

In situ FTIR spectroelectrochemical characterization of poly(3,4-ethylenedioxythiophene) films

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Abstract

The electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) and the redox behavior of poly(3,4-ethylenedioxythiophene) (PEDOT) were studied using electrochemical techniques and in situ internal reflection FTIR spectroscopy. A comparison of the IR spectra of PEDOT films taken during charging and discharging in different electrolytes is reported.

Keywords: In situ spectroelectrochemistry, electrochemical doping, infrared spectroscopy, conjugated polymers, poly(3,4-ethylenedioxythiophene)

1. Introduction

Electrochemically synthesized films of poly(3,4-ethylenedioxythiophene) (PEDOT, Fig 1b.) in organic solvents have a low redox potential in comparison to other conducting polymers and are very stable in their doped state [1]. Upon doping, the film undergoes color changes from dark blue to transparent blue. In this work the stability and the redox reactions of thin PEDOT films in different electrolytes have been studied with cyclic voltammetry and in situ FTIR internal reflection spectroscopy (technique described in [2]).

2. Results

The cyclic voltammogram of a PEDOT film in (0.1 M) TBAClO₄-CH₃CN cycled between -1 V and 1.9 V vs Ag/AgCl at a scan rate of 50 mV/s is shown in Figure 1a. In this wide potential range no significant degradation occurs. The redox peaks around 0 mV (oxidation) and at -400 mV (reduction) remain almost unaffected during cycling, showing the high stability of the polymer.

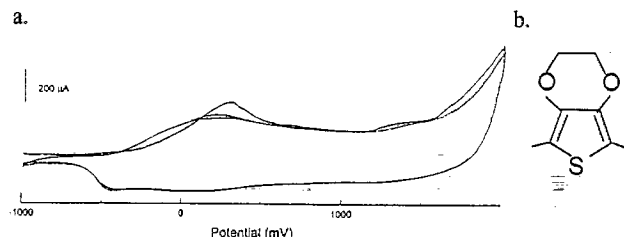


Figure 1 a. Cyclic voltammogram of PEDOT in TBAClO₄-CH₃CN, $v = 50$ mV/s. b. Structure of PEDOT

Open circuit potential measurements of PEDOT films show that neutral films are rapidly oxidized. In the present study the neutral form of the polymer was found to be stable only under applied negative potential of -700 mV. In situ FTIR spectra were recorded during potential cycling in different electrolytes (TBAPF₆, TEAPF₆, TBAClO₄) between -700 and +500 mV. Difference

spectra during the first anodic scan are shown in Figure 2 (for each spectrum 96 interferograms were coadded, resolution 4 cm⁻¹, reference spectrum at -650 mV). Below 2000 cm⁻¹ doping induced IR bands occur with maxima at 1514, 1290, 1184, 1087, 1059, 977 and 838 cm⁻¹. Small shifts in the band positions were found in different electrolytes (film electrochemically prepared and cycled in the same medium) which is explained with slightly different film morphology. In the region above 2000 cm⁻¹ the electronic absorption from free charge carriers created during doping is seen. After the reverse cycle the film reaches its original neutral state.

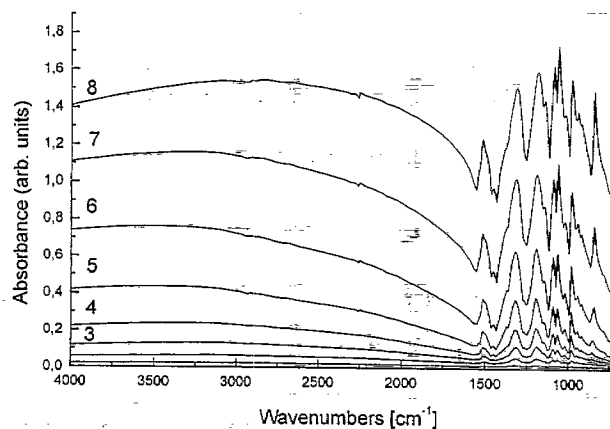


Figure 2. In situ FTIR difference spectra during oxidation of a PEDOT film in 0.1 M TBAClO₄-CH₃CN. The numbers indicate spectra each covering 120 mV in a potential scan starting at -700 mV and ending at 500 mV.

3. References

1. M. Dietrich, J. Heinze, G. Heywang and F. Jonas, *J. Electroanal. Chem.*, 369 (1994) 87.
2. H. Neugebauer and Z. Ping, *Mikrochim. Acta [Suppl]* 14 (1997) 125.