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Synthetic Metals 152 (2005) 133–136
SYNTHETIC METALS
www.elsevier.com/locate/synmet

Synthesis and characterization of inherently conducting polymers by using Scanning Electrochemical Microscopy and Electrochemical Quartz Crystal Microbalance

V. Syritski [a,*], R. E. Gyurcsányi [c], A. Öpik [a], K. Tóth [b]

[a] *Laboratory of Physical Chemistry, Department of Materials Science, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia*
[b] *Technical Analytical Research group of the Hungarian Academy of Sciences,* / [c] *Institute of General and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, 1111 Budapest, Hungary*

Abstract

Understanding ion transport processes in electrically conducting polymers is very important in the light of possible application of these materials in chemical or biosensors. In this work we have studied the ion transport in the electrochemically synthesized inherently conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) induced by the redox switching of the polymer. Mass changes during the synthesis and redox switching of the film have been monitored *in-situ* by Electrochemical Quartz Crystal Microbalance (EQCM). By doping the conducting polymer film with electroactive materials such as ferrocyanide ions (FCN) the release of the different oxidation state species during the voltage cycling of the polymeric film could be monitored on-line by Scanning Electrochemical Microscopy (SECM). Direct evidence of the exchange capability of $Fe(CN)_6]^{4-/3-}$ anions entrapped in PEDOT/FCN film with Cl^- anion from the solution and doping levels were found by computing the experimental data provided by SECM and EQCM techniques. In addition, SECM measurements showed that during reduction of the PEDOT/FCN films only the release of $[Fe(CN)_6]^{4-}$ ion occurs.

Keywords: polythiophene and derivatives, electrochemical polymerisation, electrochemical doping, scanning electrochemical microscopy, EQCM.

1. Introduction

The preparation, characterization and application of electrically conducting polymers (ECP) have received a lot of attention because of their unique optical, electrochemical, and electrical properties [1]. These materials have already found applications in a number of advanced technologies, such as energy storage [2], molecular recognition [3], chemical sensors [4-6], electromagnetic interference and opto-electronic devices [7, 8]. Using ECP in the field of electrochemical sensors [9, 10], ion-selective-electrodes [11] or electroanalysis [12, 13] supposes a clear understanding of the charge compensation processes following the redox switching of ECPs. Electrochemical Quartz Crystal Microbalance (EQCM) [14] is especially suitable for these investigations since the mass changes can be in-situ monitored during the electrochemical modulation of the film. However, EQCM provides only the net mass change with limited information about the type and charge of the species involved in the transport process. Therefore attempts have been made to gather further information about the nature of the ion transport in polypyrrole and polyaniline films by using Scanning Electrochemical Microscopy (SECM) [15, 16]. Recently, there is a lot of interest regarding poly(3,4-ethylenedioxythiophene) (PEDOT) polymer due to its high electrical conductivity [17], good stability in the p-doped state [18] and reversible electrochemistry. These properties make this material very attractive for application in sensor fabrication technologies.

This communication presents EQCM and SECM investigations of the synthesis and of the redox behavior of PEDOT films doped with ferrocyanide ions (FCN).

2. Experimental

The PEDOT/FCN films were synthesized on platinum electrodes by cycling the potential between -700 and

* Corresponding author. Tel: +372-620-28-20; fax: +372-620-20-20;
E-mail: syritski@edu.ttu.ee

0379-6779/$ – see front matter
doi:10.1016/j.synthmet.2005.07.097

1100 mV (vs. 3 M Ag/AgCl) at 50 mV/s in a solution of 0.01 M 3,4-ethylenedioxythiophene and 0.1M $K_4[Fe(CN)_6]$. For SECM experiments the electrode was mounted in the bottom of a suitable cell with the polymer film pointing up. Then the cell was filled with deoxygenated 0.1 M NaCl solution. For monitoring redox species released from the PEDOT/FCN a 150 μm Pt tip was fixed above PEDOT/FCN film at a distance of ~10 μm. The electrodes (substrate and tip) were connected to a bipotentiostat (Autolab Pgstat 10, Eco Chemie B.V., Utrecht, The Netherlands) and while the potential of the polymer film was cycled between -900 and 400 mV at a scan rate of 20 or 5 mV/s the tip was used to amperometrically detect the released species (E= +500 mV or E= 0 mV).

For EQCM investigations polished 14 mm gold-plated 10 MHz AT-cut quartz resonators with active area of 0.21 cm^2 were used. The frequency shifts caused by mass change of the polymer films during the potential scans were measured using Fluke PM 6680 Timer/Counter. The conversion of the resonant frequency shift Δf to mass change Δm was performed using the Sauerbrey equation (Eq.1):

$$\Delta m = -\Delta f / C_f \quad (1)$$

where C_f is the sensitivity factor for the 10 MHz AT-cut quartz resonators, $2.261 \cdot 10^8$ Hz cm^2 g^{-1}.

3. Results and discussion

3.1 Electropolymerization of EDOT

EQCM was used to simultaneously monitor the charge and mass gain during electrodeposition of the PEDOT film (Fig. 1). It is rather difficult to make the correlation between the frequency change and the deposited mass in aqueous solution, but for sufficiently thin and rigid films the linear dependence, known as the Sauerbrey equation (Eq. 1) can be used [19]. The oxidation and reduction peaks of FCN can be clearly seen at 460 mV and 75 mV, respectively. The oxidation of the monomer started at 900 mV, which is indicated by the increasing anodic current and mass. The current due to the redox switching of FCN increases slightly from sweep to sweep indicating that the redox reaction cannot take place solely at the electrode surface. Meanwhile the mass of the deposited polymer film increased after each cycle. For the first four cycles the polymer mass increased only at the end of the oxidative cycle remaining approximately constant in the rest of the potential range. However, starting from the fifth cycle a mass gain appears also during film reduction. Possibly, a part of hydrated cations remains in the film causing the more than expected mass change.

Calculating the mass change Δm vs. the charge ΔQ for electropolymerization of monomers, the theoretical value of the doping level y can be calculated [20] with the following equation:

$$y = (-2F\Delta m/\Delta Q + M_{EDOT})/(zF\Delta m/\Delta Q - M_A) \quad (2)$$

where M_{EDOT} is the molar mass of the monomer unit in the polymer (140 g/mol), M_A is the molar mass of the doping anion, z is its electrical charge and F is Faraday's constant. The redox current due the $[Fe(CN)_6]^{4-/3-}$ couple overlaps with that due to the polymerization and redox switching of the polymer and does not allow the direct calculation of $\Delta m/\Delta Q$. Therefore, for each cycle a corrected value of the charge was calculated by subtracting the contribution of the FCN redox couple from the overall current. Thus, the doping level for this synthesis condition was about 0.1, which corresponds to $2.5 \cdot 10^{-8}$ mol cm^{-2} of FCN anions in the obtained 40.5 μg cm^{-2} of PEDOT/FCN film.

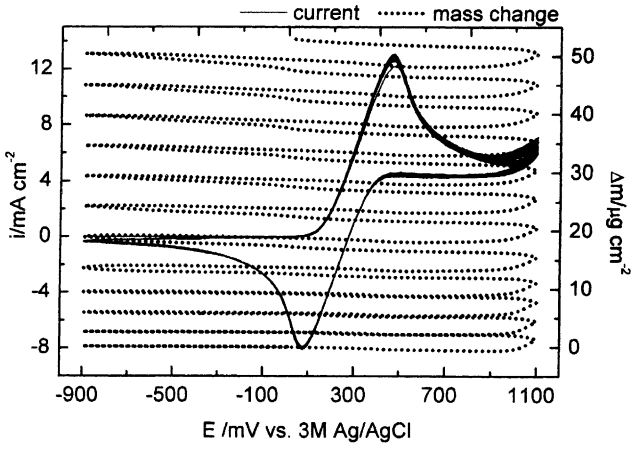

Fig. 1. Current and mass responses during potentiodynamic deposition of PEDOT/FCN recorded by EQCM. Scan rate 50 mV/s.

3.2 Redox properties of the PEDOT/FCN film

Current and mass changes for the PEDOT/FCN film as function of the applied potential in 0.1 M NaCl solution are shown in Fig. 2. The oxidative and reductive peaks in the cyclic voltammograms (CV) are related with the redox switching of FCN ions incorporated in the polymeric film and with the anion and cation release/uptake that accompanies changes in the oxidation state of the polymer. It is interesting that during the reduction of the polymer, a slight mass decrease related with anion expulsion could only be detected in the 0.40-0.18 V potential window. In the rest of the potential domain a large mass gain was observed, which indicates a predominant cationic transport in the film.

After the first cycle the CVs (Fig. 2) showed a significant decrease of the reduction peak at -800 mV and in the oxidation current attributed to the FCN redox couple. With the exception of the first cycle where a clear mass gain was observed the mass of the film continuously decreased, which can be most likely explained by an overall exchange of FCN to Cl^-. In order to find the amount