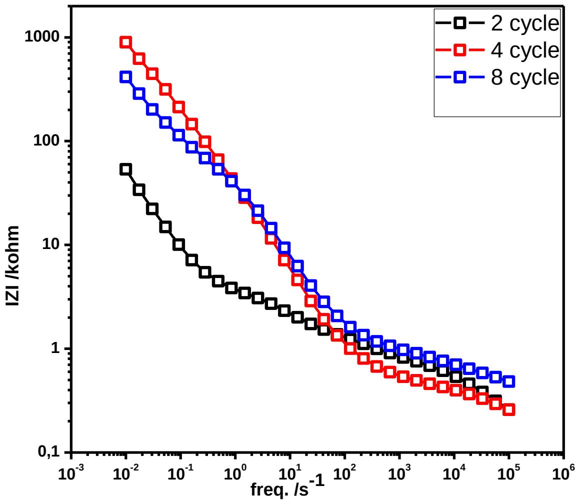


Figure 4. Impedance graphs. a. Nyquist graph, b. Bode-Phase graph, c. Bode-magnitude graph. (Working electrode: ITOPET coated with poly (T-2-TB); electrolyte-solvent: Bu_4NPF_6-PC, monomer free, different coating thickness)

Low frequency capacitance (C_{lf}-Specific capacitance) value was calculated from the related Nyquist graph by using the Equation (1) [17, 20, 30, 31].

$$C_{lf} = \frac{1}{2\pi f Z_{im}} \quad (1)$$

Double layer capacitance (C_{dl}) values were calculated by using average of Z (|Z|) which is obtained from Bode-Magnitude plot. C_{dl} is proportional to 1/|Z| [17, 20, 30, 31]. The C_{lf} and C_{dl} values that showed how coating thickness affected on capacitance and impedance values were calculated and were given in Table 1.

Table 1: The effect of coating thickness on capacitance and impedance values (Z).

Condition	Z_{im}/kohm	C_{lf}/mFcm^{-2}	Phase angle/degree		IZI/kohm	C_{dl}/mFcm^{-2}
			0.01Hz	0-100Hz		
2 cycle	50.69	0.31	67.47	23.26	3.83	0.26
4 cycle	320.73	0.049	52.10	66.32	37.10	0.027
8 cycle	248.76	0.064	56.08	64.03	37.10	0.027

As the coating thickness was increased, its impedance values changed and its capacitance property decreased. According to data from Table 1When the C_{lf} of electrode with 2 cycle coating was 0.31 mF/cm^2, in case of 8 cycles coating the capacitance value was 0.064 mF/cm^2.
To determine the effect of applied voltage on impedance and capacitance values, firstly polymerization was carried out at different voltage (0, 0.2; 0.4and 0.6V). Obtained impedance graphs were given in Fig 5, which were Nyguist , Bode-Phase and Bode-Magnitude.

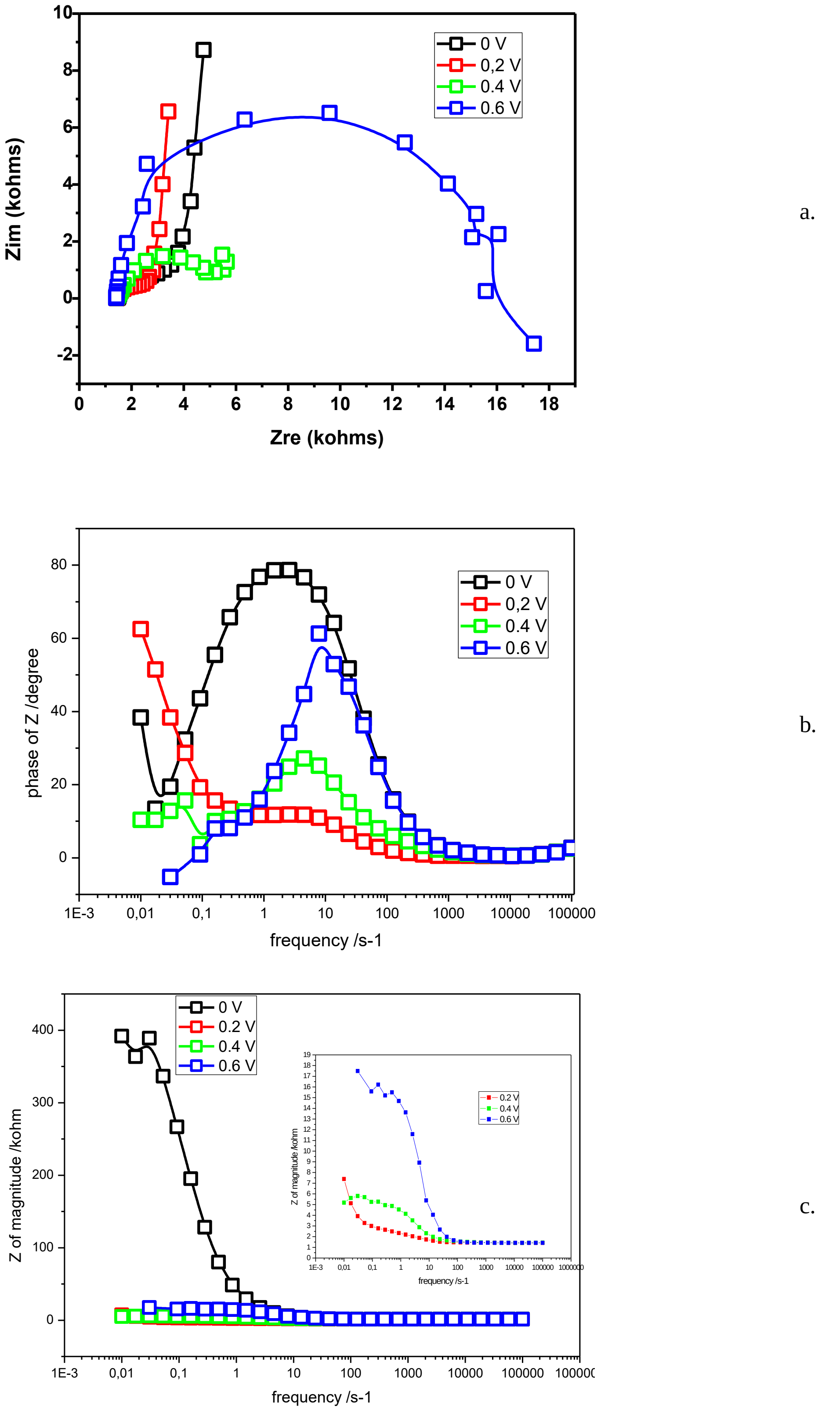


Figure 5. Impedance graphs. a. Nyquist Graph, b. Bode-Phase Graph, c. Bode- Magnitude Graph. (working electrode: ITOPET coated with poly(T-2-TB);electrolyte-solvent: Bu_4NPF_6-PC, monomer free, different applied voltages)

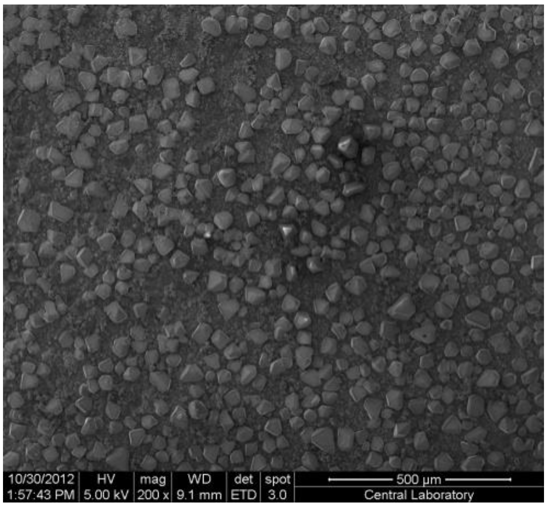
The C_{lf} and C_{dl} values that showed how applied voltage affected on capacitance and impedance values were calculated and were given in Table 2. If it is examined the Table it can be seen that when the applied potential on the poly (T-2-TB) coated electrode was increased the structure of the polymer was degraded and its capacitance was decreased. It say that can be applied potentials are 0V and 0.2V.

Table 2: The effect of applied voltages on capacitance and impedance values (Z)..

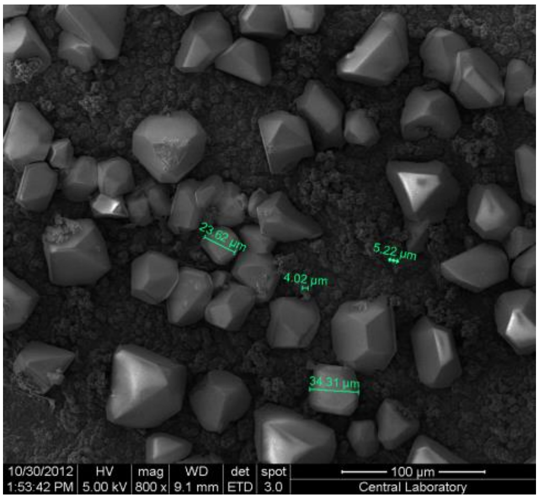
condition	Z_{im}/kohm	C_{lf}/mFcm^{-2}	Phase angle/ degree		IZI/kohm	C_{dl}/mFcm^{-2}
			0.01Hz	0-100Hz		
0.0V	8.66	1.884	38.37	78.63	44.94	0.022
0.2V	6.51	2.45	62.44	11.91	2.36	0.42
0.4V	-	-	10.52	26.68	4.64	0.22
0.6V	-	-	0.6	62.11	14.82	0.067

2.3. Scanning Electron Microscopy (SEM):

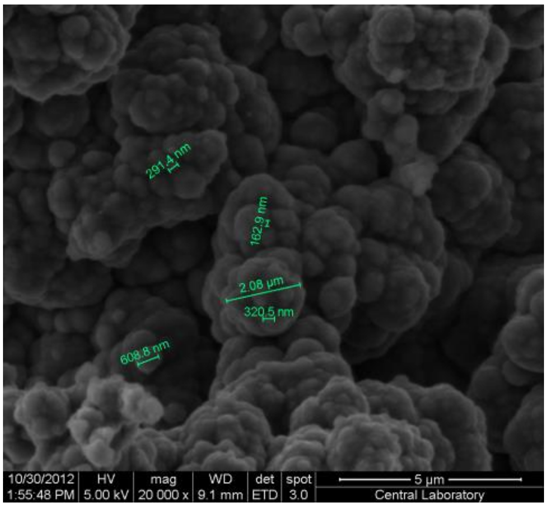
SEM images were taken to investigate the surface of poly (T-2-TB) in way of morphological. Chosen sizes were 500, 100 and 5 µm for imagining in detail the polymer surface. The images were given in Fig. 6. As seen from the images, typical cauliflower structure suggested [31] for polythiophene and their derivatives were distinguishable on surface and the particles were observed on the polymer surface, which was estimated due to potassium, probably.



a) surface (500 um)



b) particle (100 um)



c) polymer ground (5 um)

Figure 10. The SEM images of Poly(T-2-TB).

3. Conclusion

As a result, the monomer PT-2TB including boron(B) was polymerized on the surface of ITOPET in 5 mL of 0.1M Bu4PF6-PC solution at the 0-1.7 V of potential range and by using the 50 mV/s of scan rate, electrochemically. Its electrochemically and capacitance properties were investigated. The effect of coating thickness and applied external potential on impedance and capacitance values of poly(T-2-TB) coated ITOPET was determined. According to obtained results, as coating thickness was increased, its impedance values changed and its capacitance property decreased. When the C_{lf} of electrode with 2 cycle coating was 0.31 mF/cm^2, the that of 8 cycle coating was 0.064 mF/cm^2. On the other hand, when the applied potential on the poly(T-2-TB) coated electrode was increased the structure of the polymer was degraded and its capacitance was decreased. It say that can be applied potentials are 0V and 0.2V. In morphological investigation, the particles were observed on the polymer surface, which was estimated due to potassium, probably. Nevertheless, cauliflower structure accepted as a typical for Polythiophene was observed on the surface.

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