



Voltammetric, electrochemical quartz crystal microbalance and in situ conductance studies of conducting polymers based on ethylenedioxythiophene and N-ethylcarbazole

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ABSTRACT

Previous electrochemical studies on the redox transformation of 3,6 bis(3,4-ethylenedioxythiophenyl)-9-ethylcarbazole (Ed-ECz-Ed) have been completed by further electrochemical, electrochemical quartz crystal microbalance (EQCM) and in situ conductance measurements. Effect of electrode gap for in situ conductivity measurements, cycle number and potential range were investigated. The EQCM measurements results showed the conductance in the n-doping range and conductivities were high enough to use the 20 μm microarray electrodes.

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1. Introduction

3,4-Ethylenedioxythiophene (EDOT) has been used as a building block in several conjugated systems that incorporate unique properties such as electrochromic behavior and low band gap polymers [1,2]. On the other hand, N-ethylcarbazole (ECz) is a cheap starting material, a fully aromatic unit providing better chemical and environmental stabilities. N-groups help polymer solubility and tune the optical and electrical properties and it has reversible electrochromic behavior [3–6]. To obtain, electrochromic materials a number of studies have focused on the synthesis of bis-heterocycle substitute arylene monomers [7]. Bis[2-(3,4-ethylenedioxy)thienyl]carbazole is one of these famous monomers that polymerize easily to form stable electroactive polymers [8–10]. In the fully reduced form (at -1.0 V), polymer is yellow which gradually changes to green upon mildly oxidizing potential ($\sim 0.4\text{ V}$) and at higher potential it turns to reddish brown ($\sim 0.9\text{ V}$). This type of multicolor behavior is not common which is important for electrochromic materials.

Use of in situ conductivity measurements together with other techniques is a useful tool in qualitatively mapping the electronic, redox, optic properties of p- and n-doping polymers. In situ

conductivity measurements of conducting polymers were firstly done by Wrighton and co-workers using microelectrode arrays for some conducting polymers and the other scientists continued [11–32]. On the other hand, EQCM is a very sensitive in situ piezoelectric tool which is capable to control nanogram-range mass changes (10^{-8} to 10^{-9} g) [33–42]. It is especially useful in estimation of the polymerization efficiency as well as ion and solvent exchange between the polymer and the solution upon redox cycling.

With the consideration of the main results obtained by different, independent techniques suggested for the investigation of the redox transformation of polymer, the aim of the present work was to complete the electrochemical studies on poly[3,6 bis(3,4-ethylenedioxythiophenyl)-9-ethylcarbazole] P[Ed-ECz-Ed] by in situ conductance and EQCM methods.

2. Experimental

The electropolymerization measurements were performed in a three electrodes configuration Kiesele cell [43] containing acetonitrile (ACN) as the solvent and tetrabutylammonium hexafluorophosphate (TBAPF₆) (recrystallized from ethanol and dried under vacuum at 70°C for several hours) as the supporting electrolyte (0.1 M). Before electrochemical experiments, the solvents were passed through an alumina column (ICN alumina B-Super I, vacuum dried at 300°C for 2 h immediately before use), until

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a good background in the required potential range was obtained. Cyclic voltammetry was performed by means of a JaisleIMP88PC potentiostat–galvanostat connected with an EG&GPAR model 175 universal programmer. Pt and Ag wires were used as the counter and quasi-reference electrodes, respectively. Potentials measured were then rescaled versus Ag/AgCl calibrated with the ferrocene/ferrocenium redox couple (0.35 V vs. Ag/AgCl).

2.1. In situ conductance measurements

In situ conductance measurements were carried out on a Pt microarray working electrode (5–20 μm gap) with an electrode area of 2.1 cm^2 . The working electrode was separated from potentiostat with two 1 $\text{k}\Omega$ resistors [16–18]. A bias of $E = 10$ mV was applied to the microarray electrode and third 1 $\text{k}\Omega$ resistor at which the potential was measured. The conductance of the polymers on the electrode was calculated according to Ohmic rules. Only relative conductivity changes have been measured because the thickness and the area of films were not known.

2.2. Electrochemical quartz crystal measurements

EQCM studies were carried out using a QCM unit (Type M3, UELKO, and Poland) combined with the potentiostat PGSTAT 30. All measurements were made at the room temperature ($20 \pm 2^\circ\text{C}$). The working electrode was Au, deposited on 10 MHz AT-cut quartz crystals (International Crystal Manufacturing Co. Ltd., Oklahoma City, OK), with piezoelectrically and electrochemically active areas of 0.21 and 0.23 cm^2 , respectively. The experiments were carried out in a conventional three-electrode cell with a platinum gauze counter electrode and Ag/AgCl, 0.1 TBAPF₆ in ACN or dichloromethane (DCM) reference electrode. ACN (Aldrich, HPLC grade with water content <0.005%) was freshly distilled over calcium hydride. The solutions were deaerated carefully before experiments and the measurements were done with Ar flow over the solution.

3. Results and discussion

Correlation of the cyclic voltammograms (CV) with the conductance profiles for electrodeposition of Ed-ECz-Ed on the microarray electrodes that have different gaps (5, 10, 20 μm) are shown in Figs. 1 and 2. During polymerization, the conductance starts to increase at the oxidation potential of the monomers and oligomers began to form in the gaps between the Pt microelectrodes (Fig. 1). For the micro array electrode of 5 μm , after 3 cycles there is no change in conductivities since the values are out of range of the device (Fig. 1a). For the micro array electrode of 10 μm , after 0.7 V, conductance decreases due to coupling reaction in the solution (Fig. 1b, inset). When the potential reaches its maximum, conductivity starts to increase again. In the reverse direction at 0.7 V it decreases due to reduction. Increase in conductivity about 0.6 V is due to the diffused species from solution to the electrode surface. When 20 μm micro array electrode was used during polymerization, similar conductivity behavior was observed with 10 μm microarray electrode (Fig. 1c.)

To obtain thicker films, polymerizations were carried out by applying further 4 cycles by using 10 and 20 μm microarray electrodes (Fig. 2a–c). Anodic limit does affect the redox and the conductivity behaviors and this effect was investigated for 10 μm microarray electrode and results are given in Fig. 2a and b. In the case of 10 μm microarray electrode, whenever the anodic limit was as high as 1.0 V, the conductivity reached its maximum value and stayed constant after four cycles (Fig. 2a). When the sweep potential limit decreased from 1.0 V to 0.75 V, the conductance continued to increase by further scanning for both 10 and 20 μm microarray

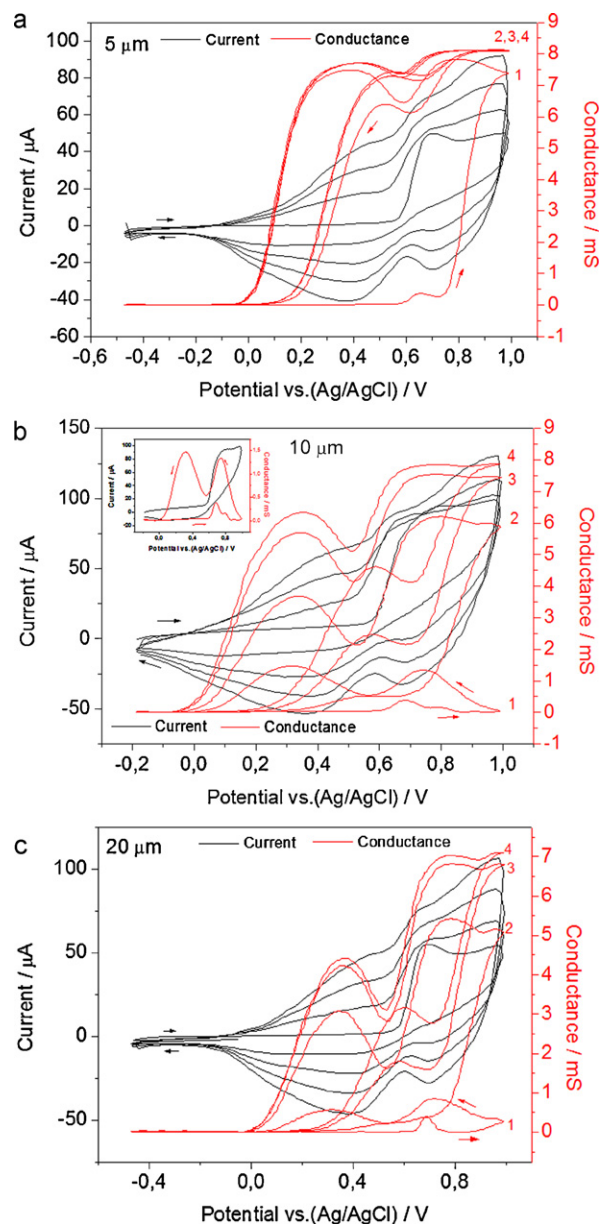


Fig. 1. Cyclic voltammograms and in situ conductivity measurements obtained simultaneously during potentiodynamic polymerization of Ed-ECz-Ed at 4 cycles in 0.1 M TBAPF₆ containing acetonitrile at the scan rate of 20 mV/s. Gap of the electrodes: 5 μm (a), 10 μm (b, inset: 1st cycle), 20 μm (c).

electrodes (Fig. 2b and c respectively). This effect was not investigated for 5 μm microarray electrode. It is also clear the conductivity values of the polymer film obtained on the 20 μm microarray electrode is lower than the 10 μm microarray electrode as expected (Fig. 2b and c).

The conductance changes during charging–discharging (p-doping reactions) of P[Ed-ECz-Ed] film were investigated in monomer free solutions. The shape of CV and the conductance depend on the scan limit. Different potential limits were chosen in Figs. 3 and 4 in order to compare the effect of potential limit on the redox behavior and conductivity of the polymeric film. P[Ed-ECz-Ed] has two redox behaviors as previously reported by voltammetric measurements [8–10].

The conductance increases within a narrow potential range, from 0.3 to 0.6 V and then it decreases in the reverse direction (Fig. 3a). A hysteresis of conductance observed upon

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