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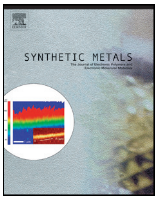

Electrochemically synthesized Sn^{2+} doped poly(3-methylthiophene) and poly(3,4-ethylenedioxythiophene) for supercapacitors

Müjdat Çağlar [a], Andaç Arslan [b,c], Ramis Kılıç [b,c], Evrim Hür [b,*]

[a] Anadolu University, Faculty of Science, Department of Physic, 26470 Eskişehir, Turkey
[b] Eskişehir Osmangazi University, Faculty of Arts and Science, Department of Chemistry, 26480 Eskişehir, Turkey
[c] Eskişehir Osmangazi University, Graduate School of Sciences, 26480 Eskişehir, Turkey

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ABSTRACT

Electrochemically synthesized tin ion (Sn^{2+}) doped poly(3-methylthiophene) (P3MeT:Sn) and poly(3,4-ethylenedioxythiophene) (PEDOT:Sn) on pencil graphite electrode (PGE) were prepared to utilize as the electrode materials for supercapacitor applications. Cyclic voltammetry (CV) method was employed for the preparation of the electrodes (PGE/P3MeT:Sn and PGE/PEDOT:Sn). The morphologies of the electrodes were analyzed by scanning electron microscopy (SEM). Electrochemical properties of the electrodes were examined by CV, electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge (GCD) and repeating chronopotentiometry (RCP) in acetonitrile (ACN) solution containing 0.10 M lithium perchlorate ($LiClO_4$). PGE/P3MeT:Sn has better electrochemical performance than PGE/PEDOT:Sn. Maximum capacitances of PGE/P3MeT:Sn and PGE/PEDOT:Sn are 181.41 and 137.89 $F\,g^{-1}$ at a scan rate of 10 $mV\,s^{-1}$, respectively. Additionally, PGE/P3MeT:Sn and PGE/PEDOT:Sn show good charge/discharge stability with the retention of 92 and 83% in electrochemical performance, respectively.

1. Introduction

Conducting polymers such as polyaniline, polythiophene and polypyrrole have attracted much attention as an alternative to metals and inorganic semiconductors in recent years. They have many advantages including high electrical conductivity, electrochemical reversibility, easy synthesis, low toxicity and cost. The conductivities and various properties of conducting polymers can be improved by doping process [1–3]. Based on these advantages, conducting polymers have gained great importance in many applications such as sensors [4], smart windows [5], electrochromic devices [6] and solar cells [7]. Also, conducting polymers have been widely used as an electrode active material for supercapacitor applications [8]. Supercapacitors also known as electrochemical capacitors or ultracapacitors are one of the most important energy storage devices. Because of their high capacitance, long cycle life, high power and energy densities, environmentally friendly and low costs, supercapacitors are very attractive power sources. Currently, supercapacitors fill the gap between batteries and conventional capacitors [9–14]. Supercapacitors are generally categorized in two types depending on the charge storage mechanism and the kind of active materials: electrical double-layer capacitors and pseudocapacitors. In electrical double-layer capacitors, energy is stored by the ionic charge separation at the electrode/electrolyte interface. Pseudocapacitors store the energy by the fast and reversible faradaic reactions which occur at the electrode surface [15,16]. The typical electrode materials for electrical double-layer capacitors are carbon-based materials with high surface area. Carbon-based materials have high cycle life in charge/discharge. However, they have poor energy density and their capacitances are low [17]. Metal oxides and conducting polymers are mainly used as electrode materials for pseudocapacitors. Conducting polymers represent a promising class of active materials for supercapacitors compared to metal oxides [18]. By contrast with carbon-based materials, conducting polymers have good electrical conductivity and large capacitance. However, they suffer from poor cycling stability during charge/discharge [19,20]. In order to form an electrode active material which have high capacitance and long cycling stability, researches have combined the advantages of electrical-double layer capacitors and pseudocapacitors. Such supercapacitors have demonstrated improvement in performance [21].

Among conducting polymers, polythiophene and its derivatives have been much interested due to their several advantages:

(i) compatibility in both aqueous and organic electrolytes
(ii) ability to work in wide potential range

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[*] Corresponding author. Tel.: +90 222 2393750/2872; fax: +90 222 2393578.
E-mail address: evrimhur@ogu.edu.tr (E. Hür).

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(iii) environmental stability
(iv) high electrical conductivity
(v) large pseudocapacitance
(vi) fast electrochemical charge/discharge process

Therefore, many researches have studied with polythiophene and its derivatives as an electrode active material for supercapacitor applications [22–24]. Pandey and Rastogi [25] synthesized poly(3,4-ethylenedioxythiophene) (PEDOT) films on graphite electrode by using two different methods that are short galvanic pulse and potentiostatic polymerization. They characterized the prepared PEDOT films by using CV and galvanostatic charge/discharge methods. They reported that morphology of galvanic pulsed PEDOT film is more porous than that of potentiostatically deposited PEDOT film and such morphology enhances the capacitive properties. High specific capacitances of 126.5 and 100.0 F g^{-1} were obtained by using galvanic pulse and potentiostatic polymerization methods, respectively.

Electrochemical characterization of undoped and cobalt ion doped poly(3-methylthiophene) and PEDOT films on PGE as an electrode active material for supercapacitor applications was reported in our previous works [26,27]. When the results of previous studies are examined, it can be clearly seen that doping of the polymer films with cobalt ion improved the electrochemical properties of the electrodes. Specific capacitances of the electrodes formed by using P3MeT and PEDOT films were enhanced from 2.62 to 131.99 and from 8.67 to 112.64 F g^{-1} with doping of cobalt ion, respectively. In this work, to further enhance the capacitive properties of P3MeT and PEDOT films, P3MeT:Sn and PEDOT:Sn films have been electrochemically synthesized on PGE using CV method. Morphologies of the prepared electrodes have been monitored by SEM. Electrochemical characterization of PGE/P3MeT:Sn and PGE/PEDOT:Sn has been realized by using CV, EIS, GCD and RCP methods. Specific capacitance of the electrodes has been determined by CV, EIS and GCD methods. While real supercapacitor performances of the electrodes have been examined by using GCD method in two electrode system, the long term charge/discharge cycling stability of the electrodes has been examined by RCP method.

2. Experimental

2.1. Chemicals and materials

3-methylthiophene (MeT, 98%) and 3,4-ethylenedioxythiophene (EDOT, 97%) monomers were purchased from Alfa Aesar. All monomers were vacuum-distilled and maintained under nitrogen atmosphere before use. ACN (99%), $HClO_4$ (70%) and $SnCl_2{\cdot}2H_2O$ (98%) were purchased from Sigma–Aldrich. $LiClO_4$ (99%) was purchased from Fluka for electropolymerization process.

A three electrode system was used with PGE as working electrode, platinum sheet as a counter electrode and pseudo Ag wire as a reference electrode for all electrochemical experiments except GCD. PGE is Tombo lead with a diameter of 0.50 mm. The PGE was prepared by cutting the leads into 3 cm long sticks and 2 cm (area 0.31 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

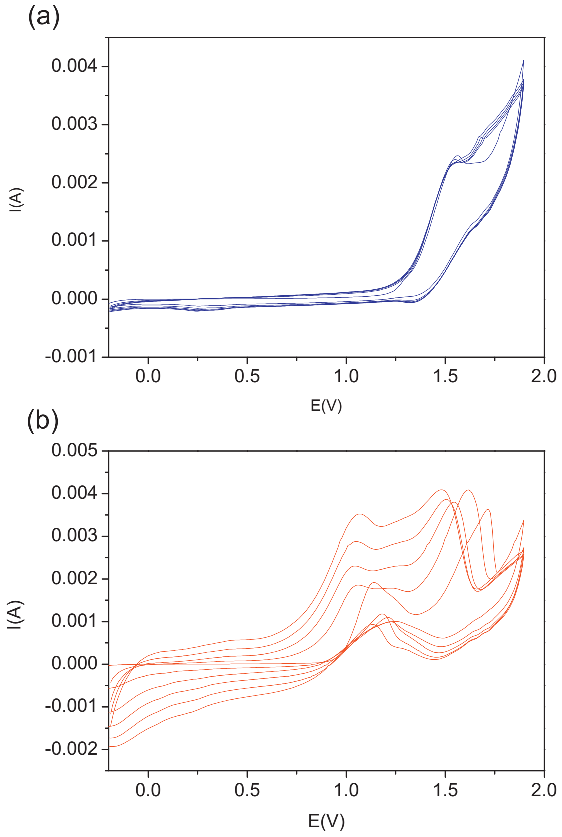

Fig. 1. Cyclic voltammograms of ACN solution containing (a) 0.01 M 3MeT, 0.10 mM $SnCl_2.2H_2O$, 0.10 M $LiClO_4$ and 0.06 M $HClO_4$, (b) 0.01 M EDOT, 0.10 mM $SnCl_2{\cdot}2H_2O$, 0.10 M $LiClO_4$ and 0.06 M $HClO_4$. Scan rate:30 mV s^{-1}, cycles:15.

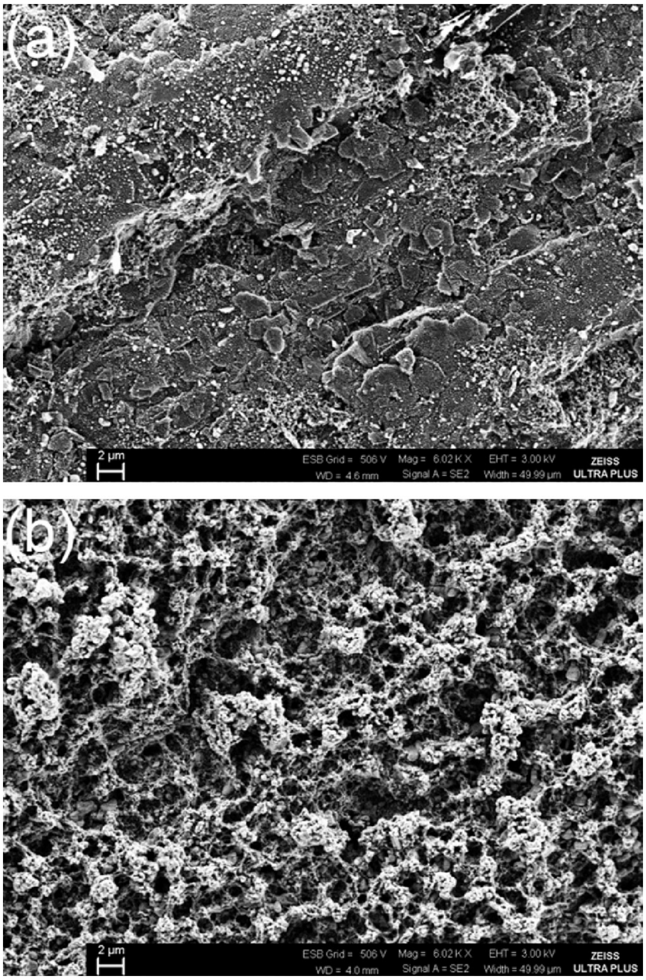

Fig. 2. SEM images of (a) PGE/P3MeT:Sn and (b) PGE/PEDOT:Sn.