

# Structural changes during the overoxidation of poly(3,4-ethylenedioxythiophene) films electrodeposited from surfactant free aqueous solutions

Gyözö G. Láng<sup>a,\*</sup>, Veniamin Kondratiev<sup>b</sup>, Mária Ujvári<sup>a</sup>,  
Soma Vesztergom<sup>a</sup>, Krisztina Szekeres<sup>a</sup>, Dóra Zalka<sup>a</sup>

<sup>a</sup>*Eötvös Loránd University, Institute of Chemistry, Department of Physical Chemistry & Laboratory of Electrochemistry and Electroanalytical Chemistry, Pázmány P. s. 1/A, H-1117 Budapest, Hungary*

<sup>b</sup>*Institute of Chemistry, Saint-Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia*

## Abstract:

Inherently conducting polymers have been of great interest to scientists since the initial discovery of polymers with metal type conductivities and this is currently one of the most active areas of research in polymer science and engineering. Conducting polymers are attractive materials for use in a variety of applications that require materials which are both electrically conducting and mechanically compliant. It is known that poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT, is relatively stable compared to other conducting polymers. The electropolymerization of 3,4-ethylenedioxythiophene (EDOT) is usually carried out in organic solvents due to the low solubility of the monomer in water. However, since organic solvents are often harmful to health and uneconomical compared to water, there is a growing interest in the preparation of PEDOT films in aqueous media. In the present study, the most important electrodeposition methods for the preparation of PEDOT films in surfactant free aqueous media are summarized. It is obvious, that the stability of polymer films is of great importance for their practical application. For this reason, results of recent studies on the electrochemical stability and degradation properties of poly(3,4-ethylenedioxythiophene) films electrodeposited from aqueous solutions are summarized, with particular emphasis on the structural changes induced by overoxidation and oxidative (electrochemical) degradation. Experimental techniques suitable for monitoring the degradation process have been discussed and the morphological changes in PEDOT films during overoxidation have been analyzed. Overoxidation mechanisms proposed in the literature have been surveyed.

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\*Tel.: +36 1 209 0555/1107; fax: +36 1 372 2592.  
E-mail address: langgyg@chem.elte.hu

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## Introduction

Intrinsically conducting organic polymers have attracted great interest due to their very good electrical conductivity and good environmental stability, combining the advantages of organic polymers and the electronic properties of semiconductors. Polymers can be made to conduct if alternating single and double bonds link their respective carbon atoms. Here, electrons can be introduced via reduction of the polymer chain, or removed via the oxidation of the polymer chain. It is known that demand for electrically conducting polymers as used in the electronics industry has in the past been met by using high loadings of metal or other conductive powders (e.g. Au, Ag, Cu, Ni and graphite) with the polymer matrix [1]. There are, however, a number of disadvantages to this approach, including high cost and deterioration in other properties of the polymer.

Intrinsically conducting organic polymers are attractive materials for use in a variety of applications that require materials which are both electrically conducting and mechanically compliant, i.e. in energy conversion/storage, optoelectronics, coatings, sensing applications and supplement the quest for powerful yet small/thin and flexible devices [2-15]. Obviously, in all these applications the long term stability of the polymer is of particular concern. This stability can be assessed in terms of the property of interest, such as: mechanical elasticity, conductivity, electrochemical activity, etc. A main characteristic feature of conducting polymers is the ability to undergo reversible redox transformations which are accompanied by the movement of “dopant” ions (or counterions). In the so called p-doped state, the main chain of the conducting polymer is oxidized, and the dopant ions are introduced for stabilizing the charge along the polymer backbone, i.e. for keeping the electron neutrality of the whole molecule. Due to the low stability of n-doping states the most investigations of conducting polymers are focused on the p-doping processes, where delocalized cation-radicals (“polarons”) and dications (“bipolarons”) play the role of charge carriers within the polymer film. The positive polaron with positive charge (formed after oxidation of chain fragments) and the negative polaron with negative charge (formed after reduction of chain fragments) are usually denoted as  $P^+$  and  $P^-$ , respectively. The bipolaron is a charge carrier that possesses double charges by coupling of two  $P^+$  or

two P<sup>•</sup> on a conjugated polymer main chain. Bipolarons have no spin. The “oxidation” of the polymer is usually considered to be reversible, while “overoxidation” can be defined as an irreversible electrochemical process which leads to excessive oxidation of polymer fragments (with formation of new oxidation centers, states) and is accompanied by gradual loss of electroactivity.

It should be noted here that the nature of the “doping” in conducting polymers is different from that of the doping of crystalline inorganic semiconductors, since in the latter case doping is realized by the introduction of impurities into a semiconductor crystal, the dopant species occupies positions within the lattice of the host material and the dopant is integrated into the lattice structure. The number of outer electrons define the type of doping. E.g. two of the most important materials Si can be doped with, are boron (3 valence electrons) and phosphorus (5 valence electrons). Other materials are aluminum, indium (3-valent) and arsenic, antimony (5-valent), i.e. elements with outer shell electrons one more or one less than Si. Elements with 3 valence electrons are used for p-type doping, 5-valued elements for n-doping.

Conducting polymers such as polyanilines, polypyrroles and polythiophenes have been studied intensively during the last decades. It has been found that poly(3,4-ethylenedioxythiophene) [14,16], often abbreviated as PEDOT, is relatively stable compared to other conducting polymers. The conjugated polymer backbone, consisting of alternating C-C double bonds, provides for  $\pi$ -orbital overlap along the molecule. PEDOT can be doped with many anions, including macromolecular polyanions such as poly(styrene sulfonate) (PSS). Previous studies have shown that PEDOT is electroactive in aqueous solutions [17-19], and exhibits a relatively high conductivity. However, although the problem of degradation and stability of organic conducting polymers is an important “real-life” problem in practical applications and it has been repeatedly discussed in the literature, there are not many papers dealing with the stability of PEDOT-modified electrodes. In most of these studies, voltammetric techniques such as cyclic voltammetry were used to investigate the electrochemical behavior of PEDOT films. For example, it has been reported [20-24] that at sufficiently positive electrode potentials, degradation of the polymer occurs. That is, when the positive potential limit of the cyclic voltammogram (CV) is extended to the region in which the “overoxidation” of the PEDOT film takes place, an oxidation peak (without a corresponding reduction peak) appears in the cyclic voltammogram. It was also shown [21-23] that PEDOT films in modified electrodes undergo structural changes during the overoxidation process.

The possible stages involved in the overoxidation/degradation process are the following:  
1) Stress generation in the PEDOT film during overoxidation [25]. 2) Crack formation due to

internal stresses. 3) After the formation of the line cracks, the film stress is partially released. 4) The products of the degradation of the polymer can leave the polymer layer. 5) The partial delamination of the polymer layer leads to the exposure of the underlying metal substrate to the electrolyte solution.

Besides morphological changes, overoxidation can also affect the charge structure of the polymer film. Poly(3,4-ethylenedioxythiophene) is a redox polymer that incorporates counterions from the electrolyte solution to maintain electroneutrality; thus its charging processes involve a detectable counter-ion flux leaving the film [26]. It should be emphasized here that the polymer film still present on the substrate after overoxidation remains electroactive, and its internal structure may be an interesting subject for further studies, since according to literature reports conducting polymers in different overoxidation states show unique features useful for analytical, sensing and biomedical applications [27-30]. For example, (over)oxidized PEDOT films were successfully used for sensing perchlorate [31], and overoxidized poly(3,4-ethylenedioxythiophene) film-modified screen-printed carbon electrodes exhibited superior sensitivity and selectivity to dopamine [32]. However, the basis for the observed selectivity of overoxidized polymer films is still not entirely clear [15,23,33].

As can be seen from the above discussion, it is not easy to give a general definition of "electrochemical degradation of conductive polymers" due to the complexity of the phenomenon involving several parallel processes and the large amount of parameters which must be considered. On the other hand, as a rule, the electrochemical degradation of polymer modified electrodes is strongly associated with overoxidation. That is why, although the two terms "electrochemical oxidative degradation" and "overoxidation" do not have exactly the same meaning they are frequently used as synonyms.

In this review recent studies on the electrochemical stability and degradation properties of poly(3,4-ethylenedioxythiophene) films are surveyed, with particular emphasis on the structural changes induced by overoxidation and electrochemical degradation. The most important electrodeposition methods for the preparation of PEDOT films in aqueous media are also summarized, and techniques suitable for monitoring the degradation process are discussed.

## **The electrochemical synthesis of PEDOT**

Poly(3,4-ethylenedioxythiophene) can be synthesized both by electrochemical and chemical methods [15,34]. The electropolymerization of 3,4-ethylenedioxythiophene (EDOT) is usually carried out in organic solvents such as acetonitrile [35-39] or propylene carbonate

[36,40] due to the low solubility of the monomer in water. Nevertheless, since organic solvents are often harmful to health and uneconomical compared to water, there is a growing interest in the electropolymerization of PEDOT films in aqueous media. This is sometimes achieved by the application of surfactants that can prevent the aggregation of EDOT molecules in aqueous solutions. The most often used surfactants are poly(sodium 4-styrenesulphonate) (NaPSS) and sodium dodecyl sulphate (SDS), however the electrodeposition of PEDOT films may also be carried out in aqueous media that do not contain any surface active agent, i.e. when the aqueous solution contains only the monomer and an inorganic salt. There are several papers that reported the electropolymerization of PEDOT in absence of any surfactants or macromolecules (in most cases only for comparison of the films prepared with and without surfactant) but only a few of these studies deal specifically with the dependence of the film structure on the deposition methods and parameters [11,17,41-43]. In this section some of the most common “direct” electrochemical deposition techniques (i.e. the methods that can be used for the deposition of PEDOT in surfactant free aqueous media) are summarized.

### **Deposition in surfactant free aqueous solutions by using potentiostatic methods**

Du and Wang [44] prepared PEDOT films by potentiostatic deposition on a 2 mm diameter Pt disk from a 0.01M EDOT + 0.1 M LiClO<sub>4</sub> aqueous solution under constant stirring (in order to maintain the same hydrodynamic conditions). The potential was varied between 0.8 and 1.5 V vs. KCl-saturated calomel electrode (SCE), and the same charges (0.2 C) were passed at the different synthesis potentials. The capacitance of the film exhibited a minimum, while the film resistance and the deposition time (i.e., the time required for the passing of 0.2 C charge) exhibited a maximum at 1.2 V. Over 1.1 V deposition potential overoxidation of PEDOT takes place parallel to the EDOT oxidation and polymerization.

Potentiostatic electropolymerization of PEDOT on gold can be sensitively followed using the electrochemical quartz crystal microbalance (EQCM) and by spectroelectrochemistry [45]. According to [45] the PEDOT films were deposited from a 3 mM aqueous EDOT solution containing 0.3 M LiClO<sub>4</sub> as supporting electrolyte at different electrode potentials (0.75 V, 0.80 V, 0.85 V and 0.90 V vs. Ag / AgCl / 3 M KCl). The electrolysis time was 360 s. The applied potentials were chosen carefully in order to avoid the overoxidation of the polymer. At 0.75 V vs. Ag / AgCl / 3 M KCl, there was no frequency change of the EQCM, indicating that no deposition occurred at this potential. At electrode potentials more positive than 0.80 V, the absolute value of the frequency shift monotonically increased (i.e. the resonant frequency of the QCM sensor decreased) with the positive shift of the potential.

Lupu et. al. [46] deposited PEDOT potentiostatically and using sinusoidal voltage perturbation from 0.01 M EDOT and 0.1 M LiClO<sub>4</sub> containing solution (the electrolysis time was 300 s). The DC bias was fixed at 0.95 V vs. SCE. The amplitudes of the applied AC perturbations were 5 and 50 mV. In case of the 5 mV perturbation the properties of the film were similar to those of PEDOT prepared by a regular potentiostatic method. In case of 50 mV amplitude the porosity of the film became higher. The advantage of the sinusoidal method is that it allows the estimation of electrochemical parameters, such as charge transfer resistance and exchange current during the polymerization process.

The oligomers occluded in electrochemically synthesized PEDOT were investigated by Ventosa et al. [47]. The films were grown on different substrates potentiostatically by applying an anodic potential of +1.00 V vs. Ag / AgCl / KCl (3 M) for 250 s in 0.003 M EDOT + 0.2 M LiClO<sub>4</sub> aqueous solution. Both spectroelectrochemical and scanning electrochemical microscopy (SECM) measurements showed that in a 0.2 M LiClO<sub>4</sub> solution the oligomer release started at 0.70 V. From the mass spectroscopy results it can be concluded that the most stable oligomeric forms are the tetramer and the hexamer and only traces of the longest oligomeric compounds are released to solution.

### **Deposition in surfactant free aqueous solutions by potentiodynamic methods**

PEDOT films have been deposited on indium tin oxide (ITO) by using a potentiodynamic method (cyclic voltammetry) from 0.1 M KNO<sub>3</sub> + 0.01 M EDOT solution in different potential ranges [48]. The negative limit of the CVs was 0.4 V (vs. SCE), the total charge density was 0.17 C/cm<sup>2</sup>. The structure of the film changed by increasing the positive potential limit: the globules grew larger and many globules became well separated, leading to an increased roughness. The capacitance of films prepared with the application of the positive potential limit of 1.4 V was less than that of films polymerized using potential limits of 1.05 or 1.2 V. These findings are related to the overoxidation of the PEDOT films. The microstructure – which is based on lamellas and nanosheets – does not change with increasing oxidation limit.

The effect of the solubilizing agent during potentiodynamic and potentiostatic deposition was investigated as well [42]. The solution used for the deposition contained 10.0 mM EDOT, 0.5 M NaNO<sub>3</sub> and different solubilizing agents. Voltammetric curves were recorded between 0.0 V and 1.0 V (vs. Ag/AgCl/3 M NaCl) at 100 mV/s polarization speed, and potentiostatic deposition was performed at 1.0 V (up to charge density 6.25 mC/cm<sup>2</sup>). It was concluded that anodic solubilizing agents favor polymerization by lowering the oxidation potential of EDOT and by eliminating the induction period. The films had longer conjugation length,

showed higher transparency and increased conductivity compared to films prepared without surfactant addition. Cationic surfactants increased the oxidation potential and exhibited slow polarization kinetics.

### **Deposition in surfactant free aqueous solutions by using galvanostatic methods**

In Refs. [21-24] Au | PEDOT films were prepared from  $0.01 \text{ mol} \cdot \text{dm}^{-3}$  ethylenedioxythiophene (EDOT)/ $0.1 \text{ mol} \cdot \text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  solution at a constant current density of  $0.2 \text{ mA} \cdot \text{cm}^{-2}$  for 900 s, 1800 s or 7200 s. The thickness of the film can be controlled by changing the deposition time. The structure of the PEDOT film was globular, cauliflower-like.

Glassy carbon | PEDOT films were synthesized by Zanfognini et.al. [49] from a 0.01 M EDOT / 0.1 M  $\text{LiClO}_4$  solution by applying a constant current density of  $0.4 \text{ mA} \cdot \text{cm}^{-2}$  for 20 s. The chronopotentiogram ( $E - t$  transients) exhibited a maximum potential of +0.92 V, later the potential was stable around +0.90 V vs. Ag / AgCl / 3 M KCl reference.

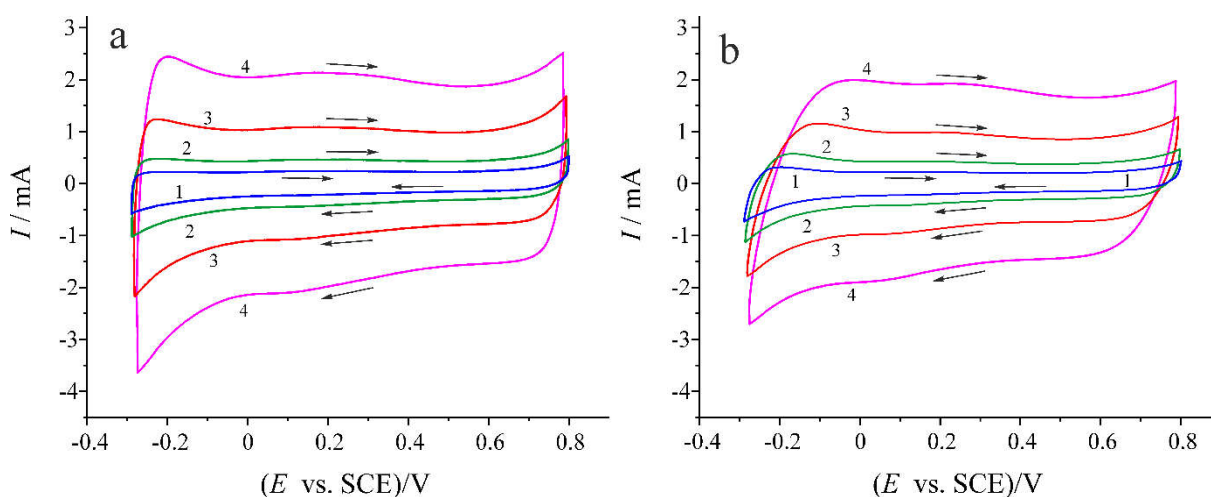
King et. al. [41] deposited PEDOT on different substrates (Au and Pd sputtered glass, as well as ITO on glass and Pt/Ir balls) and in the presence of various counterions. The applied preparation method involved a galvanostatic electrolysis at a current density of  $0.5 \text{ mA}/\text{cm}^2$  for 12 min from solutions containing 0.01 M EDOT and 0.01 M of the studied counterion. They characterized the structure of PEDOT films deposited from aqueous poly(styrene sulfonate), chloride, perchlorate, PBS: phosphate buffered solution containing 0.001 M  $\text{KH}_2\text{PO}_4$ , 0.15 M NaCl and 0.0057 M  $\text{Na}_2\text{HPO}_4$ , *para*-toluenesulfonate, heparin, glutamate, hyaluronic acid, bovine serum albumine, poly(*D*-lysine), and biotin solutions, and found that the selection of counter-ions for PEDOT deposition affects both the electrical properties and the morphology of the obtained film.

Bobacka et. al. have reported the galvanostatic deposition of PEDOT on glassy carbon [11] and Pt [17]. They used a solution that contained 0.01 M EDOT and 0.1 M supporting electrolyte (either KCl, NaCl or NaPSS with an average molar mass of 7000). A glassy carbon rod was used as counter electrode in both cases. The reference electrode was either Hg /  $\text{Hg}_2\text{Cl}_2$  / 3 M KCl [11] or Ag / AgCl / 3 M KCl [17]. In each experiment, the current density was kept constant ( $j = 0.2 \text{ mA} \cdot \text{cm}^{-2}$ ) while the deposition time was varied between 71 and 1071 s.

### **Electrochemical and structural characterization of overoxidized PEDOT films**

## Cyclic voltammetry

Cyclic voltammetry (CV) is one of the standard techniques used for characterization of polymer modified electrodes. As mentioned in the introduction it is an effective tool also for the investigation of the electrochemistry of PEDOT. It has been found that when the positive potential limit of the CV is extended into the region in which the overoxidation of the polymer film takes place, an oxidation peak (without a corresponding reduction peak) appears [20], but only minor changes can be observed in the shape of the cyclic voltammograms recorded in the “stability region” before and after overoxidation. The influence of the electropolymerisation potential on the properties of PEDOT films obtained in aqueous solutions has been studied in [44,45]. It has been concluded in [48] that strong overoxidation of the PEDOT film takes place when the electropolymerisation potential is more positive than +1.10 V vs. SCE, and the extent of overoxidation is smaller when the potential ranges from +0.80 to +1.10 V.

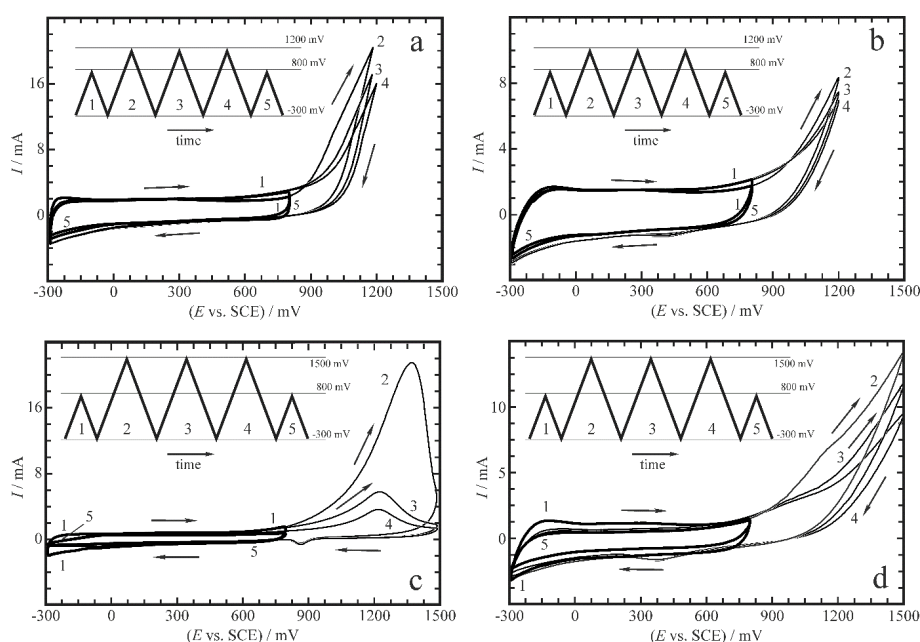


**Figure 1** Cyclic voltammograms of PEDOT films electrodeposited on gold-on-glass (a) and platinum-on-glass strips (b) recorded in  $c = 0.1 \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{SO}_4$  solution at different sweep rates. 1:  $\nu = 10 \text{ mVs}^{-1}$ ; 2:  $\nu = 20 \text{ mVs}^{-1}$ ; 3:  $\nu = 50 \text{ mVs}^{-1}$ ; 4:  $\nu = 100 \text{ mVs}^{-1}$ ; Geometric electrode area:  $2.0 \text{ cm}^2$ .  $E$ : electrode potential,  $I$ : current [15].

Overoxidation of PEDOT films prepared electrochemically under “normal” conditions has been investigated in several studies [15,21-24]. A series of cyclic voltammograms of pristine Au|PEDOT|0.1 M sulfuric acid (aq.) and Pt|PEDOT|0.1 M sulfuric acid (aq.) electrodes recorded at different sweep rates ( $\nu = 10, 20, 50, 100 \text{ mVs}^{-1}$ ) are shown in Figure 1 (geometric surface area of the electrode:  $2.0 \text{ cm}^2$ ). The rectangular-like shape of the CV curves indicates capacitive behavior of the electrodes (Figure 1a and Figure 1b). The charge associated with the



charging/discharging process is approximately the same for both electrodes [22], i.e. between  $-0.3$  and  $0.8$  V vs. KCl-saturated calomel electrode (SCE) the oxidation-reduction process of the PEDOT films is reversible. It is known from published data [15,21] that irreversible oxidation of the PEDOT film starts at or above  $0.8$  V vs. SCE. This means that at potentials more positive than  $0.8$  V vs. SCE irreversible degradation of the polymer layer occurs as it can be seen in Figure 2, where a series of cyclic voltammetric curves recorded for Au|PEDOT|0.1 M sulfuric acid (aq.) (Figure 2a) and Pt|PEDOT|0.1 M sulfuric acid (aq.) (Figure 2b) electrodes at a sweep rate of  $\nu = 50 \text{ mV s}^{-1}$  are shown [22].



**Figure 2** The series of cyclic voltammetric curves recorded according to the potential programs indicated by the saw-tooth like inserts (sweep rate:  $\nu = 50 \text{ mV s}^{-1}$ ). One “narrow-range” CV (curve 1) taken immediately before and one (curve 5) taken immediately after the 3 cycles (curves 2-4) recorded in the potential range  $-300 \text{ mV vs. SCE} — 1200 \text{ mV vs. SCE}$  (a,b) and  $-300 \text{ mV vs. SCE} — 1500 \text{ mV vs. SCE}$  (c,d), respectively, are presented. (a): Au | PEDOT | 0.1 M sulfuric acid (aq.); (b): Pt | PEDOT | 0.1 M sulfuric acid (aq.); (c): Au | PEDOT | 0.1 M sulfuric acid (aq.); (d): Pt | PEDOT | 0.1 M sulfuric acid (aq.). Geometric electrode area:  $2.0 \text{ cm}^2$ .  $E$ : electrode potential,  $I$ : current [15].

The potential programs applied to the electrodes are given in the inserts. After “moderate” (or “mild”) overoxidation (up to  $1.2$  V vs. SCE) there are only small differences between the voltammograms recorded in the  $0.3$  V to  $0.8$  V potential range before and after overoxidation (curves 1 and 5 in Figures 2a and 2b). Both in the cases of Au|PEDOT and Pt|PEDOT

the shapes of the cyclic voltammograms change considerably if the positive limit of the electrode potential is extended to 1.5 V vs. SCE (“strong” overoxidation, curves 2-4 in [Figures 2c and 2d](#)). In case of Au|PEDOT a broad oxidation peak at about 1.30-1.35 V with no corresponding reduction peak can be observed in the first cycle. The voltammetric behavior of Pt|PEDOT in the potential range of -0.3 to 1.5 V vs. SCE is similar to that of Au|PEDOT, however, no distinct peak appears on the voltammograms. As it can be seen from [Figures 2c and 2d](#), the effects of overoxidation on the oxidation current are common for both electrodes: the peak current decreases with the number of scanning cycles (curves 2-4). This quite rapid decrease of the oxidation current with the number of cycles and the absence of the reduction peak suggest that the oxidation process lead to irreversible changes in the polymer film. Indeed, the cyclic voltammograms recorded before and after overoxidation (curves 1 and 5 in [Figures 2c and 2d](#)) are similar in shape and show typical capacitive behavior in the “narrow” potential range ( -0.3 V to 0.8 V vs. SCE), but the redox capacity of the (over)oxidized polymer film is considerably smaller than that of the freshly prepared film.

### Electrochemical-mechanical properties of the PEDOT films

According to experimental results, during oxidation or reduction processes the mechanical properties of conductive polymers may change significantly [50,51]. E.g. by using a micro-mechanical cantilever-based sensor considerable stress changes have been detected in dodecylbenzenesulfonate-doped polypyrrole films during potential cyclization [52]. The “bending cantilever” or “electrochemical bending beam” method [53-56] can be effectively used in electrochemical-mechanical experiments, since the changes of the stress in a thin film ( $g_f$ ) or other conducting layer on one side of an insulator strip (cantilever) in contact with an electrolyte solution can be estimated from the changes of the radius of curvature of the strip. If the potential of the electrode changes, electrochemical processes resulting in the change of  $g_f$  induces a bending moment and the strip bends (the scheme of the experimental setup is similar to that presented in Figure 1 in the chapter entitled “Interface stress measurements in an electrochemical environment” of this Encyclopedia). The change of  $g_f$  can be obtained by an expression based on a generalized form of Stoney’s equation [25,53,57,58]

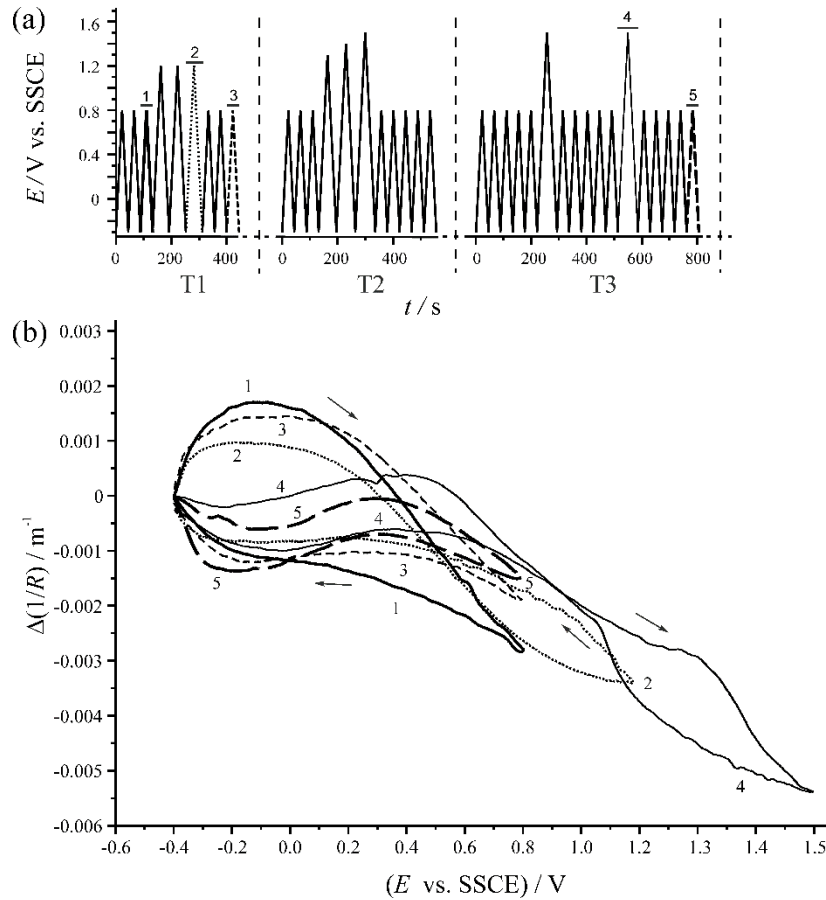
$$\Delta g_f = k_i \Delta(1/R) \quad [1]$$

where  $k_i$  depends on the design of the electrode, and  $R$  is the radius of curvature of the cantilever. The change in the curvature of the cantilever,  $\Delta(1/R) = \Delta g_f / k_i$  can be calculated, if the changes of the deflection angle  $\Delta\theta$  of a laser beam mirrored by the metal layer on the plate are measured

using an appropriate experimental setup. If the deflection of the cantilever is small, the following approximate equation can be derived [53,59-61]:

$$\Delta\left(\frac{1}{R}\right) \approx \frac{\Delta\theta}{2n_{s,a}h} \approx \frac{\Delta b}{2n_{s,a}hl}, \quad [2]$$

where  $h$  is the distance between the level of the solution in the cell and the reflection point of the laser beam (measured e.g. with the help of a cathetometer);  $l$  is the distance between the electrode and the position sensitive photo detector (PSD),  $\Delta b$  is the change of the position of the light spot on the PSD, and  $n_{s,a}$  is the refractive index of the solution with respect to air.



**Figure 3** (a) The potential program applied to the Au | PEDOT | 0.1 M sulphuric acid electrode. Sweep rate:  $\nu = 50 \text{ mV s}^{-1}$ . (b) The voltdeflectograms recorded in time intervals “1” - “5” (see Fig. 6a). E: electrode potential, R: radius of curvature of the cantilever (Film thickness:  $d \approx 1.4 \text{ }\mu\text{m}$ ) [15].

As discussed above, between  $-0.3$  and  $0.8 \text{ V}$  vs. SCE the oxidation-reduction process of the PEDOT films is reversible, but at potentials  $E > 0.8 \text{ V}$  vs. SCE irreversible degradation of the polymer layer occurs. In ref. [24] a series of voltdeflectograms ( $\Delta(1/R)$  vs.  $E$  curves) has

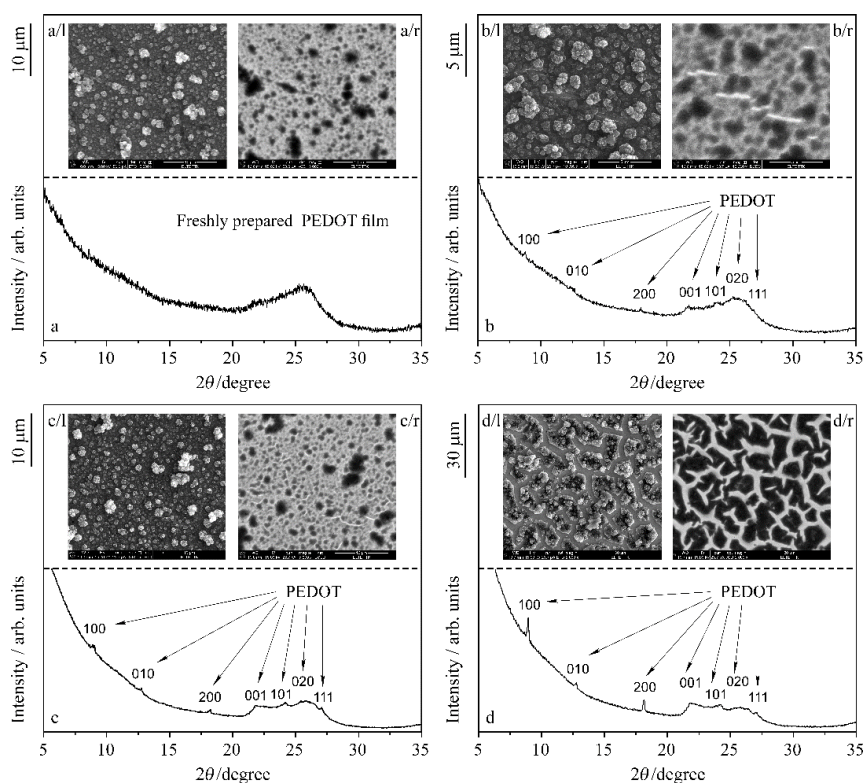
been recorded for a Au | PEDOT | 0.1 M sulfuric acid (aq.) electrode (geometric surface area: 4.0 cm<sup>2</sup>) at a sweep rate of  $\nu = 50 \text{ mV s}^{-1}$ . Some of these curves are shown in Figure 3b. (Volt-deflectograms for the Pt | PEDOT | 0.1 M sulfuric acid (aq) electrode can be found in ref. [22].) The potential program applied to the electrode is given in Figure 3a. The corresponding voltammograms showed capacitive behavior if the potential limit is kept below 0.8 V. If the polarization potential exceeded this critical value an oxidation peak without corresponding reduction peak appeared (“overoxidation cycles”). The shapes of the  $\Delta(1/R)$  vs.  $E$  curves before and after moderate oxidation were similar, but the change in  $1/R$  (between minimum and maximum) was slightly greater in the case of the pristine film.

After extending the positive potential limit up to 1.5 V vs. NaCl-saturated calomel electrode (SSCE), the shape of the  $(1/R)$  vs.  $E$  curves changed dramatically (curves 4 and 5 in Figure 3b) and begins to resemble more and more that of the  $(1/R)$  vs.  $E$  curve for bare Au [21,22,25].

### SEM micrographs and X-ray diffractograms of pristine and overoxidized PEDOT layers

In Figure 4 scanning electron microscope (SEM) images together with X-ray diffractograms of freshly prepared PEDOT films (deposited on gold) are presented [23,24]. One can see in the secondary electron (SE) SEM images, that well-separated globules (or cauliflower-like particles) are present on the top of the polymer layer (Figure 4a/l, i.e. the SEM image on the left hand side of Figure 4a, see also refs. [15,21,22]). The backscattered electron (BSE) micrograph taken from the same area (which characterizes a thicker layer compared to SE) shows that the globules are attached to an underlying smoother polymer layer (Figure 4a/r). The X-ray diffraction (XRD) pattern indicates that the as-prepared sample is highly amorphous (Fig. 4a).

In Figure 4b X-ray diffractogram and SEM images of the polymer film after moderate overoxidation (after the completion of 3 potential cycles up to 1.2 V vs. SSCE) can be seen. The most striking difference between the micrograph shown in Figure 4b/l and that of the freshly prepared sample in Figure 4a/l is the appearance of narrow cracks or crevices in the SEM image of the oxidized film. The cracks resulted in bright spots (“islands”) in the backscattered SEM image (Figure 4b/r). The XRD spectrum is still characteristic for amorphous state but small peaks appear indicating the presence of some crystalline material. After further oxidation the XRD peaks corresponding to the crystalline polymer are growing (Figure 4c), the SEM images show interconnected crevices (Figures. 4c/l-c/r).



**Figure 4** (a): X-ray diffractogram of the freshly prepared PEDOT film. (a/l): Secondary electron SEM image. (a/r): The corresponding backscattered SEM image taken from the same area. The length of the vertical black bar left to the images corresponds to 10  $\mu\text{m}$ . (b): X-ray diffractogram of the oxidized PEDOT film after moderate overoxidation (recorded at the end of time interval “T1” in Fig. 6a). (b/l): Secondary electron SEM image. (b/r): The corresponding backscattered SEM image taken from the same area. (X-ray diffractogram and SEM micrographs were recorded at the end of time interval “T1” in Fig. 6a). The length of the vertical black bar left to the images corresponds to 5  $\mu\text{m}$ . (c): X-ray diffractogram of the oxidized PEDOT film at the end of time interval “T2” in Fig. 6a. (c/l): Secondary electron SEM image. (c/r): The corresponding backscattered SEM image taken from the same area. The length of the vertical black bar left to the images corresponds to 10  $\mu\text{m}$ . (d): X-ray diffractogram of the oxidized PEDOT film after strong overoxidation (recorded at the end of time interval “T3” in Fig. 6a). (d/l): Secondary electron SEM image. (d/r): The corresponding backscattered SEM image taken from the same area. The length of the vertical black bar left to the images corresponds to 30  $\mu\text{m}$  [15].

On the other hand, well-separated X-ray diffraction peaks can be observed after the completion of 3 potential cycles up to 1.5 V vs. SSCE (i.e. after strong overoxidation) (Figure 4d). The diffraction peaks of crystalline PEDOT were indexed on the basis of published data [62,63]. These works identified this phase as orthorhombic structure. According to Figures 4b, 4c and 4d the diffraction peaks of PEDOT became sharper and more intensive after the

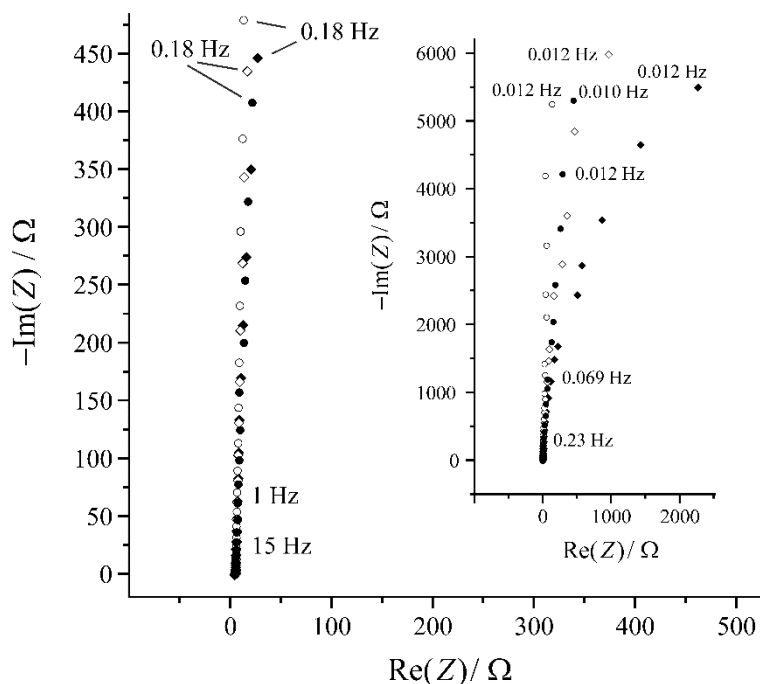
electrochemical treatment. This indicates that besides the degradation of the PEDOT film its crystallinity gradually increased with increasing the number of oxidation cycles. After strong overoxidation the cauliflower-like structure can still be identified in the SEM micrographs, but the film forms islands separated by cracks on the surface of the substrate (Figure 4d/l). According to the backscattered SEM micrographs (Figure 4d/r) the crevices of about 2-3  $\mu\text{m}$  width form a widespread network. Energy dispersive X-ray (EDX) composition analysis proved that only Au is present at the bottom of the crevices [21-24].

### Electrochemical impedance spectroscopy (EIS) – impedance measurements

Unfortunately, there are only few studies in the literature dealing directly with the impedance of overoxidized PEDOT films, only some tentative or qualitative interpretations of such impedance spectra can be found in recent studies and reviews [15,21,22,24]. For instance, impedance spectra of freshly prepared and overoxidized Au/PEDOT in 0.5 M  $\text{H}_2\text{SO}_4$  solution are presented in [15]. In Figure 5 impedance spectra (complex plane plots) of freshly prepared Au/PEDOT in 0.5 M  $\text{H}_2\text{SO}_4$  solution at different electrode potentials are shown ( $t_f \approx 0.7 \mu\text{m}$ , geometric area  $\approx 1 \text{ cm}^2$ ). In the frequency range 0.1 Hz – 10 kHz and at electrode potentials ranging from 0.1 V to 0.7 V vs. SCE the impedance spectra indicate an almost purely capacitive behavior (the “low frequency capacity” of the film is  $C_L \approx 2.9 \text{ mF}\cdot\text{cm}^{-2}$  at 0.1 V vs. SCE and  $C_L \approx 2.7 \text{ mF}\cdot\text{cm}^{-2}$  at 0.4 V vs. SCE). However, at electrode potentials  $E > 0.7 \text{ V}$  vs. SCE the medium/low frequency “arc” (see the insert in Figure 5) indicates the presence of an interfacial charge transfer process, which can most probably be attributed to the slow (over)oxidation of the PEDOT film. The impedances of freshly prepared electrodes at medium and low frequencies ( $\omega < 50 \text{ Hz}$ ) can be well approximated in terms of a constant phase element (CPE):

$$Z(\omega) = R_u + \frac{1}{B} (i\omega)^{-\alpha}, \quad [3]$$

where  $\omega$  is the angular frequency,  $R_u$  is the uncompensated ohmic resistance,  $B$  and  $\alpha$  are the CPE parameters, and  $i$  is the imaginary unit. The values of  $\alpha$  are close to unity. At higher frequencies a small capacitive arc can be identified in the complex plane plot which can be observed more clearly in the spectra recorded after overoxidation, i.e. after repetitive cycling of the electrode potential between  $-0.3$  and  $1.5 \text{ V}$  vs. SCE. On the other hand, it has been found that for thin PEDOT films in very clean solutions the CPE parameter  $\alpha$  is close to unity which indicates a nearly perfect capacitive behavior.



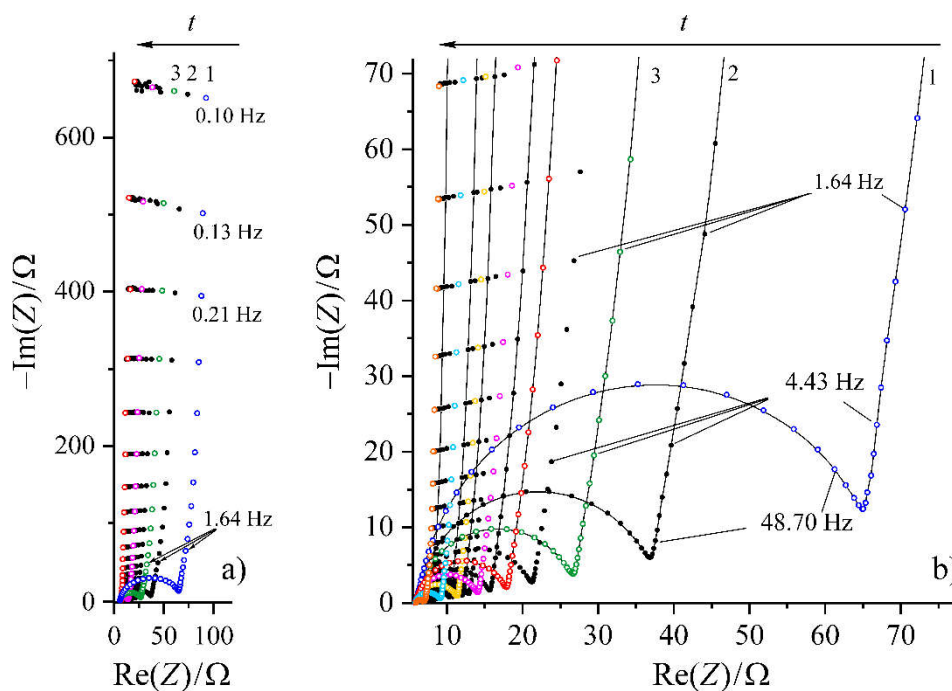
**Figure 5** Impedance spectra (complex plane plots) of freshly prepared Au/PEDOT in 0.5 M aqueous  $\text{H}_2\text{SO}_4$  solution at different electrode potentials.  $\bullet$ :  $E = 0.10$  V vs. SCE;  $\circ$ :  $E = 0.40$  V vs. SCE;  $\diamond$ :  $E = 0.70$  V vs. SCE;  $\blacklozenge$ :  $E = 0.80$  V vs. SCE. Adapted from [21].

It should be noted here, that although the theory of the impedance method for an electrode with diffusion restricted to a thin layer is well established [64], in the case of polymer-modified electrodes an ‘ideal’ response, i.e., a separate Randles circuit behavior at high frequencies, a Warburg section at intermediate frequencies, and a purely capacitive behavior due to the redox capacitance at low frequencies can rarely be observed.

As it can be seen from Figure 6, the impedance spectra of overoxidized PEDOT on gold differ from those measured for freshly prepared Au/PEDOT [15]. In this experiment the film was oxidized by cycling the potential between -0.4 V and 1.5 V vs. SCE. The most interesting feature is the appearance of an arc (or a “depressed semicircle”) at high frequencies in the complex plane impedance plot. The “low frequency capacity” of the degraded film is about  $2 \text{ mF}\cdot\text{cm}^{-2}$  at 0.35 V vs. SCE. The increase of the charge transfer resistance with the level of degradation is in accordance with the results for polypyrrole on Pt published in [65]. The decreasing capacitance and the increasing charge transfer resistance suggest that during overoxidation the electrochemical activity of the film decreases and the charge transfer process at the metal/film interface becomes more hindered than in the case of pristine films. On the other hand, the time evolution of the impedance spectra is a remarkable feature of the electrodes with overoxidized PEDOT films [66]. According to this observation, the charge transfer resistance



( $R_{ct}$ ) at the (electronically conductive) substrate/polymer film interface decreases continuously over several hours when the potential is held in the “stability region” after overoxidation of the film. The results imply that a “healing process” may occur at the film/substrate interface. A better understanding of this effect may have an impact on practical applications.



**Figure 6** a) Successive impedance diagrams of the Au | PEDOT | 0.1 M H<sub>2</sub>SO<sub>4</sub> at E = 0.4 V vs. SSCE recorded after overoxidation; b) High frequency part of the Argand diagrams. The solid lines are to guide the eye only: not curve fits. Adapted from [66].

## Suggested overoxidation mechanisms

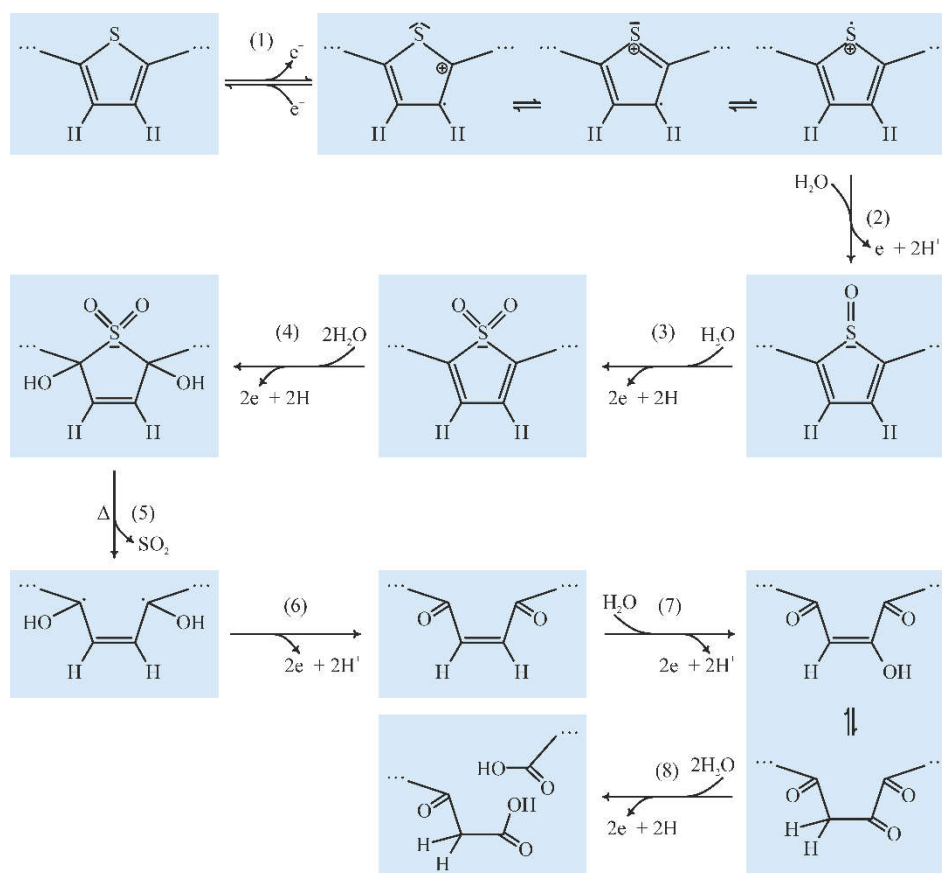
Degradation or the lack of electrochemical stability severely limits the operational lifetime of devices based on conducting polymers. Although basic studies of the properties of PEDOT have been pursued since the 1990's and the electrochemical properties of PEDOT are continuously under investigation, the number of mechanistic studies dealing with the anodic degradation of PEDOT is very limited and a thorough kinetic-mechanistic study of the overoxidation of PEDOT has not been published yet. Nevertheless, the oxidative degradation of polythiophenes in general was relatively widely studied, and this may provide an insight into the overoxidation mechanism of PEDOT as well.



Electrochemical studies accompanied by electron microprobe analysis as well as NMR and IR spectroscopic investigations [67] revealed that the first (reversible) stage of anodic polythiophene oxidation is often accompanied by the substitution of nucleophiles on the 3<sup>rd</sup> or 4<sup>th</sup> position of the thiophene units. The nucleophiles are either solvents or counter ions (e.g., water, hydroxide, methanol or halides); the resulting polymers are still conductive and electroactive, with a new optical gap induced by the substitution [68,69]. However, the proposed reaction pathways and oxidation mechanisms are describing the oxidation of poly-3-methylthiophene and poly-thiophene and not that of PEDOT where the 3 and 4 position of the ring is blocked by carbon bonds what may lead to different reaction schemes.

On the other hand, it has been reported [70] that by strong (over-)oxidation, polythiophenes are irreversibly transformed to a non-conducting state, and the voltammograms of polythiophene films in contact with wet acetonitrile solutions exhibit an irreversible anodic peak at sufficiently positive electrode potentials. It has been shown by IR spectroscopy [71] that at this potential range the thiophenic sulphur of polythiophene is oxidized, resulting in the formation of SO or SO<sub>2</sub> groups. According to the proposed mechanism (Figure 7) the oxidation of the thiophene unit (i.e. the sulphur in the thiophene ring) is followed by an oxidative SO<sub>2</sub> elimination and the formation of carbonyl groups at the 2<sup>nd</sup>, 3<sup>rd</sup> and 5<sup>th</sup> positions on the thiophene rings. The electrical conductivity of the polythiophene film gradually decreases due to an interruption of conjugation routes by the formed carbonyl groups. Further oxidation may lead to the cleavage of C—C bonds and the formation of terminal carboxylic groups. It has been suggested [69] that the above mechanism describing the overoxidation of polythiophenes *in general* should also be valid for the case of PEDOT *in particular*. On the basis of results of Fourier-transformed infrared and X-ray photoelectron spectroscopy of pristine and over-oxidized PEDOT:PSS, it was hypothesized that the presence of ethylene-dioxy groups does not create fundamental differences between the overoxidation mechanism of PEDOT and the scenario described in [71] for polythiophene. The results of cyclic voltammetry confirmed that the anodic onset potential of the overoxidation of PEDOT depends strongly on the pH. At pH > 10 where the amount of OH<sup>-</sup> ions in the electrolyte solution becomes more significant, PEDOT films can be more easily overoxidized than at more acidic pH values [69]. This indicates that the amount of counterions (nucleophiles) in the solution may also play a significant role in the overoxidation process.

Nevertheless, further research is needed to conclusively clarify these points and to elucidate the mechanism of the overoxidation process.



**Figure 7** Mechanism of the overoxidation of polythiophene. Step (1) proceeds reversibly (doping/dedoping), while steps (2) and (3) are irreversible. A sequence of two further  $2e^-$  steps, (4) and (5), leads then to the elimination of  $\text{SO}_2$ , initiated by a 2,5-hydroxylation. Thereafter, 2,5-diketones are formed in step (6) and a hydroxylation in the 3-position follows in step (7). The mesomer of the formed enol yields a vicinal 2,3-diketon, the C—C bond of which is easily cleaved in the last anodic step (8) to yield two carboxylic groups. Altogether the reaction involves two  $1e^-$  steps and five  $2e^-$  steps [15].

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## Nomenclature

Symbols and Units

$B$

CPE parameter

$E$	electrode potential
$g_f$	film stress (Pa)
$i$	imaginary unit
$I$	current
$\text{Im}(Z)$	imaginary part of the impedance
$j$	current density
$n_{s,a}$	refractive index of the solution with respect to air
$R$	radius of curvature of the cantilever
$R_{ct}$	charge transfer resistance
$\text{Re}(Z)$	real part of the impedance
$R_u$	uncompensated ohmic resistance
$t$	time
$Z$	electrode impedance ( $\Omega$ )
$\alpha$	CPE parameter (exponent)
$v$	sweep rate ( $\text{mV s}^{-1}$ )
$\Delta\theta$	deflection angle
$\omega$	angular frequency

#### Abbreviations and Acronyms

AC	alternating current
BSE	backscattered electron
CPE	constant phase element
CV	cyclic voltammetry, cyclic voltammogram
DC	direct current
EDOT	3,4-ethylenedioxythiophene
EIS	electrochemical impedance spectroscopy
EQCM	electrochemical quartz crystal microbalance
IR	infrared
ITO	indium tin oxide
NMR	nuclear magnetic resonance
PEDOT	poly(3,4-ethylenedioxythiophene)
PSD	position sensitive (photo)detector
PSS	polystyrenesulfonic acid

SCE	KCl-saturated calomel electrode
SDS	sodium dodecyl sulphate
SE	secondary electron
SECM	scanning electrochemical microscopy
SEM	scanning electron microscope
SSCE	NaCl-saturated calomel electrode
STM	scanning tunneling microscope
XRD	X-ray diffraction

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