

# The study of polythiophene, poly(3-methylthiophene) and poly(3,4-ethylenedioxythiophene) on pencil graphite electrode as an electrode active material for supercapacitor applications



Evrin Hür\*, Görkem Ali Varol, Andaç Arslan

Department of Chemistry, Faculty of Arts and Science, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey

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## ABSTRACT

Films of polythiophene (PTh), poly(3-methylthiophene) (PMeT) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been grown using cyclic voltammetry (CV) in acetonitrile (ACN) solution containing lithium perchlorate ( $\text{LiClO}_4$ ) and perchloric acid ( $\text{HClO}_4$ ) on pencil graphite electrode (PGE). The morphologies of the electrodeposited films have been monitored using scanning electron microscopy (SEM). The utilities of the polymer coated electrodes (PGE/PTh, PGE/PMeT and PGE/PEDOT) as an electrode active material for supercapacitor applications have been investigated in ACN solution which contains 0.1 M  $\text{LiClO}_4$ . The values of specific capacitance of the electrodes have been evaluated by CV and electrochemical impedance spectroscopy (EIS) methods. Measured specific capacitances of PGE/PTh, PGE/PMeT and PGE/PEDOT are 1503.20, 2621.76 and 8668.58  $\text{mF g}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$  according to CV measurements, respectively. Cycling stabilities of the electrodes have been examined by 1000 consecutive cycles using repeating chronopotentiometry (RCP) method.

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## 1. Introduction

Electrochemical capacitors, also known as supercapacitors or ultracapacitors, have received interests as a novel environmentally friendly power storage device in recent years. They fill the band gap between batteries and conventional solid state and electrolytic capacitors [1]. When compared to other energy storage devices, supercapacitors have rapid charge–discharge rate, excellent energy density, high power density and long cycle life [2]. Because of these properties, they are used in high power applications such as electric vehicles, military weapons and space equipments and in low power applications such as power buffer applications or for memory back-up in toys, cameras, video recorders and mobile phones. Therefore, much effort has been devoted to the developments of electrode active materials for supercapacitors. Conducting polymers, such as polypyrrole, polyaniline, polythiophene (PTh) and its derivatives, represent an interesting electrode active material for supercapacitor because of their several advantages; (i) they can be cheaply and easily produced, (ii) they are compatibility in both aqueous and organic electrolytes and ability to work in wide potential ranges, (iii) their electrochemical charge–discharge processes are fast and (iv) they have large pseudo capacitance when compared to carbon based electrical double layer capacitance due to redox reactions

take place at the electrode materials [3–5]. Among the conducting polymers, polythiophene and its derivatives have drawn a wide interest in supercapacitor applications because of their unique electrical properties and environmental stability as well as high room temperature conductivity [6,7]. However, the poor stability of conducting polymers in charge–discharge processes is a disadvantage to form electrode active materials for supercapacitor applications. This is because the redox sites in the conducting polymer backbone are not sufficiently stable for repeated redox processes. Although capacitance values of carbon materials are lower, they have a higher cycle life than those of conducting polymers [8,9]. Carbon materials have good electronic conductivity and excellent stability due to the high surface area and porosity. High amounts of electric charges within the capacitor electrolyte can accumulate on the electrode surface and ions of opposite charge are arranged in the electrolyte side, resulting in an electric double-layer capacitance [10,11]. In terms of long cycle life and high specific capacitance, carbon materials and conducting polymers have been recognized as promising electrode active materials for supercapacitors. Among carbon materials, pencil graphite electrode (PGE) has some advantages, including low cost, good electrical conductivity, high reproducibility and easy accessibility. Thus, these interesting properties make them attractive materials for several electrochemical applications [12].

In this work, we have reported the electrochemical synthesis of PTh, poly(3-methylthiophene) (PMeT) and poly(3,4-ethylenedioxythiophene) (PEDOT) films on PGE and the electro-

\* Corresponding author. Tel.: +90 222 2393750; fax: +90 222 2393578.  
E-mail address: [evrimhur@ogu.edu.tr](mailto:evrimhur@ogu.edu.tr) (E. Hür).

chemical studies of the obtained electrodes to investigate utilities of these electrodes as electrode active materials for supercapacitor applications for the first time. Therefore, their capacitive behaviors have been systematically examined. Cyclic voltammetry (CV) method has been used to investigate electrochemical stabilities of the films and the effect of the scan rate on specific capacitance values of the obtained electrodes. At the same time, electrochemical impedance spectroscopy (EIS) method has been used to characterize the frequency response of the electrodes for supercapacitor applications. The long term charge–discharge cycle life of the electrodes has been tested by repeating chronopotentiometry (RCP) method. The morphological characterization of the electrodes has been carried out by using scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Chemicals and apparatus

Thiophene (Th, 99%), 3-methylthiophene (MeT, 98%) and 3,4-ethylenedioxythiophene (EDOT, 97%) monomers were purchased from Alfa Aesar. All monomers have been vacuum-distilled and maintained under nitrogen atmosphere before use. ACN (99.0%) and  $\text{HClO}_4$  (70%) were purchased from Sigma–Aldrich as a solvent and oxidative ingredient, respectively.  $\text{LiClO}_4$  (99%) which was used as supporting electrolyte and doping salt was purchased from Fluka for electropolymerization process.

Electropolymerization and all other electrochemical experiments were carried out in a conventional three electrode system using PGE as working electrode, platinum sheet as a counter electrode and pseudo Ag wire as a reference electrode, which all potentials were referenced. PGE is Tombo lead with a diameter of 0.50 mm. The PGE has been prepared by cutting the leads into 3 cm long sticks and 2 cm (area 0.31  $\text{cm}^2$ ) was dipped in electrolyte. A Rotring Tikky pencil model was used as a holder for PGE. Electrical contact with the PGE was obtained by soldering a metallic wire to the metallic part of the holder. All electrodes were cleaned in ACN using ultrasonic bath (Bandelin Sonarex) and dried before each experiment. The all electrochemical measurements were carried out using A Gamry 3000 potentiostat/galvanostat/ZRA system (Wilmington, USA) and obtained data were analyzed using Gamry CMS-300 (version 5.50b) framework/analysis software. All experiments were carried out at 25 °C and at open air atmosphere.

### 2.2. Preparation of PTh, PMeT and PEDOT coated PGE

Polymer films were synthesized by electropolymerizations of monomers from ACN solution containing  $\text{LiClO}_4$  and  $\text{HClO}_4$  using CV from  $-0.20\text{ V}$  to  $+1.90\text{ V}$  at a scan rate of  $30\text{ mVs}^{-1}$  for 5 cycles. After the electrodeposition of the polymer films, PGE/PTh, PGE/PMeT and PGE/PEDOT were removed from the polymerization medium and rinsed with ACN to remove monomer molecules before being dried in air.

### 2.3. Electrochemical stabilities of PTh, PMeT and PEDOT films

Polymer films were investigated in ACN solution which contain 0.10 M  $\text{LiClO}_4$  via CV in the potential range that coatings were done at a scan rate of  $100\text{ mVs}^{-1}$  for 100 cycles to research electrochemical stability.

### 2.4. Capacitive properties of PGE/PTh, PGE/PMeT and PGE/PEDOT

Capacitive properties of PGE/PTh, PGE/PMeT and PGE/PEDOT which are suggested as electrode active material for supercapacitors were investigated in ACN solution which contains 0.10 M  $\text{LiClO}_4$ . CV and potentiostatic EIS methods were used to determine

these properties and calculate specific capacitance values of these electrodes. CV measurements were carried out in the potential range that coatings were done at different scan rates. All impedance measurements were recorded at open circuit potential (OCP) in the frequency range from  $10^5$  to  $10^{-2}$  Hz using AC amplitude of 10 mV. Charge–discharge behaviors of the electrodes were investigated at double current ( $\pm 2.00\text{ mA}$ ) for 1000 cycles by using RCP method.

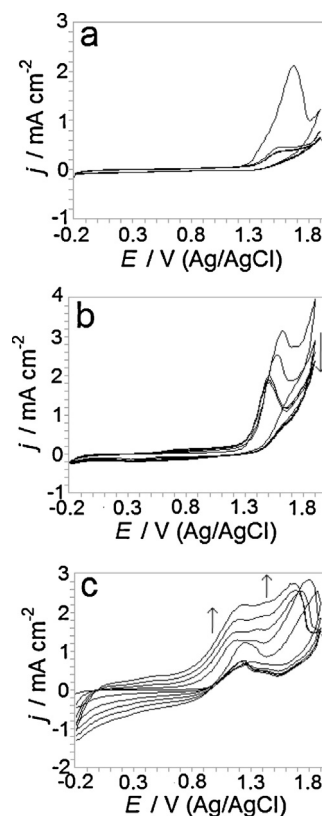
### 2.5. Surface morphologies of PGE/PTh, PGE/PMeT and PGE/PEDOT

The surface morphologies of PGE/PTh, PGE/PMeT, PGE/PTh/PMeT and PGE/PMeT/PTh were analyzed by using a Zeiss Ultraplus model field emission scanning electron microscopy (FESEM).

## 3. Results and discussion

### 3.1. Electrochemical synthesis of PTh, PMeT and PEDOT films

PTh, PMeT and PEDOT films were synthesized on PGE in ACN solution containing 0.01 M Th + 0.10 M  $\text{LiClO}_4$  + 0.05 M  $\text{HClO}_4$ , 0.01 M MeT + 0.10 M  $\text{LiClO}_4$  + 0.06 M  $\text{HClO}_4$  and 0.01 M EDOT, 0.10 M  $\text{LiClO}_4$  and 0.06 M  $\text{HClO}_4$ , respectively. Synthesis were performed by using CV in the potential range between  $-0.20\text{ V}$  and  $+1.90\text{ V}$  at  $30\text{ mVs}^{-1}$  of scan rate for 5 cycles. Fig. 1a–c shows the voltammograms recorded for PTh, PMeT and PEDOT growth on PGE, respectively. It can be seen from Fig. 1a, monomer oxidation peak potential value of Th is  $+1.71\text{ V}$  shifts to cathodic direction ( $+1.52\text{ V}$ ). In Fig. 1b, monomer oxidation peak potential value of MeT is  $+1.61\text{ V}$  shifts to cathodic direction ( $+1.51\text{ V}$ ). On the other



**Fig. 1.** Cyclic voltammograms recorded during the synthesis of (a) PTh in ACN solution containing 0.01 M Th, 0.10 M  $\text{LiClO}_4$  and 0.05 M  $\text{HClO}_4$ , (b) PMeT in ACN solution containing 0.01 M MeT, 0.10 M  $\text{LiClO}_4$  and 0.06 M  $\text{HClO}_4$ , (c) PEDOT on PGE in ACN solution containing 0.01 M EDOT, 0.10 M  $\text{LiClO}_4$  and 0.06 M  $\text{HClO}_4$  on PGE (potential region:  $-0.20$  and  $+1.90\text{ V}$ , scan rate:  $30\text{ mVs}^{-1}$ , cycles: 15).

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