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

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Abstract

The electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT), in different electrolyte–solvent media was studied with cyclic voltammetry, in situ UV–VIS-spectroelectrochemistry, electrochemical quartz crystal microbalance technique (EQCM) and with in situ Fourier transform infrared (FTIR) spectroscopy using external and internal reflection techniques. The effect of polymerization current density and monomer concentration on the formation of the film structure was studied. The redox reactions and the stability of charged films of different thickness were studied with cyclic voltammetry and open circuit potentiometric measurements. FTIR spectra were recorded in situ during step-wise and continuous potential cycling of the polymer films in different electrolytes. A characterization of the doping induced IR-bands has been made. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Among the efforts in getting more ordered polymeric materials, different alkylendioxy substituted thiophenes are of great interest [1]. With these substances, the 3- and 4-positions in the thiophene rings are occupied, thus facilitating the formation of linear polymer chains which should lead to increased conjugation length. The 3,4-substitution also lowers the oxidation potential at which the monomer polymerizes. Of the poly(alkylendioxy)thiophenes reported, poly(3,4-ethylenedioxythiophene) (PEDOT) has been shown to have most promising properties. PEDOT is very stable in its

doped state [2] and reaches conductivity as high as 200 Scm^{-1} [3]. The conductivity has been found to be stable up to 1000 h at 120°C in laboratory atmosphere. PEDOT has a low redox potential and the color changes upon doping are from dark blue to transparent blue. PEDOT has been reported to undergo fast redox changes where the charging reaction was found to be faster than the discharging reaction [4]. The diffusion coefficient of the charge carriers in the film was found to be three orders of magnitude higher than for other conducting polymers in contact with a polymer electrolyte [4].

PEDOT has a low bandgap (approx. 1.6–1.7 eV) due to the presence of the two electron donating oxygen atoms coupled to the thiophene ring [3]. Charged PEDOT films are almost transparent which makes them suitable in applications as electrochromic

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displays, antistatic transparent films [5] and as transparent anode in polymer light-emitting diodes [6,7]. PEDOT can be synthesized chemically both in organic [1] and in aqueous solutions [8]. Jonas et al. [8] reported that processable aqueous PEDOT solutions are obtained by oxidative polymerization in presence of polystyrenesulfonic acid using potassium peroxydisulfate as oxidizing agent. EDOT can also be polymerized electrochemically in either organic or aqueous solutions. The possibility to prepare PEDOT from aqueous solutions enables the potential use of PEDOT in biosensor applications. Results on electropolymerization of EDOT in phosphate buffer has been reported [9]. The system PEDOT (polystyrene sulfonate) was found to be more stable than the corresponding polypyrrole system when used in biosensor operating condition. Electropolymerization of EDOT in the presence of sodiumdodecyl sulfate water solution was reported to take place at a lower potential than in acetonitrile-electrolyte solutions [10]. Heinze et al. [2] studied the optical behavior and the electrochemistry of electrochemically synthesized PEDOT in organic solvents and compared it with the reactions of 3,4-trimethylenedioxythiophene. Electrode potential induced volume changes in electrochemically prepared PEDOT in organic solvents was reported by Inganäs et al. [11]. The electrochemical polymerization of EDOT was found to occur more easily than its relating thiophene derivatives (3,4-trimethylenedioxythiophene) [2] and 3,4-methylenedioxythiophene [12]. Although the polymerization of dialkoxythiophenes should lead to a linear chain with no possibility for crosslinking, the redox behavior of in particular PEDOT has turned out to be complex, which has been explained by several redox processes taking place in the PEDOT material [13].

In this work we have studied the polymerization of EDOT and the p-doping redox reactions of PEDOT by in situ external and internal reflection FTIR spectroscopy. In addition, potentiometric, in situ UV–VIS and electrochemical quartz microbalance measurements were made on PEDOT films of different thickness.

2. Experimental

2.1. Chemicals

3,4-Ethylenedioxythiophene (EDOT) was obtained from Bayer, AG. Acetonitrile (Lab Scan) was stored over molecular sieves and in nitrogen atmosphere. Tetrabutylammonium- and tetraethylammonium-hexafluorophosphate, (TBAPF₆, TEAPF₆) and tetrabutylammoniumperchlorate, (TBAClO₄ all obtained from Fluka) were dried at 100°C for 48 h before use.

2.2. Electrochemical measurements

A three-electrode electrochemical cell was used in the cyclic voltammetric experiments. A Pt-electrode (area 7 mm²) served as working electrode and a glassy carbon rod was used as auxiliary electrode. The reference electrode was Ag/AgCl/Cl⁻ (3 M) used with a glass bridge. The charges during polymerization were recorded with a Metrohm Coulometer type E 211. Cyclic voltammograms were obtained with a EG&G Princeton applied research potentiostat model 366 A. Open circuit experiments were made on PEDOT covered Pt electrodes. After film preparation the electrode was kept in electrolyte solution (0.1 M TBAPF₆-acetonitrile) and a potential was applied for 2 min. The potential vs. time data were recorded immediately after the potential was switched off and the film was under open circuit conditions.

2.3. In situ UV–VIS spectroscopy

The in situ UV–VIS spectroelectrochemical cell and equipment are described in detail elsewhere [14]. In a one-compartment cell the working electrode was ITO coated glass, and a Ag/AgCl wire and a stainless steel plate were used as reference and auxiliary electrodes, respectively. A thin PEDOT film was polymerized galvanostatically on the ITO electrode ($i = 1$ mA/cm², $q = 30$ mC/cm²). The spectra were recorded with an optical multichannel analyzer equipped with a diode array detector (PAR M1461) [15].

2.4. In situ FTIR spectroscopy

In the in situ external reflection FTIR spectroelectrochemical measurements a modified electrochemical cell was used. A Pt electrode (area 0.4 cm²) served as working electrode and as auxiliary electrode a Pt-net around the working electrode was used. The thin electrolyte layer between the Pt electrode and the ZnSe window was refreshed by drawing the electrode back from the window. Prior to each spectrum recording the system was readjusted again. Details of the measurement procedure have been published elsewhere [16]. The potential values are vs. an Ag/AgCl/Cl (3 M) electrode with a glass bridge filled with the electrolyte. In the setup for the external reflection technique the reference electrode was used with a Luggin capillary ending close to the working electrode. The in situ internal reflection FTIR measurements were performed with the attenuated total reflection technique. An electrochemical cell was attached to a reflection element of germanium covered with Pt ($A = 0.63$ cm²) which was used as working electrode. The technique has been described in detail elsewhere [17–19]. The external reflection FTIR spectra

were recorded by a Mattson Cygnus 100 spectrometer with a MCT detector. The internal reflection FTIR measurements were made on a Bruker IFS66S spectrometer. For each spectrum 150 interferograms (external reflection) or 96 interferograms (internal reflection) with a resolution of 4 cm^{-1} were coadded. All measurements were performed in nitrogen atmosphere and prior to measurements the solutions were purged with nitrogen for 10 min.

2.5. Electrochemical quartz crystal microbalance

The EQCM measurements were performed with a quartz analyzer (model QCA917, EG&G Seiko) electrochemically connected to a potentiostat/galvanostat

(model 283 EG&G PAR). A thin PEDOT film ($q = 10\text{ mCcm}^{-2}$) was electropolymerized galvanostatically ($i = 0.1\text{ mAcm}^{-2}$) on a Pt coated AT-cut quartz crystal (8.9 MHz Seiko). The polymerization solution contained 0.1 M EDOT and 0.1 M TBAPF₆ in acetonitrile. The frequency changes during potential cycling of the film in monomer free electrolyte solution were followed in situ. Since the film was very thin the rigidity condition can be assumed to hold and the use of the Sauerbrey Eq. (1) to calculate the corresponding mass changes is valid.

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\rho_q \mu_q}} \quad (1)$$

In Eq. (1) Δf stands for the change in resonance

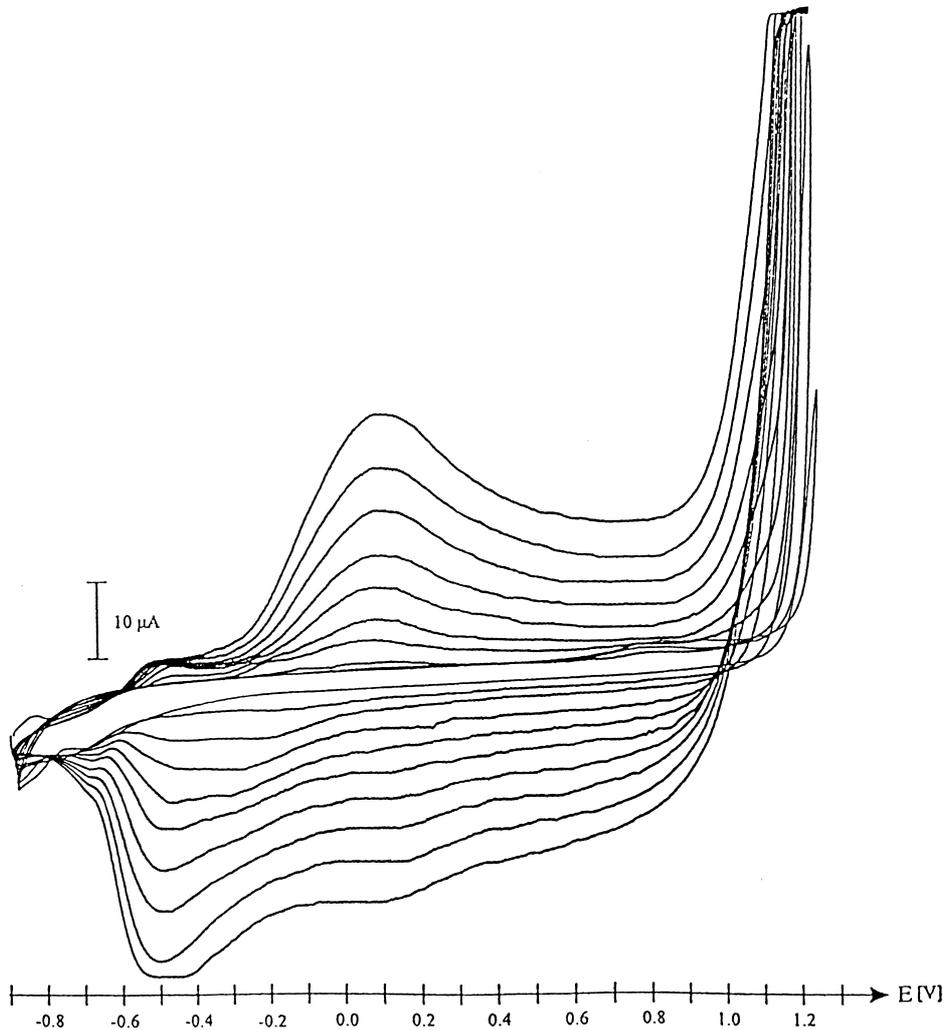


Fig. 1. Polymerization by potential cycling between -0.9 V and 1.25 V of a 25 mM EDOT solution in 0.1 M TBAPF₆-acetonitrile. Scan rate 100 mV/s .

frequency, Δm the change in mass, f_0 the resonance frequency of the fundamental mode of the quartz crystal, A the area of the electrode, ρ_q the density of

quartz and μ_q the shear modulus of quartz. The active surface area of the Pt coated quartz crystal was 0.196 cm^2 .

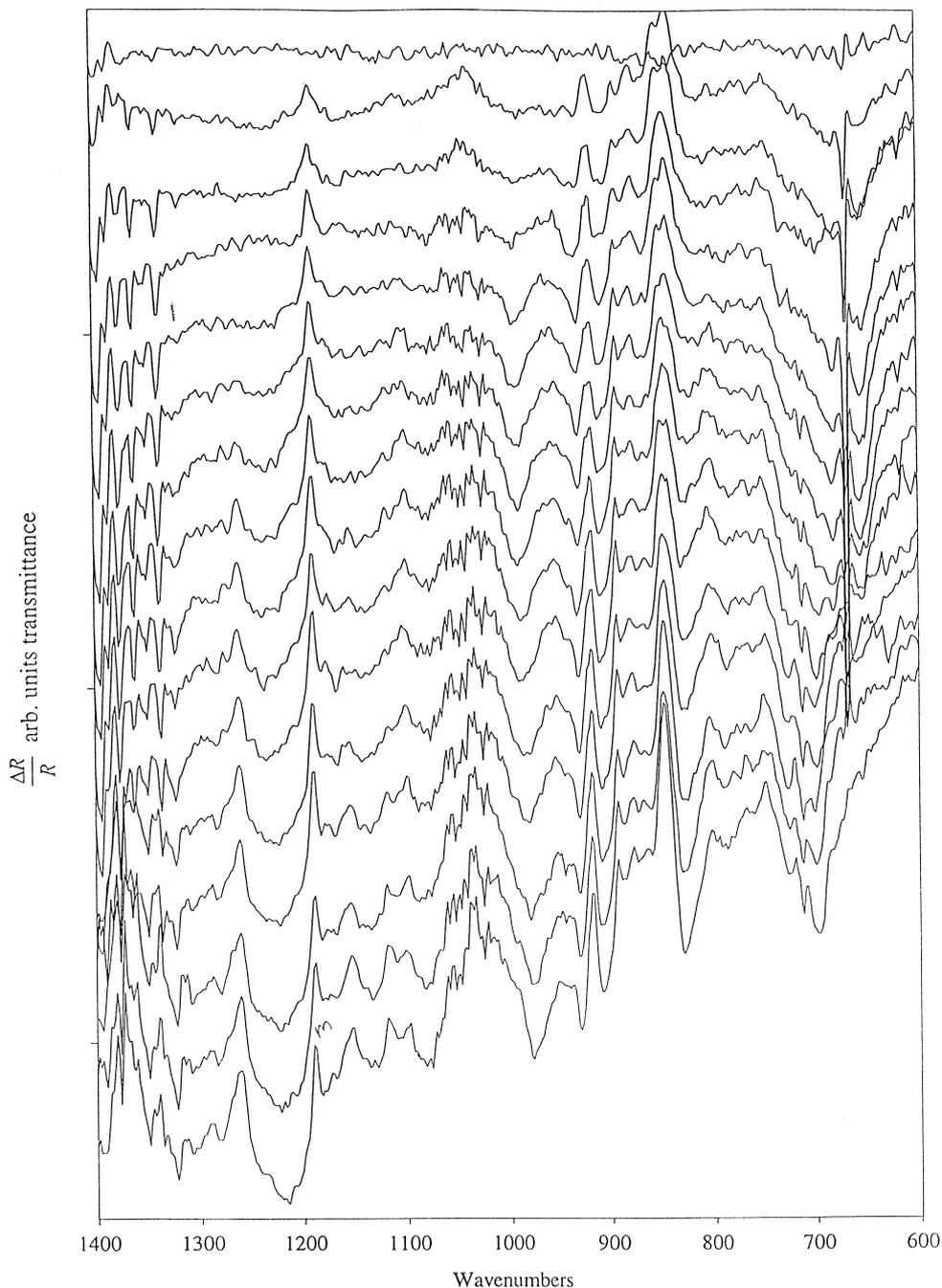


Fig. 2. In situ external reflection FTIR spectra during the polymerization of 25 mM EDOT in 0.1 M TBAPF₆-acetonitrile solution at constant potential 1.07 V. First spectrum at the top of the figure, time between the spectra 45 s. The spectra are separated.

3. Results and discussion

3.1. Electropolymerization of EDOT

The oxidation potential of the monomer EDOT is approximately 1.1 V and upon polymerization a fast adsorption on the working electrode takes place resulting in a smooth and flexible film. The polymerization proceeds easily even when low monomer concentrations are used. The polymerization made by potential scanning between -0.9 and 1.25 V in 25 mM EDOT in acetonitrile containing 0.1 M TBAPF₆ is shown in Fig. 1. The increasing peak currents from the redox processes of the film with every potential cycle indicate a continuous growth of material on the electrode.

In situ external reflection FTIR spectra were recorded during a polymerization at constant potential (1.07 V). The polymerization solution was the same as mentioned in Fig. 1. The relatively low polymerization potential was chosen in order to slow down the reaction rate. In Fig. 2 in situ spectra in the wavenumber region 1400 – 600 cm^{-1} can be seen. The first spectrum is at the top in Fig. 2 and the time difference between the spectra is 45 s. A spectrum taken at open circuit of the cell containing monomer solution was used as reference spectrum. Bands extending upwards denote material that has been expelled or diffused from the electrode surface, bands extending downwards represents the adsorption of material taking place during polymerization. In the beginning of the polymerization (from the second spectra on in Fig. 2) the decrease of

monomer material close to the electrode can be seen in upwards extending bands at 1056 cm^{-1} and in the region 900 – 800 cm^{-1} . The upwards extending band with the highest intensity at 839 cm^{-1} is from the anionic part of the electrolyte salt TBAPF₆. (A sharp peak at 677 cm^{-1} comes from remaining CO₂ in the FTIR device).

Table 1 lists the main vibrations appearing in the region 1400 – 600 cm^{-1} in the in situ external reflection spectra taken during polymerization shown in Fig. 2. Bands both from the formed oligomeric material as well as from the simultaneous doping reaction appear. Additionally, in Table 1 proposed assignments reported in the literature on similar substituted polythiophenes are given.

Vibrations at 1512 , 1454 [20] (not shown in Fig. 3) 1394 , 1370 and 1168 cm^{-1} originates from the stretching of C=C and C–C in the thiophene ring [20,21]. Further vibrations from the C–S bond in the thiophene ring can be seen at 930 , 830 , 727 and 697 cm^{-1} [20,21]. Vibrations at 1183 , 1144 – 1128 , 1093 – 1076 and 1052 – 1047 cm^{-1} are assigned to stretching in the alkylenedioxy group [25,26]. For comparison, the spectrum of the neutral PEDOT film measured with internal reflection is shown in Fig. 3 together with a KBr-pellet spectrum of the monomer, EDOT.

3.2. Redox behavior of PEDOT

PEDOT films all showing reproducible redox behavior when cycled in 0.1 M TBAPF₆-acetonitrile electrolyte can be made from polymerization solutions containing 20 – 50 mM EDOT. A typical cyclic voltammogram (100 mV/s) of a (6 mC) PEDOT film made in

Table 1

Proposed assignments for the main vibrations in the in situ spectra during polymerization

| Wavenumbers (cm^{-1}) | Assignments | References |
|----------------------------------|--|--------------|
| 1370 | $\nu(\text{C}-\text{C})_{\text{ring}}$ | [21] |
| 1323–1290 | doping-induced band | [21, 23, 24] |
| 1247–1199 | doping-induced band | [21–24] |
| 1183 | $\nu(\text{C}=\text{C})_{\text{ring}}$, $\nu(-\text{COROC}-)$ | [20, 25] |
| 1168 | $\nu(\text{C}-\text{C})_{\text{ring}}$ | [20] |
| 1144–1128 | $\nu(-\text{COROC}-)$ | [26] |
| 1090 | doping-induced band | [21, 24] |
| 1093–1076 | $\nu(-\text{COROC}-)$ | [26] |
| 1052–1047 | $\nu(-\text{COROC}-)$ | [26] |
| 978–1026 shift | doping-induced band | [23, 24] |
| 943–930 | $\nu(\text{C}-\text{S})_{\text{ring}}$ | [20] |
| 830 | $\nu(\text{C}-\text{S})_{\text{ring}}$ | [20] |
| 787 | $\gamma(\text{CH})$ | [23] |
| 760 | $\gamma(\text{CH})$ | [27] |
| 727 | $\delta(\text{C}-\text{S})$ | [21] |
| 697 | $\delta(\text{C}-\text{S}-\text{C})_{\text{ring}}$ | [28] |

ν represents stretching, δ in-plane deformation, γ out-of-plane deformation and $\text{R} = \text{CH}_2-\text{CH}_2$.

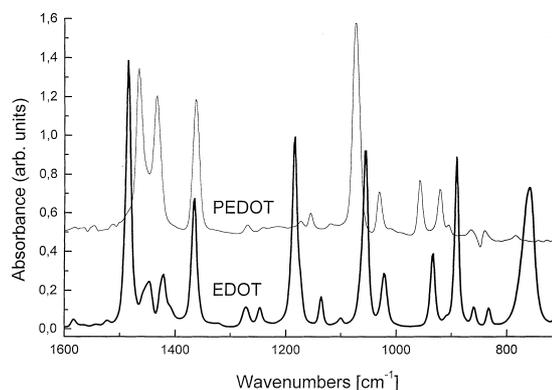


Fig. 3. Lower spectrum: transmission IR spectrum of monomer EDOT, (KBr pellet). Upper spectrum: internal reflection IR spectrum taken in situ at -1 V of a PEDOT film in 0.1 M TBAClO₄-acetonitrile solution. The film was made in 25 mM EDOT solution in 0.1 M TBAClO₄-acetonitrile.

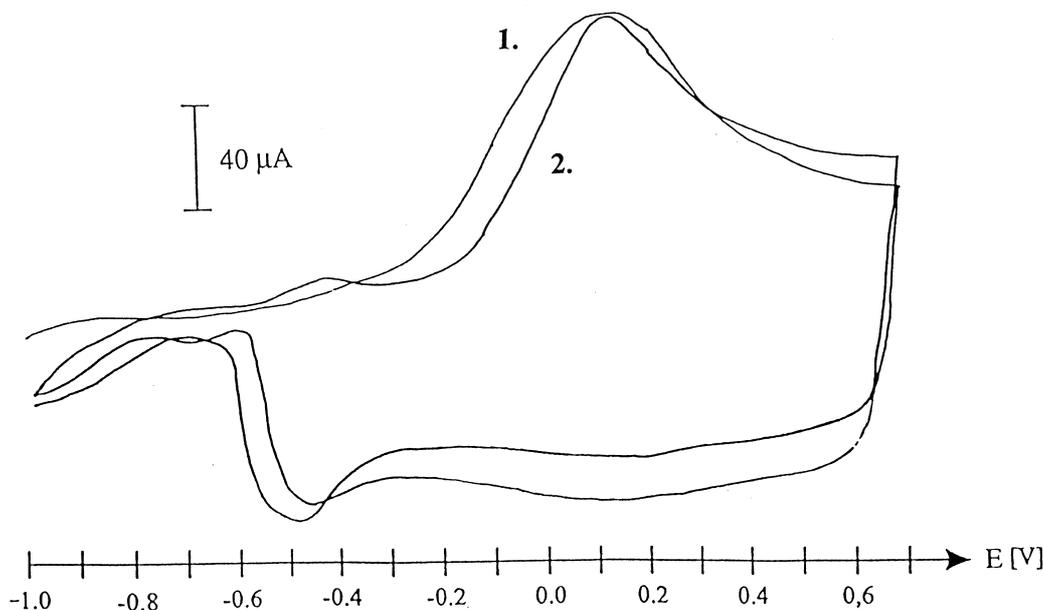


Fig. 4. The first two cycles between -1 and 0.7 V of a PEDOT film in 0.1 M TBAPF₆-acetonitrile solution. The film was made galvanostatically using 6 mC of charge for polymerization. Scan rate 100 mV/s.

(50 mM) EDOT- (0.1 M) TBAPF₆-acetonitrile solution is shown in Fig. 4.

The peak potential for the oxidation is at 0.1 V and for the reduction at -0.5 V. Depending on the synthesis conditions, scan rate and film history, i.e. time and potential at which the film has been kept before cycling, an additional oxidation peak at -0.4 V and a broad reduction process around 0 V can be seen. The film can be continuously cycled between -1 and 0.7 V without any changes in the cyclic voltammogram (except for the first scan).

In situ UV-VIS spectra were recorded during cycling a polymer film in monomer free electrolyte solution between -1.0 and 0.6 V. The polymerization solution was the same as in Fig. 1. The growth and change of the spectra as a function of potential are shown in Fig. 5. The spectral feature during oxidation shows a similar behavior that has been published previously [2]. The absorbance assigned to a $\pi-\pi^*$ -transition at 580 nm decreases continuously as the doping proceeds while a new absorbance above 700 nm is evolving. The potential range where the main spectral changes occur coincides well with the potentials where the current peak of the film is observed in the cyclic voltammogram.

Open circuit measurements were made on films of different thickness (made galvanostatically using 1.8 , 6 and 12 mC of charge for polymerization). Films were kept in neutral state or charged to different levels before the open circuit behavior was measured. The films were kept at potentials close to the oxidation

peak potential (approximately 0.1 V) or slightly higher (up to 0.35 V). For obtaining neutral films -700 mV was applied. The results of the 1.8 and 12 mC films are shown in Fig. 6. A common feature for all the films in slightly or heavily doped state was that they showed a slow decrease in the potential for the first minutes, but at longer time scales the change in potential was very small. In contrast, neutral films showed a rapid change in their open circuit potential indicating that the films were oxidized by impurities or traces of water in the electrolyte solution. The E vs. t responses

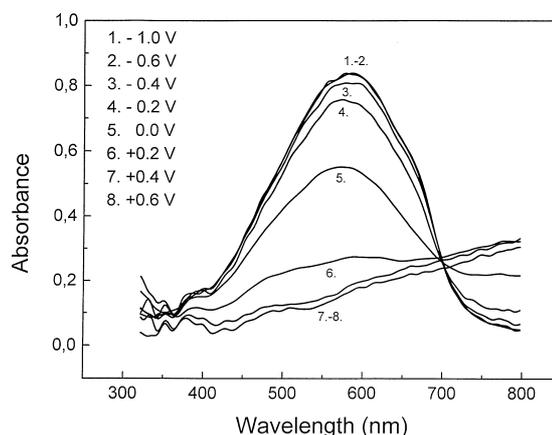


Fig. 5. UV-VIS absorption spectra of PEDOT film on ITO during the oxidation process in 0.1 M TBAPF₆-acetonitrile. The potential range is -1.0 – $+0.6$ V, scan rate 100 mV/s.

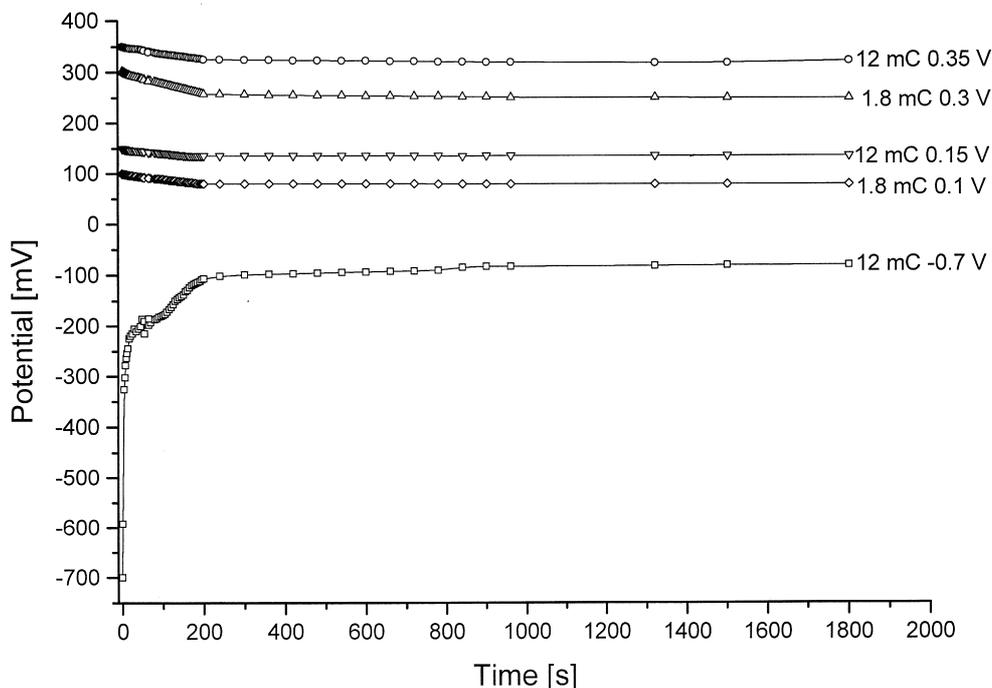


Fig. 6. Open circuit behavior of a 1.8 mC and a 12 mC PEDOT film kept for 2 min at the indicated potential. Electrolyte solution was 0.1 M TBAPF₆-acetonitrile.

show that PEDOT is very stable in its doped state which is explained by its low oxidation potential. The film thickness has no significant influence on the open circuit behavior.

FTIR spectra taken in situ during stepwise oxidation and reduction of a PEDOT film in 0.1 M TBAPF₆-acetonitrile solution are shown in Fig. 7. Spectra are gathered at constant potential every 200 mV of a potential cycle starting and ending at -1 V. The anodic switching potential was at 0.7 V. A spectrum of the PEDOT film in electrolyte solution in the cell at -1 V was used as reference spectrum. The stepwise oxidation is shown in Fig. 7a and the reduction in Fig. 7b, respectively. At -0.4 V (the potential which corresponds to the first oxidation peak in the cyclic voltammogram) the spectra change significantly. Doping induced bands originating from changes in the conjugated backbone due to electron withdrawing (oxidation) from the polymer chain and counterion balancing (also seen during electrochemical polymerization) appear at 1319, 1200, 1100 and 978 cm^{-1} . In addition, bands of lower intensity also appear at 1147, 1058, 1014 and at 944 cm^{-1} , which are interpreted to be from stretching in the ethylenedioxy ring and from the C-S bond. In the spectra around 0.1 V, the potential where the main oxidation peak is seen in the cyclic voltammogram, (spectrum at 0 and 0.2 V in Fig. 7a) the intensities of the doping induced band have increased and some broadening of

the bands has taken place. Spectral features from unsuccessful subtraction of the absorption bands of the electrolyte can be seen as upwards extending peaks in the spectra at 1040, 918 and 839 cm^{-1} . In addition, peaks pointing upwards at 1070 cm^{-1} and at 957 cm^{-1} from the neutral form of the polymer can be seen due to the conversion of the material into its oxidized form. The reduction is shown in Fig. 7b where the first spectrum taken at 0.2 V is at the bottom of the figure. The reference spectrum is the same as in Fig. 7a. Between -0.4 and -0.6 V the spectral changes indicate a transition of the film towards a discharged state. The spectrum at the potential of the main reduction peak in the cyclic voltammogram (-0.6 V) has the same band shapes as the spectrum from the oxidation of the film at -0.4 V indicating a hysteresis in the oxidation/reduction process. At -1 V the film is back in its neutral state and all bands have disappeared from the spectrum.

Earlier studies on the redox behavior of PEDOT where the bending beam technique was used have been reported by Inganäs et al. [13]. In their studies they observed a rapid contraction in volume of the film in the beginning of the oxidation and a slow swelling upon further oxidation. The contraction was explained to be due to structural changes taking place in the polymer. The cyclic voltammogram of a thin PEDOT film on a quartz electrode with simultaneous mass

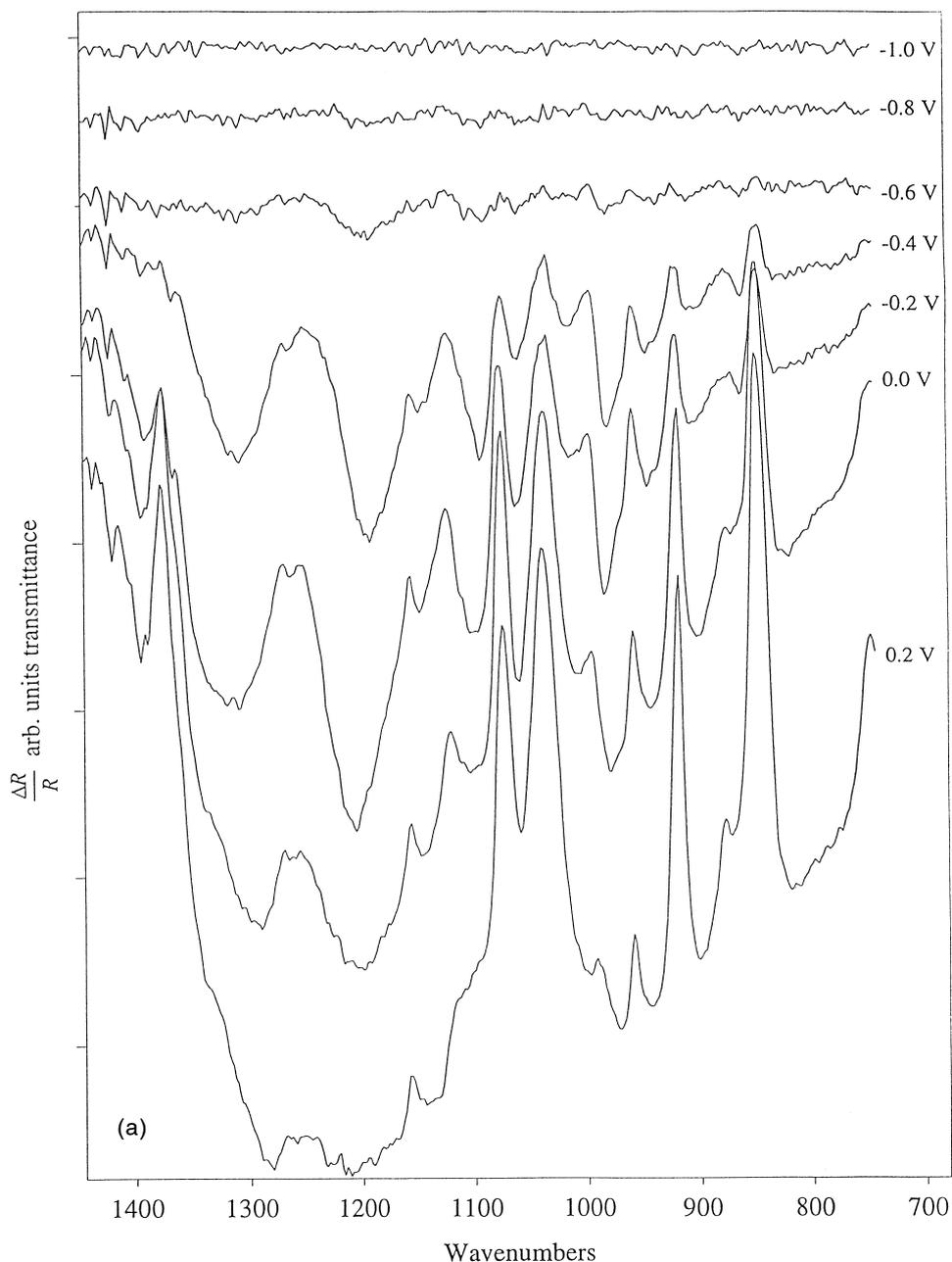
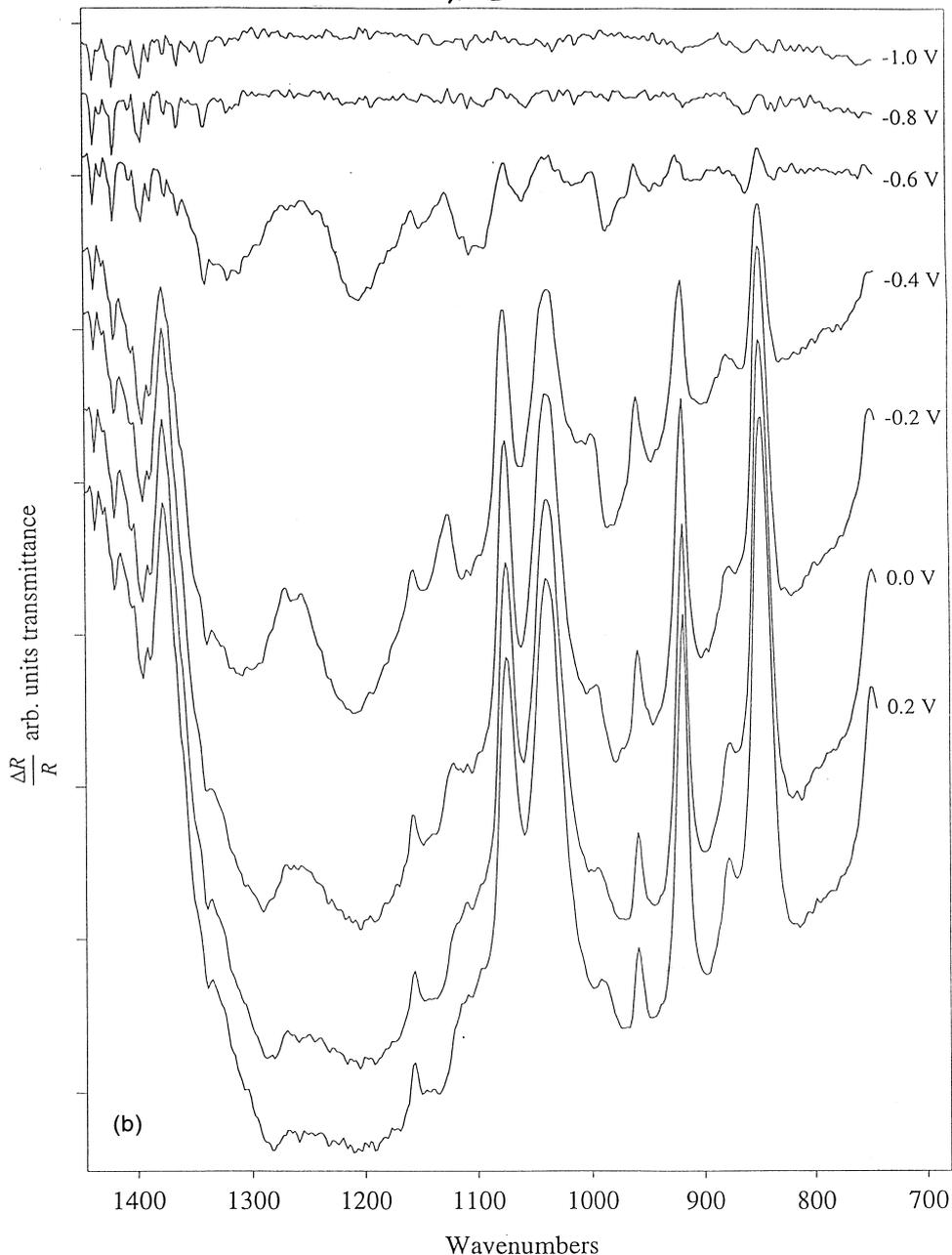


Fig. 7. In situ external reflection FTIR spectra of step wise oxidation and reduction of a PEDOT film made potentiostatically at 1.14 V for 10 min. Reference spectrum at -1 V. The spectra are separated. (a) Oxidation, first spectrum at the top of the figure. (b) Reduction, first spectrum at the bottom of the figure.

changes obtained from changes in the resonance frequency is shown in Fig. 8. The voltammogram is measured at 10 mV/s and differs slightly from that obtained at 100 mV/s shown in Fig. 4. At a lower scan rate only one anodic and cathodic peak is observed, the peak separation is over 500 mV. A similar scan rate dependency of a PEDOT film was observed pre-

viously by Inganäs et al. [13] and was explained to be due to more than one single redox reaction in the film. The mass changes in Fig. 8 show a decrease in mass in the beginning of the oxidation. Usually a mass decrease during electrochemical oxidation of conducting polymer films has been explained by expulsion of cations from the film (with or without solvent

Fig. 7. *continued.*

molecules) and a mass increase by the incorporation of anions (with or without solvent molecules) in the film. The mass decrease in the beginning of the oxidation is approximately 10% of the total mass change during the cycle. The result shows that some amount of solvent and electrolyte is incorporated inside the layer in its neutral state and upon oxidation cations are expelled from the film. As the potential is increased

above 0 V, the mass starts to increase again due to insertion of anions. During the reverse scan a mass decrease is seen due to expulsion of anions and solvent. The mass decreases to a lower value than for the film at the initial state and reaches the initial mass only after some minutes at -0.9 V.

In situ FTIR spectra were also recorded using the internal reflection technique. The results of the

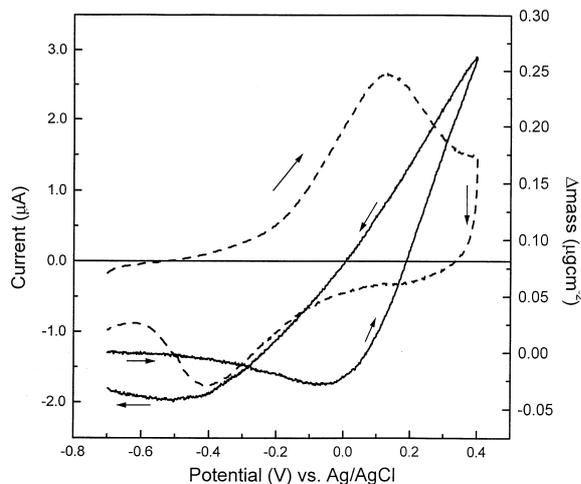


Fig. 8. Potential scan characteristics of current (dashed) and Δ mass (solid) of a PEDOT layer on Pt coated quartz crystal in 0.1 M TBAPF₆-acetonitrile solution. Scan rate 10 mV/s.

oxidation of a PEDOT film in 0.1 M TBAClO₄-acetonitrile are shown in Fig. 9. Similar spectral features as in the external reflection measurements were obtained. In addition, the electronic absorption due to the formation of free carriers during charging of the film can be seen in the internal reflection spectra above 2000 cm⁻¹. The infrared bands obtained with external and internal reflection techniques in different electro-

lytes are summarized in Table 2. The small shift in the band positions using different electrolyte salts can be explained with slightly different film structures.

If the film thickness exceed 2 µm, the spectral behavior during charging and discharging measured by the external reflection technique in 0.1 M TBAPF₆-acetonitrile was found to be partly irreversible. Some of the spectral features of the oxidized form (similar to the spectrum at -0.6 V during oxidation) are visible in the reduced film after one potential cycle. The partly irreversible behavior of thick films might be due to an impeded ion transport through the material which slows down the discharging process.

3.3. Stability of PEDOT films

The stability of PEDOT films at high anodic potentials was studied by extending the potential scan in positive direction. In Fig. 10 a PEDOT film made by potential cycling between -1 and 1.25 V (three cycles) is cycled between -1.0 and 1.9 V in 0.1 M TBAPF₆-acetonitrile solution. No distinct decrease in the current from the redox reaction of the film can be seen despite continuous cycling in this potential range. When the potential range is extended to higher positive potentials, a strong oxidation peak is growing above 2 V. Upon consecutive cycling the oxidation peak slightly shifts towards lower potential values and the peak current decreases simultaneously with a slow

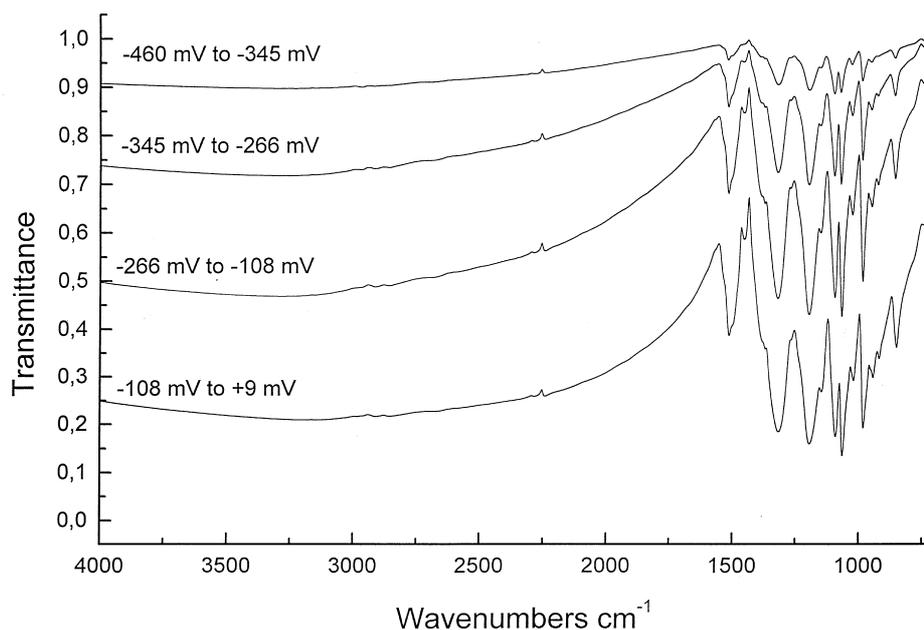


Fig. 9. In situ FTIR internal reflection spectra of the oxidation of a PEDOT film made potentiodynamically by cycling between 0–1.2 V. The spectra are recorded during potential scanning and each spectra covers a range of about 120 mV in the cyclic voltammogram. The first spectrum is at the top of the figure. Reference spectrum at -700 mV.

Table 2
Comparison between bands arising upon oxidation in PEDOT films in different electrolytes

| Wavenumber (cm^{-1}) | | | Assignment |
|---------------------------------|-------------------------|--------------------------|---|
| TBAPF ₆ e.r. | TEAPF ₆ i.r. | TBAClO ₄ i.r. | |
| 1450 | 1450 | 1450 | $\nu(\text{C}=\text{C})_{\text{ring}}$ |
| 1394 | | 1404 | $\nu(\text{C}=\text{C})_{\text{ring}}$ |
| 1290 | 1311 | 1290 | doping-induced band |
| 1205–1189 | 1184 | 1180 | doping-induced band |
| | | | $\nu(\text{C}=\text{C})_{\text{ring}}, \nu(-\text{COROC}-)$ |
| 1147 | 1140 | 1139 | $\nu(-\text{COROC}-)$ |
| 1090 | | | doping-induced band |
| | 1087 | 1077 | $\nu(-\text{COROC}-)$ |
| 1058 | 1059 | 1049 | $\nu(-\text{COROC}-)$ |
| 990–1014 | 1020 | 1020 | |
| 977 | 977 | 966 | doping-induced band |
| 943 | 939 | 940 | $\nu(\text{C}-\text{S})_{\text{ring}}$ |
| 898 | | | |
| | 838 | 831 | $\nu(\text{C}-\text{S})_{\text{ring}}$ |
| 871 | | | |

The films were electropolymerized in the same electrolyte as the doping was performed, e.r. = external reflection, i.r. = internal reflection.

decrease in the redox response of the film. The results show that PEDOT is very stable in comparison to other substituted thiophenes were the inactivation of the film takes place already at 1.4 V [29]. For a full inactivation the PEDOT film has to be oxidized above 2.2 V, where breakdown of the polymer film occurs and the redox response vanishes.

4. Conclusions

The electrochemical experiments show that electropolymerization of EDOT takes place easily, even when

a low monomer concentration and a low polymerization potential is used. The redox behavior of the films is dependent on the scan rate with which they are cycled in electrolyte, but not on moderate changes in different polymerization parameters as monomer concentration, electrolyte salt and polymerization potential. The low redox potential of the polymer makes it very stable under ambient conditions in its oxidized state. The neutral form of the film is maintained by applying a sufficiently high negative potential (–700–1000 mV) at the electrode. Due to its low redox potential the polymer tends to get into its oxidized state under open circuit conditions. Doping induced

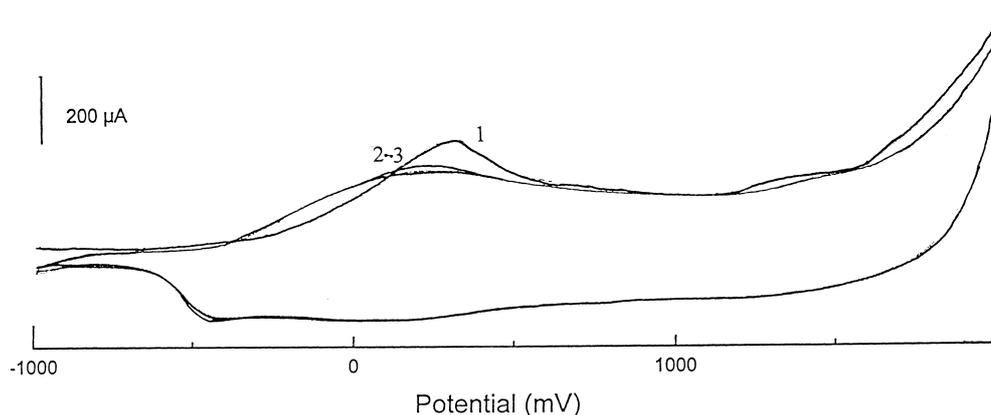


Fig. 10. The first three potential cycles between –1.0 and 1.9 V of a PEDOT film made by potential cycling between –1 and 1.25 V (three cycles at 50 mV/s). Electrolyte solution 0.1 M TBAPF₆–acetonitrile, scan rate 100 mV/s.

IR-bands appear in the spectrum immediately when a Faradic current from the redox response can be detected, i.e. at -400 mV. The EQCM measurements show a mass decrease in the film during the early state of oxidation which indicates that the neutral film is able to load electrolyte inside itself. The presence of electrolyte in the film favors the fast oxidation process taking place in a neutral film during an open circuit experiment where traces of water or impurities in the electrolyte are able to oxidize the polymer. The potential range in which the polymer is stable under ambient conditions is one of the widest ever recognized for any conducting polymer, i.e. between -400 mV (slightly oxidized form) up to 1900 mV (highly oxidized form) which makes it a promising candidate for potential applications.

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