

Electrochemical synthesis of high charge capacity Poly(3,4-ethylenedioxythiophene) using pulse polymerization technique

Using pulse electrochemical polymerization technique we prepared high charge capacity polymer of 3, 4-Ethylenedioxythiophene (PEDOT) on glassy carbon (GC) substrate. The effect of pulse time on the growth processes and charge capacity of (PEDOT) has been investigated. Pulse on time plays an important role in controlling chain size and chain defects whereas pulse off time contributes in polymer conjugation and orientation. Stable PEDOT films with good electrochemical reversibility, high doping degree and high charge capacity were obtained by applying ultra short on time current pulse for polymerization. The characterization using scanning electron microscopy confirmed that the obtained PEDOT deposits were firstly formed as a thin layer followed by rough, nodular growth which produces an open and porous structure. A charge capacity up to 114 Fg^{-1} was obtained at time on of 10 ms.

Keywords: pulse electrochemical polymerization, 3, 4-Ethylenedioxythiophene, charge capacity

1. INTRODUCTION

Conducting polymeric systems have been studied for the last two Decades [1] because the wide range of promising applications in the field of energy storage [2-5], electrocatalysis, organic electrochemistry, photoelectrochemistry, electroanalysis, biosensors [6], electrochromic displays [7-10], and corrosion protection [11,12.] etc.

In recent years, poly(3,4-ethylenedioxythiophene) PEDOT has been of considerable interest because of the possibility of producing a material with linear chains due to the blocking of the 3,4-positions of the thiophene ring [13–17]. This polymer has been reported to exhibit superior stability of conductivity compared to polypyrrole [18]. PEDOT is one of the most stable conducting polymers available at present, where its monomer units have electron donating oxygen atoms stabilizing the monomer radical cation, so lower the oxidation potential as well as lowering the bandgap (approx. 1.6-1.7 eV) of the polymer [19]. These properties made PEDOT applicable in many areas such as antistatic coatings [20,21], electrode material in solid-state capacitors [22], substrates for electrolysis metal deposition in printed circuit boards [19].

Electropolymerization of 3,4-ethylenedioxythiophene monomer (EDOT) is one of important method to prepare the (PEDOT). Many studies on the electropolymerization of EDOT and the electrochemical

characterization of PEDOT have been carried out usually in organic solution [23,24] and also in aqueous solutions [25-27]. When PEDOT was synthesized through electrochemistry method, the electropolymerization conditions, such as the solvent, the electrode, supporting electrolyte, polymerization potential and applied electropolymerization method, have significant effects on the properties of the obtained polymer [28].

Many electropolymerization techniques were used to prepare PEDOT such as cyclic voltammetry and chronoamperometry [28]. In this work, a preliminary study was carried out on the electrochemical polymerization of EDOT using pulse polymerization technique. The surface morphology of the resulting polymer films have been characterized using scanning electron microscope and their charge capacity was measured by cyclic voltammetry.

2. EXPERIMENTAL

The monomer 3,4-ethylenedioxythiophene EDOT, was product of Bayer company. Acetonitrile, ACN, was used as solvent is HPLC-grade (Merck), tetrabutylammonium hexflorophosphate TBAPF₆, (Aldrich, 98%), Glassy carbon rode 3 mm diameter bought from SIGRADUR company Germany.

The working glassy carbon GC disk electrode was prepared by sealing 1 cm long x 3 mm diameter GC rod in glass tube and connected by copper wire using indium (Aldrich). Prior to experiment the GC electrode was polished with alumina powder (1 and 0.5 μm) to a mirror finish, then rinsed with water, dried in air and used immediately.

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All electrochemical experiments were carried out using Variable Multi-channel Potentiostat (VMP2, Princeton Applied Research) connected to a computer with EC-Lab software. The electrochemical cell was a conventional three electrodes with a platinum mesh as the counter electrode and Ag/Ag⁺ (10 mM AgNO₃/ACN) reference electrode. The solution used for the polymerization contained ACN as solvent, 50mM TBAPF₆ as supporting electrolyte and 10mM EDOT as monomer. Prior to use, the solution was purged with argon gas for 20 min and maintained over during all the experiments. Polymerization was carried out at constant current (0.4 mA, 5.7 mAcm⁻²) pulses for a very short period of time. Pulse on time was varied from 10 ms to 200 s and pulse off time was chosen as constant 100 ms no current was applied during off period. Polymerization charge was constant in all the growth experiments by keeping the total growth time as 200 s with applied current of 0.4 mA. Total numbers of on pulses were set to complete a growth time equivalent of 200 s. The produced polymer films were characterized by cyclic voltammetry in 50 mM TPAPF₆ in ACN and the scanning electron microscopy, SEM, (JEOL 6400) was used to study the film morphology.

3. RESULTS AND DISCUSSION

The PEDOT films were obtained by passing 80 mC total charge using chronopotentiometric (DC) and pulsed polymerization technique from solution containing 10 mM EDOT in 50 mM TBAPF₆ in ACN.

The DC polymerization was carried out by applying 0.4 mA for 200s. Pulse polymerization was carried out by applying constant current 0.4 mA for a very short period of time, pulse on time was varied from 10 ms to 200 s and pulse off time was chosen as constant 100 ms no current was applied during off period.

Fig. 1 shows a typical cyclic voltammograms at 10 mVs⁻¹ in 50 mM TBAPF₆/ACN solution for the PEDOT electrodeposited using DC and pulse polymerization at different pulse time. The voltammograms clearly demonstrate the significant enhancement on the capacitance of the PEDOT electrodeposited using the pulse deposition over DC polymerization. The voltammetric behavior of all polymer films was similar and showing capacitive-like responses which nearly has a rectangular shape and the CV stable for 50 cycles. It is important to note that the electrodeposition charge for all the polymer films is same; therefore all the obtained polymer films likely had the same mass. The specific capacitance of the PEDOT electrodes can be estimated from equation 1:

$$C = Q/\Delta Em \quad (1)$$

Where C is the specific capacitance (Fg⁻¹), Q is the voltammetric charge (C), ΔE is the potential window, and m is the mass of the polymer material (g) [29].

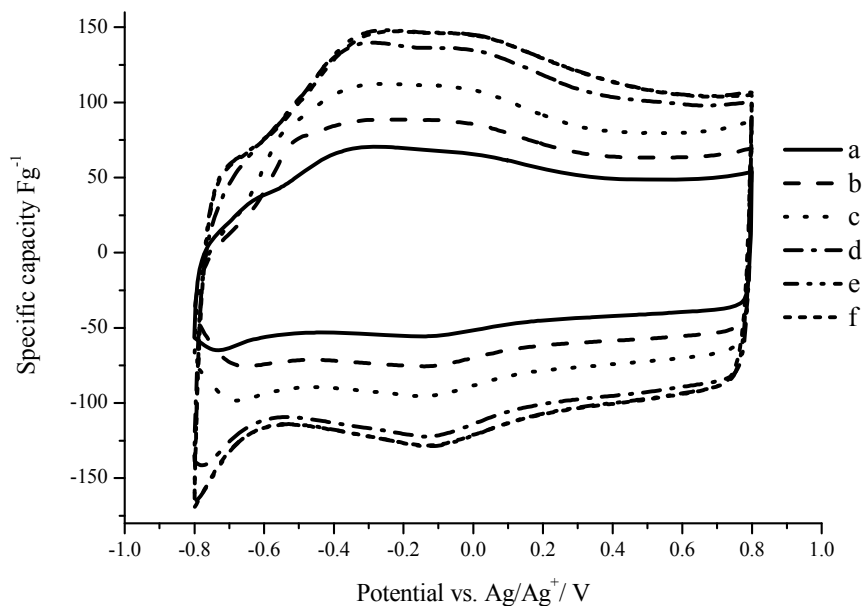


Fig. 1 - Cyclic voltammograms for PEDOT at 10 mVs⁻¹ in 50 mM TBAPF₆/CAN of the PEDOT film electrodeposited by (a) DC polymerized film at 0.4 mA for 200 s. Pulse polymerized film; on current 0.4 mA, puls

Suggesting the electropolymerization efficiency is 100%, the specific capacitance of the polymer film electrodeposited using DC Current was 56 Fg^{-1} while using pulse polymerization technique the specific capacity increased gradually with decreasing the pulse on time and reach up to 114 Fg^{-1} at pulse on time of 10 ms.

Fig. 2 shows the relation between the specific capacity of the PEDOT polymer films and pulse on time. The data clearly show that the specific capacitance increase by decreasing pulse on time and there is no significant change in specific capacity at pulse on time less than 50 ms.

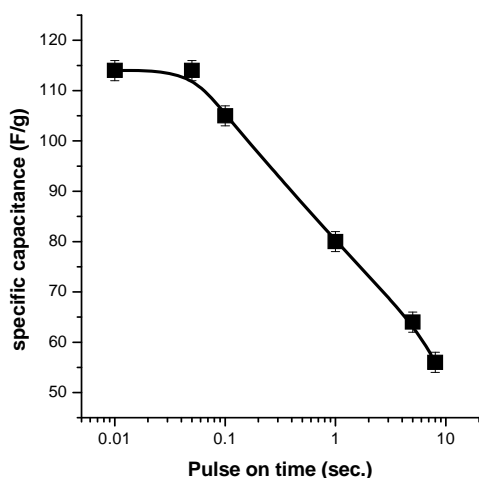


Fig. 2. Relation between specific capacitance and pulse on time for PEDOT prepared by pulse polymerization

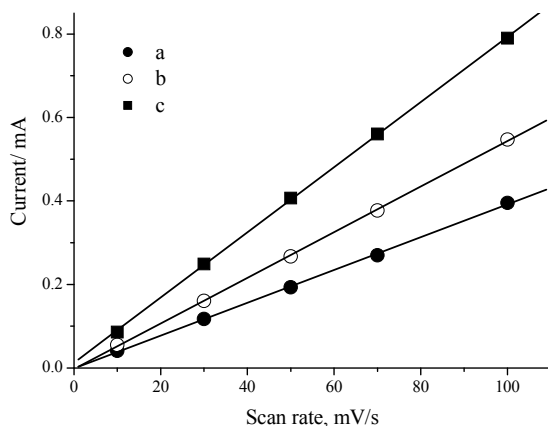


Fig. 3. Kinetics of charge doping/dedoping of the PEDOT film (a) DC polymerized film at 0.4 mA for 200 s. Pulse polymerized film; on current 0.4 mA, pulse off time 100 ms and pulse on time (b) = 0.1 s, (c) = 10 ms

Fig. 3 shows the linear variation in capacitive currents of pulsed and DC PEDOT electrodes as a function of scan rates. Slope for pulsed polymer is

two time higher than DC one which can attributed to higher capacitance

During the process of doping and dedoping, when a reducing potential is applied to the oxidized conducting polymer chain, electrons are transferred to the polymer backbone and the cations enter the material in response to the electric field. This mass insertion is responsible for the volume increase [30].

The work by Otero *et al.* [31] showed that of the polymerization using pulse process with repetitive on and off time duration is useful to create space between the polymer chains in order for the ions to enter and the ion current on chain movement. The application of ultra short on current pulse for polymerization has definite effect on the polymer structure and the chain length is obviously short in comparison to DC electrochemical method of polymerization. Moreover the short polymer chains are the ideal structures for many applications such as supercapacitor [22].

During on current the pulse is charged and allows polymer chain to nucleate over the substrate surface only for a very short period followed by the off time pulse that do not initiate fresh nucleation but terminate the growing chains [32]. Relatively longer off time help the already grown chains to oxidize completely and orient over the surface with fullest conjugation before the next pulse charges and another polymer chain nucleates over it. During the off pulse growth on the initial sites of the electrode is frustrated and hence the growth on the fresh sites of the electrode is more probable, consequently a large number of equivalent nucleation and growth sites formed [33]. Thus the PEDOT obtained from short pulse on time (50 and 10 ms) are supposed to have shorter polymer chain length, higher degree of conjugation and complete orientation in oxidized state.

The polymer surface characterization using SEM as shown in fig. 4, is confirming that pulsed PEDOT deposits at first as a thin layer followed by rough and nodular growth which results in an open, porous structure where DC PEDOT grows as a smooth and dense film.

4. CONCLUSION

In summary, we have demonstrated a facile and convenient method to synthesize high charge capacity PEDOT using pulse polymerization of monomer in organic medium. It was observed that the application of short on time current pulse, less than 50 ms, yields high specific capacity PEDOT, 114 Fg^{-1} , where the PEDOT obtain from DC method has specific capacity 54 Fg^{-1} . It was observed that increasing specific capacity with decreasing pulse on time.

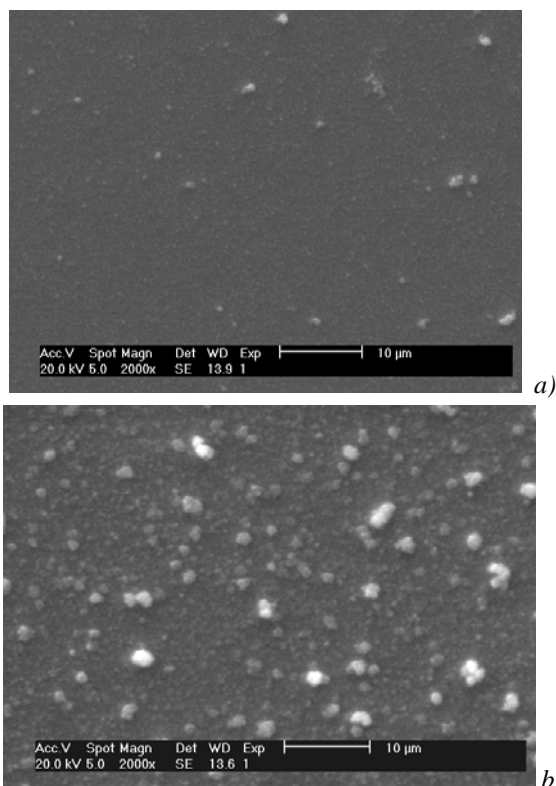


Fig. 4 - Scanning electron micrographs of the PEDOT film (a) DC polymerized film at 0.4 mA for 200 s. Pulse polymerized film; on current 0.4 mA, pulse off time 100 ms and pulse on time and (b) = 0.1 s.

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