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Original scientific paper

## Electrochemical behaviour of poly(3,4-ethylenedioxythiophene) modified glassy carbon electrodes after overoxidation – the influence of the substrate on the charge transfer resistance

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### Abstract

*Time dependence of the electrochemical impedance of an overoxidized glassy carbon|poly(3,4-ethylenedioxythiophene) (PEDOT)|0.1 mol·dm<sup>-3</sup> sulfuric acid (aq.) electrode has been investigated. To follow the changes occurring at the film/substrate interface after the overoxidation procedure, successive impedance measurements were carried out. Although the system is intrinsically nonstationary, the charge transfer resistance ( $R_{ct}$ ) corresponding to different time instants could be determined by using the so-called 4-dimensional analysis method. The same post-experimental mathematical/analytical procedure could be used also for the estimation of the charge transfer resistance corresponding to the time instant just after overoxidation of the PEDOT film. The increase of the charge transfer resistance of the overoxidized system with respect to that of the pristine electrode suggests that during overoxidation the electrochemical activity of the film decreases and the charge transfer process at the metal/film interface becomes more hindered. After the overoxidation procedure, when the electrode potential was held in the “stability region” (at  $E = 0.4$  V vs. SSCE in the present case) the  $R_{ct}$  decreased continuously with experiment time to a value somewhat higher than that of the pristine electrode. By comparing the properties of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> and the Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrodes a possible mechanistic explanation for the observed behavior has been proposed. This is based on the assumption that in the case of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode two processes may occur simultaneously during the impedance measurements: (a) reduction of the oxidized surface of the GC substrate, including the reduction of the oxygen-containing surface functionalities and (b) read-sorption of the polymer chains (polymer chain ends) on the surface.*

### Keywords

Non-stationary system; 4-dimensional analysis method; substrate-polymer interaction; oxidation of glassy carbon.

\* This paper is dedicated to the memory of our friend and colleague Professor Zdravko Stoyanov in recognition of his great contribution to electrochemistry.

## Introduction

Intrinsically conducting organic polymers such as polythiophenes, polyanilines and polypyrroles have been studied intensively during the last decades. Poly(3,4-ethylenedioxythiophene) [1], often abbreviated as PEDOT, and its derivatives are 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 highly insoluble in most solvents, electroactive in aqueous solutions [2-4], and exhibits a relatively high conductivity. The behavior of PEDOT in electrochemical systems is a hot topic nowadays due to its important applications in a variety of fields. Many studies have been performed recently to investigate the electrochemistry of PEDOT in more detail by using voltammetric techniques (in most cases cyclic voltammetry). It has been found in Refs. [5-9] that at sufficiently positive electrode potentials, degradation of the polymer occurs. The oxidative degradation of polypyrroles, polythiophenes is known as „overoxidation“. That is, when the positive potential limit of the cyclic voltammogram (CV) is extended to the region in which the “overoxidation” of the polymer film takes place, an oxidation peak (without a corresponding reduction peak) appears in the 1<sup>st</sup> CV (with a maximum in the vicinity of 1.4 V vs. SCE in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution). The oxidative degradation of PEDOT has been studied most frequently using cyclic voltammetry, impedance spectroscopy (EIS) or electron spin resonance (ESR) spectroscopy [5,10-13]. On the other hand, in Refs. [6-8] it has been shown that PEDOT films in modified electrodes undergo structural changes during the degradation process. The most probable stages involved in the overoxidation/degradation process are:

- 1) Overoxidation results in stress generation in the PEDOT film [14].
- 2) Formation of cracks due to internal stress.
- 3) The products of the degradation of the polymer leave the polymer layer.
- 4) After the formation of the line cracks, the film stress is partially released.
- 5) The partial delamination of the polymer layer leads to the exposure of the underlying metal substrate to the electrolyte solution.

Nevertheless, the polymer film still present on the substrate after overoxidation remains electroactive; and the areas with the polymer form a barrier between the metal substrate and the surrounding electrolyte solution. Apart from the morphological changes, overoxidation can also affect the charge structure of the polymer film. Poly(3,4-ethylenedioxythiophene) is a redox conductive polymer that incorporates counterions from the electrolyte solution to maintain electroneutrality; thus, its charging processes involve a detectable counter-ion flux leaving the film [15]. The above conclusions seem to be confirmed by the experimental data, but they give no information about the processes occurring after overoxidation of the polymer film.

For instance, it is known that the impedance spectra of overoxidized poly(3,4-ethylenedioxythiophene) (PEDOT) films on gold recorded in aqueous sulphuric acid solutions differ from those measured for freshly prepared films [12]. The most interesting feature is the appearance of an arc (or a “depressed semicircle”) at high frequencies in the complex plane impedance plot. The time evolution of the impedance spectra is another remarkable feature of the electrodes with overoxidized PEDOT films [16,17]. 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. This means that the impedance spectra recorded using the consecutive frequency sweep

mode (typical of EIS) are corrupted by typical errors caused by the system evolution during the experiment. According to the usual interpretation of the concept of impedance, impedance is not defined as time-dependent and, therefore, there should not exist an impedance out of stationary conditions. This means that if the requirement of stationarity in impedance spectroscopy is in conflict with the essential properties of the object, the measured data points are not “impedances”, the obtained sets of experimental data are not “impedance spectra” and they cannot be used in any analysis based on impedance models.

There are some methods proposed in the literature to deal with a non-stationary behavior. Stoynov proposed a method of determining “instantaneous” (“calculated”, “corrected” or “synthetic”) impedance diagrams for non-stationary systems based on a four-dimensional approach [18-22] (see Supplementary Material). Recently, the method have been successfully applied for the determination of the charge transfer resistance and some other characteristic impedance parameters of the gold|poly(3,4-ethylenedioxythiophene) (PEDOT)| sulfuric acid (*aq*) electrode corresponding to different time instants, including the time instant just after the overoxidation of the polymer film, demonstrating that the 4-dimensional analysis method can not only be used for the correction of the existing (experimentally measured) impedance data, but it opens up the possibility of the estimation of the impedance spectra outside the time interval of the impedance measurements. According to the results presented in [16,17], the high and medium frequency regions of the impedance spectra are stronger affected by the time evolution than the values measured at low frequencies.

In ref. [17] the following explanation was given for the decrease of the charge transfer resistance with time after overoxidation: During overoxidation at sufficiently positive potentials a significant fraction of the polymer chains become detached from the substrate surface (i.e. “desorption”, “deactivation” or “delamination” occurs). In contrary this, at a less positive potential the readsorption of the polymer chains (polymer chain ends) becomes possible, that is the number of the polymer chains directly contacted with (adsorbed on) the substrate surface is increasing with the passing time. This means that during overoxidation the “effective” coverage of the substrate by the polymer decreases, and at less positive potentials the coverage may start to increase again. The direction of the change in  $R_{ct}$  is in complete agreement with this hypothesis. On the other hand, there are also objections that can be raised against the above arguments. For instance, an opponent could argue that the gold oxide layer formation on the gold substrate surface plays the most important role in the observed relaxation process by preventing adsorption (or readsorption) of the polymer chains on the surface. However, this would mean that the behavior of the pedot/gold system is special, and in case of other substrates (*e.g.* glassy carbon) the post-overoxidation properties of the PEDOT-modified electrodes are different.

In the present study the electrochemical properties of poly(3,4-ethylenedioxythiophene) films deposited on glassy carbon substrates have been investigated in aqueous sulfuric acid solutions with the aim to reveal the similarities and differences between the behavior of PEDOT-modified glassy carbon (GC) and gold electrodes.

## Experimental

All electrochemical measurements were performed with a computer driven electrochemical workstation (Zahner IM6 controlled by a Thales software package) in a three-electrode arrangement.

**Electrodeposition of PEDOT:** Poly(3,4-ethylenedioxythiophene) films were prepared by galvanostatic deposition on both sides of thin gold and glassy carbon plates from  $0.01 \text{ mol}\cdot\text{dm}^{-3}$  ethylenedioxythiophene (EDOT) solution containing  $0.1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{Na}_2\text{SO}_4$  supporting electrolyte. Analytical grade 3,4-ethylenedioxythiophene (Aldrich), *p.a.*  $\text{Na}_2\text{SO}_4$  (Fluka), and ultra-pure water (specific resistance  $18.3 \text{ M}\Omega \text{ cm}$ ) were used for solution preparation. All solutions were purged with oxygen-free argon (Linde 5.0) before use and an inert gas blanket was maintained throughout the experiments.

The deposition was performed with galvanostatic method. The gold or glassy carbon plate in contact with the solution served as the working electrode (WE). A Pt wire immersed in the same solution served as the counter electrode (CE), and a KCl-saturated calomel electrode (SCE) as the reference electrode (RE). A constant current density of  $j = 0.2 \text{ mA}\cdot\text{cm}^{-2}$  ( $I = 0.2 \text{ mA}$ ) was applied for 1000 s (the geometric surface areas of the working electrodes were  $A = 1.0 \text{ cm}^2$ ). The film thickness was estimated from the polymerization charge by using the charge/film volume ratio determined earlier by direct thickness measurements [2,23,24]. The average thickness of the PEDOT film was about  $0.8 \mu\text{m}$ , the structure of the PEDOT film was globular, cauliflower-like[8,9], i.e. the thickness of the film was non-uniform.

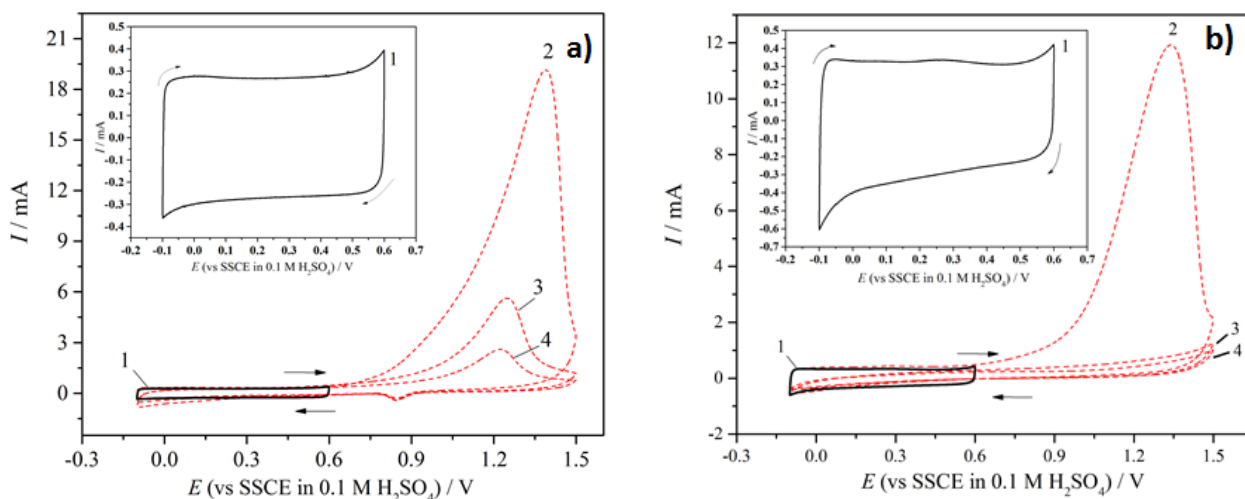
**Cyclic voltammetry and impedance measurements:** Solutions used for cyclic voltammetric and impedance measurements were prepared with ultra-pure water and *p.a.*  $\text{H}_2\text{SO}_4$  (Merck). The solutions were purged with oxygen-free argon (Linde 5.0) before use and an inert gas blanket was maintained throughout the experiments. In the conventional three-electrode cell configuration the PEDOT-modified gold or glassy carbon substrate in contact with the solution was used as the working electrode (WE), a bended gold plate immersed in the same solution as the counter electrode (CE), and a NaCl-saturated calomel electrode (SSCE) as the reference electrode (RE). The counter electrode was arranged cylindrically around the working electrode to maintain a uniform electric field. The overoxidation of the PEDOT film was carried out in  $0.1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  solution a day after the deposition.

## Results and discussion

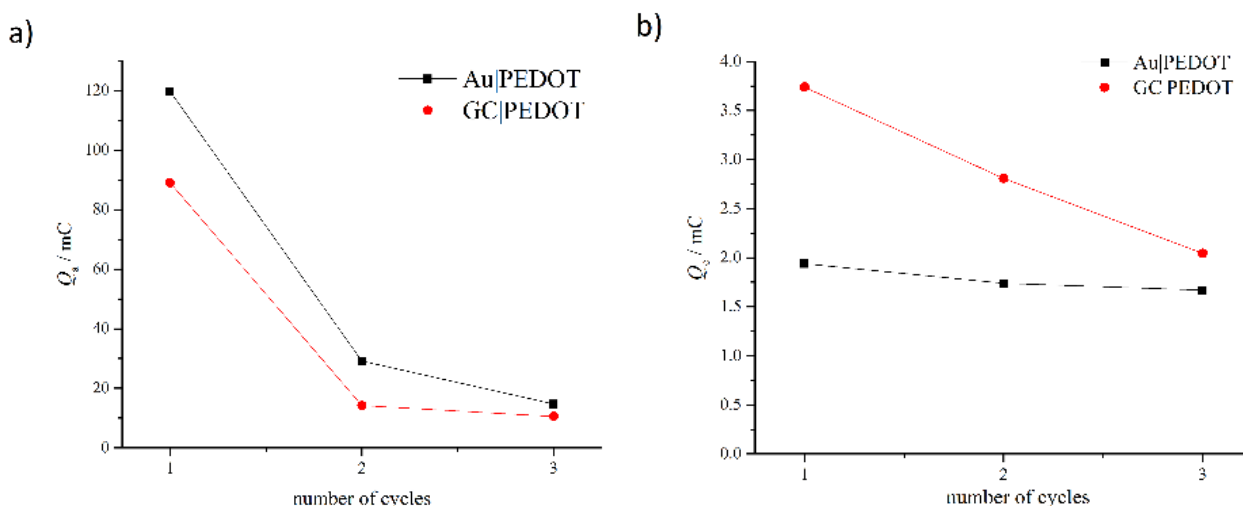
### Cyclic voltammetry

According to Fig.1 cyclic voltammograms in the potential range  $-0.1 - 0.6 \text{ V}$  vs SSCE were recorded before the overoxidation. Both in the cases of Au |PEDOT and GC |PEDOT the cyclic voltammograms change significantly if the positive limit of the electrode potential is extended to  $1.5 \text{ V}$  vs. SCE ("strong" overoxidation, curves 2–4 in Fig. 1a and 1b). It is well known [5-9,12,25] that between  $-0.3$  and  $0.8 \text{ V}$  vs. SSCE the oxidation-reduction process of the PEDOT films is reversible. However, at more positive potentials irreversible degradation of the polymer layer occurs. As it can be seen in Fig. 1a and in Fig. 1b (curve 1), the cyclic voltammograms of PEDOT-modified electrodes show almost pure capacitive behavior in the potential range between  $-0.1 \text{ V}$  and  $+0.6 \text{ V}$ , i.e. if the positive potential limit is kept below  $0.8 \text{ V}$  vs. SSCE. If the polarization potential exceeds this critical value an oxidation peak without corresponding reduction peak appears (see curves 2-4 in Fig. 1a and 1b).

As can be seen from Fig. 2 the charge consumed during the oxidation process is different for the two types of electrodes. According to the results the overoxidation is more intensive in the case of Au|PEDOT electrodes than in the case of the GC|PEDOT system. The different shapes of the 2<sup>nd</sup> and 3<sup>rd</sup> CV-s may indicate that the anodic overoxidation results in a more passive surface in the case of the GC substrate.



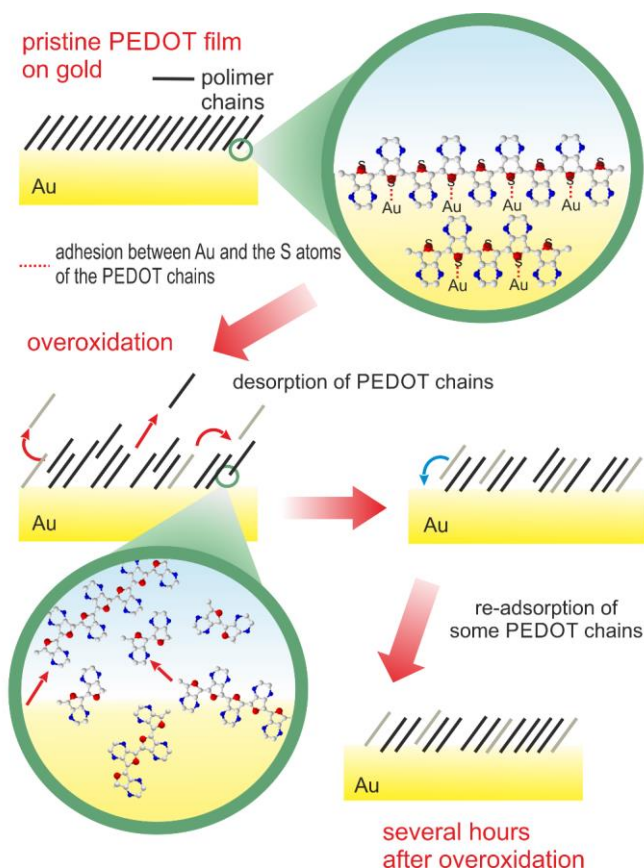
**Fig. 1.** Curve 1: Cyclic voltammograms recorded before overoxidation a) Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> b) GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode in the potential range from -0.1 V to 0.6 V vs. SSCE. Curves 2-4: Successive cyclic voltammograms („overoxidation cycles”) recorded on a) Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> b) GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode in the potential range from -0.1 V to 1.5 V vs. SSCE. The sweep rate was  $\nu = 50$  mV/s in all case



**Fig. 2** Change of the (a) anodic and (b) cathodic charges with the number of overoxidation cycles.

The decrease in the cathodic charges of the (over)oxidized polymer films are considerably smaller.

Fig. 3 shows the schematic representation of the suggested process in connection with the Au|PEDOT system. In the beginning, *i.e.* in the pristine films, the sulfur atoms of the PEDOT chains are connected to the gold surface. As already mentioned in the introduction, during overoxidation at sufficiently positive potentials a significant fraction of the polymer chains become detached from the substrate surface. In parallel with this process the oxidation of the electrode leads to the formation of a gold oxide layer. This atomic oxide layer can block the active surface temporarily and ad interim hinders the adhesion interactions with the polymer chains. This effect may be operative in the present case too. On the other hand, after the overoxidation treatment, at a less positive potentials the readsorption of the polymer chains (polymer chain ends) becomes possible. This means that during overoxidation the “effective” coverage of the substrate by the polymer decreases, and at less positive potentials the coverage may start to increase again. The direction of



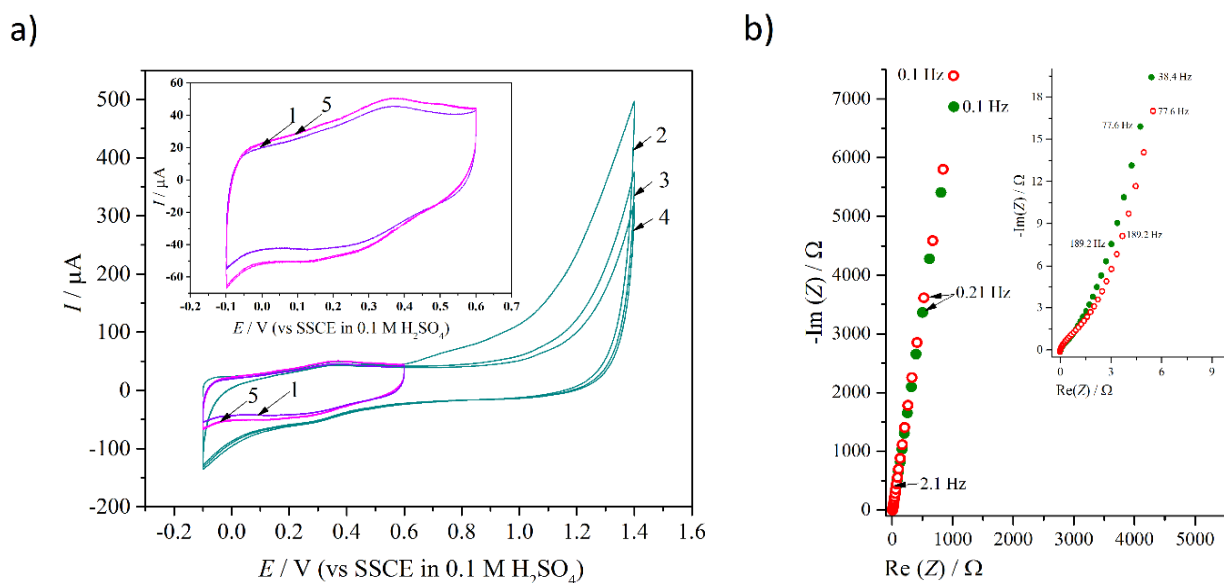
**Fig.3** The suggested mechanism of the desorption and re-adsorption polymer chains during the overoxidation process and after overoxidation (when the potential is held in the "stability region").

[27]. The Jenkins–Kawamura [28] model suggests that glassy carbon consists a long, narrow and imperfect aromatic ribbons. More recent studies have revealed that glassy carbon be made up of graphitic  $sp^2$  ribbons (*i.e.* the structure of glassy carbon consists of long, randomly oriented microfibrils, however, it has also been suggested that glassy carbon comprises a fullerene-type structure [29]) and hybridized carbon atoms with oxygen-containing groups (including oxygen-containing surface functionalities as hydroxyl, phenol, lactone, carbonyl, o-quinone and p-quinone, *etc.*) along the edges of these ribbons where the graphite layer terminates [30,31]. PEDOT that contains ethylenedioxy-bridge and sulfur atom at the end of the polymer chain can easily grow on and strongly adhere to the GC surface. Cyclic voltammograms recorded in 0.1 M sulfuric acid solution reveal that irreversible oxidation of the (bare) glassy carbon surface takes place at electrode potentials more positive than about 0.6 V vs. SSCE (Fig 4a). The negative limit of this potential range roughly coincides with the PEDOT overoxidation onset potential region therefore the surface oxidation may occur in parallel with the (gradual) desorption of the polymer chains.

On the other hand, the smooth surface of the pristine polished GC becomes roughened with electrochemical oxidation [32,33], the surface becomes more and more porous and the effective surface area increases. The electrolyte solution can penetrate into the pores, which leads to the increase of the capacitance.

The contribution of pseudo-capacity to double-layer charging/discharging currents originates mostly from fast faradaic reactions of redox active surface carbon oxygen containing species (*e.g.* hydroquinone/quinone couple), formed at the exposed edge plane sites of carbon [34]. As it can be seen in Fig 4b there is no significant difference between cyclic voltammograms obtained before

the change in  $R_{ct}$  is in agreement with this hypothesis. In the case of glassy carbon substrate, the overoxidation of PEDOT can take place in the same way in the polymer chains, however, no reduction peak can be observed in the cyclic voltammograms of the GC|PEDOT|0.1 M  $H_2SO_4$  electrode (see Fig. 1b). This difference can be explained on the basis of the electrochemical properties of the two substrates. It is well known that the electrochemical behavior of gold in aqueous media has been thoroughly studied, and the voltammetric behavior of gold in acidic media can be explained by monolayer oxide formation/removal and adsorption phenomena. The structure and electrochemical characterization of vitreous or glassy carbon has been the subject of research since it was first produced in the early 1960s. Some early structural models assumed that both complex  $sp^2$ - and  $sp^3$ -bonded carbon atoms were present, but this idea is now discarded and many of the properties suggest a 100 %  $sp^2$  bonding

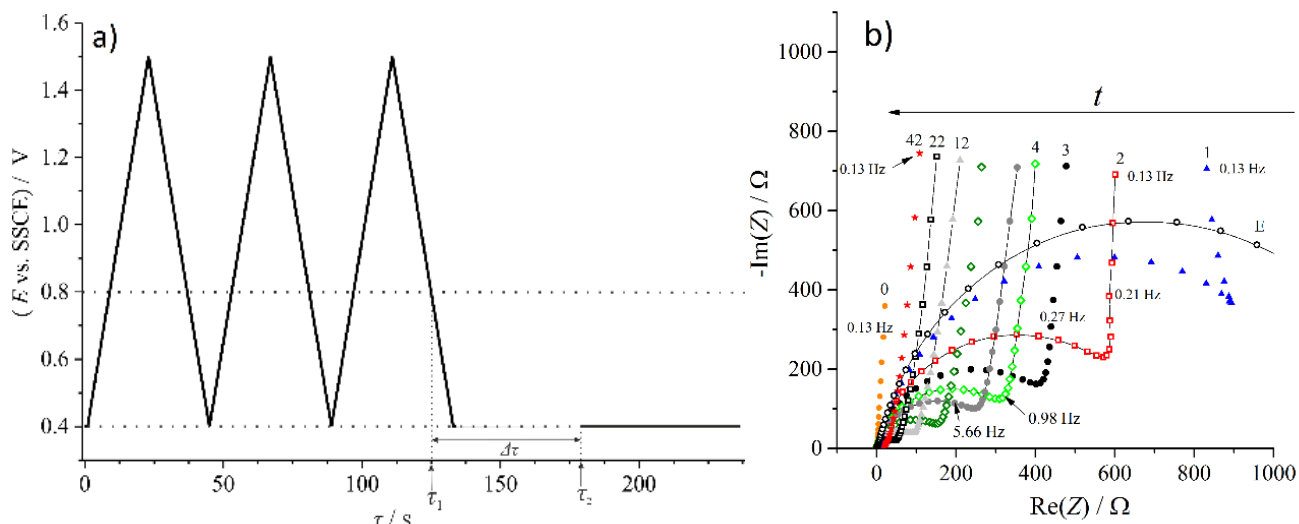


**Fig. 4.** a) Cyclic voltammograms recorded on bare glassy carbon in 0.1 M  $H_2SO_4$  vs SSCE. Curve 1 was recorded before, and curve 5 after the three subsequent oxidation cycles (curves 2-4). The sweep rate was 50 mV/s. b) Complex plane impedance diagram of the bare GC in 0.1 M  $H_2SO_4$  recorded at 0.4 V vs. SSCE before (○) and immediately after (●) three oxidation cycles. The impedance spectra were recorded at 60 discrete frequencies between 0.1 Hz and 100 kHz (amplitude: 5 mV rms).

and after the oxidative treatment. (It should also be noted here that the same statement is true for the charge transfer resistances determined by impedance spectroscopy before and after the oxidation.)

#### Impedance measurements

After overoxidation, subsequent impedance measurements were performed on the GC|PEDOT|0.1 M  $H_2SO_4$  electrode at the electrode potential  $E = 0.4$  V vs. SSCE over a frequency range from 100 mHz to 100 kHz as described in the experimental section (starting at  $\tau_2$  in Fig. 5a). The Fig. 5b and Fig. 5c data points were measured using AC signal amplitude of 5 mV at 60 discrete frequencies in the frequency region investigated during each scan. The time moment corresponding to  $\tau_2$  was taken as the starting time of the impedance measurements ("timestamp":  $t = 0$  s), and 63 successive impedance spectra were recorded. It is (somewhat arbitrarily) assumed that the overoxidation process stopped completely at  $\tau_1$ , i.e. at  $t = -50.0$  s and  $\Delta\tau = 50.0$  s (see Fig. 5a). The recording time of a "single" spectrum was about 346 s. In Fig. 5b and in Fig. 4b the results are presented in the complex plane (where  $Re(Z)$  is the real part and  $Im(Z)$  is the imaginary part of the complex impedance, respectively). For the sake of comparison sets of impedance data measured for an Au|PEDOT|0.1 M  $H_2SO_4$  electrode after overoxidation under similar conditions are presented in Fig. 5c. As we can see from Figs. 5b and 5c, the pristine PEDOT films show very small charge transfer resistances and close to ideal capacitive characteristics. On the other hand, the diameters of the capacitive arcs at high frequencies (and hence the charge transfer resistances) increase significantly during overoxidation both in the case of GC|PEDOT|0.1 M  $H_2SO_4$  and Au|PEDOT|0.1 M  $H_2SO_4$  electrodes. The analysis of the impedances obtained for the GC|PEDOT|0.1 M  $H_2SO_4$  electrode were carried out in the same way described in refs [16,17,21, see also Supplementary Material]. The calculation of the "instantaneous" impedance diagrams was carried out using the real and imaginary parts of the impedances measured at identical frequencies („isofrequential components"). The charge transfer resistances at  $t = 0$  s has been obtained by extrapolation of the iso-frequency dependencies to this time instant.



**Fig. 5**

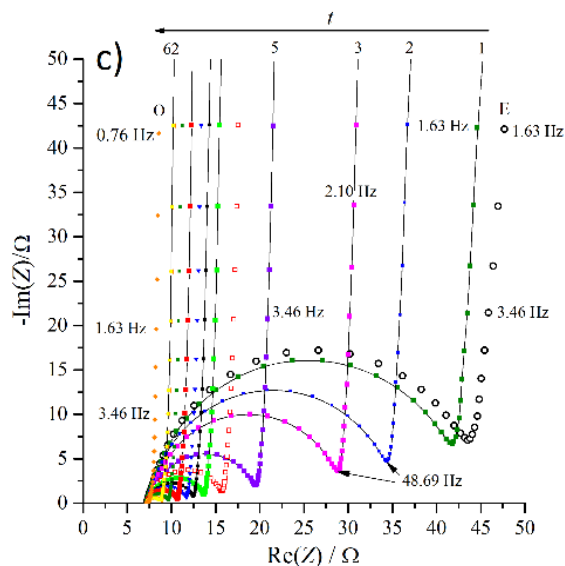
a) The potential program applied to the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode. The impedance measurements started at τ<sub>2</sub>. τ<sub>1</sub> is the estimated end of the overoxidation process. Δτ = 50 s.

b) Successive (measured) impedance diagrams recorded on the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> and

c) Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> on the electrode at E = 0.4 V vs. SSCE. The solid lines are to guide the eye only: not curve fits.

The spectra signed by E in Figs. 5 b and 5 c are calculated spectra corresponding to the presumed ends of the overoxidation processes, b) t = -50 s, c) t = -53 s, respectively.

(The spectra E were calculated using the method of Stoynov [16,17].)

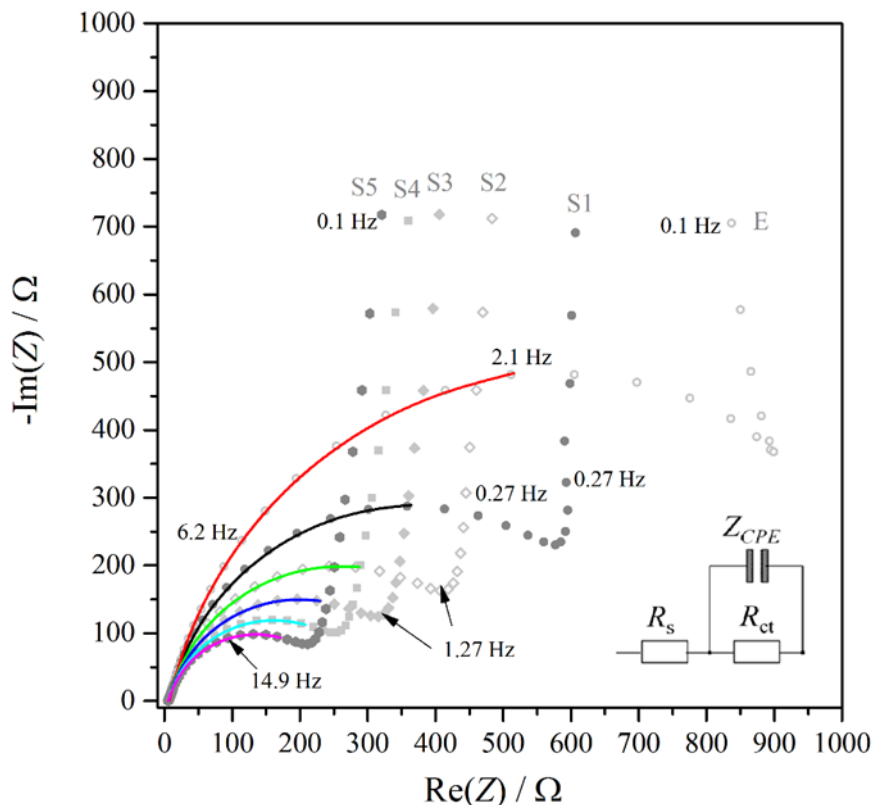


The values of the charge transfer resistances at t = 0 s and at the other time instants were estimated by fitting the high-frequency part of the “instantaneous” spectra with the impedance function (Eq. 1) corresponding to the equivalent-circuit analog shown in the inset of Fig. 6.

$$Z(\omega) = R_u + \frac{1}{B(i\omega)^\alpha + R_{ct}^{-1}} \tag{1}$$

In Eq. 1 R<sub>ct</sub> is the charge transfer resistance and R<sub>u</sub> is the uncompensated ohmic resistance (which is mainly the resistance of the electrolyte solution between the working and the reference electrode). This simple equivalent circuit is based on the model proposed e.g. in [13,35], wherein the high frequency (“double layer”) capacitance (C<sub>d</sub>) at the substrate/polymer interface has been replaced by a constant-phase element (CPE), which more accurately imitates the nonideal (distributed) behavior of the double layer (Z<sub>CPE</sub> = 1/B(iω)<sup>-α</sup>, where i is the imaginary unit, B and α are the CPE parameters, and ω is the angular frequency, respectively).

The estimated values of the parameters (obtained by complex non-linear least squares (CNLS) fitting program based on the Gauss – Newton – Levenberg - Marquardt method with inverse magnitude weighting) are shown in Table 1. The spectra calculated (simulated) by using the “best-fit” parameters are shown Fig. 6.



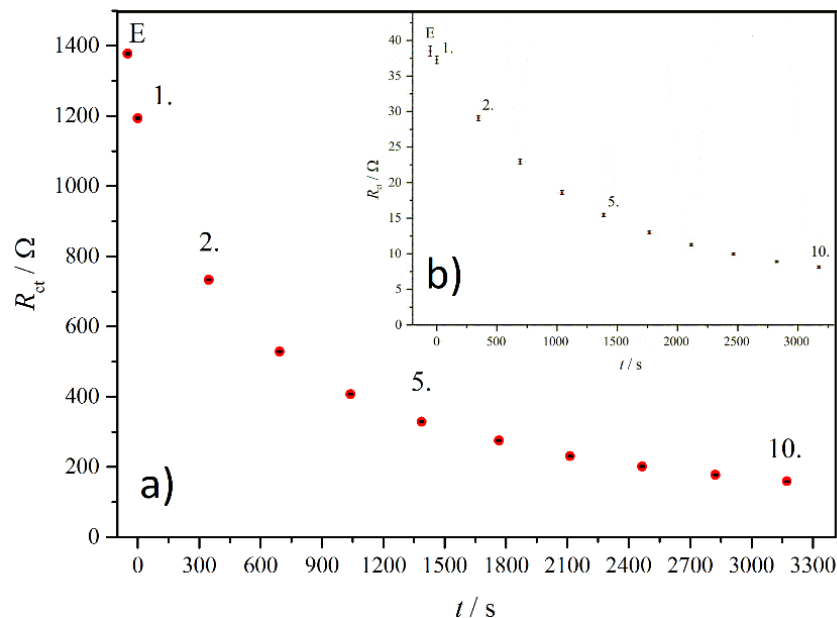
**Fig. 6.** Corrected complex plane impedance diagrams (“instantaneous impedances”) of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> system calculated for t = -50.0 s (E), t = 0 s (S1), t = 346.6 s (S2), t = 692.5 s (S3), t = 1039.4 s (S4), and t = 1386.7 s (S5), respectively. The solid curves were calculated (simulated) by using the “best-fit” parameters given in Table 1.

**Table 1.** Results of CNLS fitting of impedance data of GC|PEDOT system: the estimated values of the parameters. R<sub>u</sub> is the uncompensated ohmic resistance (resistance of the solution), R<sub>ct</sub> is the charge transfer resistance, B and α are the parameters of the CPE, ΔR<sub>u</sub>, ΔR<sub>ct</sub>, ΔB and Δα are the corresponding 95 % confidence intervals.

data set	t/s	R <sub>u</sub> /Ω	ΔR <sub>u</sub> /Ω	R <sub>ct</sub> /Ω	ΔR <sub>ct</sub> /Ω	B/Ω <sup>-1</sup> s <sup>α</sup>	ΔB/Ω <sup>-1</sup> s <sup>α</sup>	α	Δα
E	-50.0	7.8	±1.5	1391.4	±1.3	2.91·10 <sup>-5</sup>	±0.12·10 <sup>-6</sup>	0.878	±0.045
S1	0	7.22	± 0.42	1222.4	±6.7	2.55·10 <sup>-5</sup>	±0.41·10 <sup>-6</sup>	0.863	±0.019
S2	346.6	6.15	± 0.57	728.2	±6.7	2.11·10 <sup>-5</sup>	±0.64·10 <sup>-6</sup>	0.855	±0.037
S3	692.5	5.96	± 0.58	507.2	±5.3	1.82·10 <sup>-5</sup>	±0.75·10 <sup>-6</sup>	0.849	±0.047
S4	1039.4	5.99	± 0.51	384.9	±4.3	1.93·10 <sup>-5</sup>	±0.76·10 <sup>-6</sup>	0.845	±0.051
S5	1386.7	5.69	±0.54	258.6	±3.6	1.76·10 <sup>-5</sup>	±0.95·10 <sup>-6</sup>	0.831	±0.070
S6	1765.0	5.83	±0.42	219.9	±2.9	1.76·10 <sup>-5</sup>	±0.87·10 <sup>-6</sup>	0.829	±0.066
S7	2113.5	5.93	±0.33	190.7	±2.4	1.76·10 <sup>-5</sup>	±0.74·10 <sup>-6</sup>	0.828	±0.059
S8	2464.7	5.39	±0.56	172.6	±3.1	1.57·10 <sup>-5</sup>	±0.16·10 <sup>-6</sup>	0.807	±0.097
S9	2823.9	5.56	±0.42	153.7	±2.5	1.59·10 <sup>-5</sup>	±0.99·10 <sup>-6</sup>	0.809	±0.084
S10	3173.1	5.88	±0.30	138.2	±1.9	1.62·10 <sup>-5</sup>	±0.82·10 <sup>-6</sup>	0.810	±0.071
S11	3522.3	5.73	±0.20	125.6	±1.5	1.63·10 <sup>-5</sup>	±0.61·10 <sup>-6</sup>	0.811	±0.054
S12	3872.1	5.88	±0.14	114.9	±1.1	1.65·10 <sup>-5</sup>	±0.47·10 <sup>-6</sup>	0.812	±0.043

Some of the charge transfer resistance values (the R<sub>ct</sub> vs. t plot) determined for the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> by using the “instantaneous” impedances are shown in Fig. 7a. It can be seen from Table 1 (and from Fig. 7a), that the highest value of R<sub>ct</sub> is about (1391.4±1.3) Ω. This value corresponds to the time instant just after overoxidation of the film. Similarly to the Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode (see Fig. 7b), starting from this value, R<sub>ct</sub> decreases continuously with experiment time to a value somewhat higher than the charge transfer resistance of the

pristine electrode. It can clearly be concluded that the charge transfer resistances measured for the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode after overoxidation are significantly higher than those measured for the Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode, however, the relative rate of the relaxation process is apparently higher (the “half-life” of  $R_{ct}$  for GC|PEDOT is about  $t_{1/2,GC} \approx 400$  s, while for Au|PEDOT  $t_{1/2,Au} \approx 860$  s).



**Fig. 7** Time evolution of the charge transfer resistance during the experiment in the case of GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode (a) and Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode (b, see insert).

$R_{ct}$  values were determined using the calculated impedance spectra. In both cases:

The  $R_{ct}$  value designated by E corresponds to the time instant of the presumed end of the overoxidation processes:  $t = -50.0$  s (GC|PEDOT) and  $t = -53.0$  s (Au|PEDOT).

As it can be seen from the results, the direction, dynamics and nature of the temporal change in  $R_{ct}$  are consistent with the hypothesis outlined in [17] and in the introduction to this study. We can assume that during overoxidation a significant fraction of the polymer chains become detached from the substrate surface. The partial delamination of the polymer layer leads to the exposure of the underlying substrate material to the electrolyte solution. In areas where the substrate is in direct contact with the electrolyte solution, practically no charge transfer across the interface occurs (i.e. the local charge transfer resistance is close to infinite). Nevertheless, the polymer film still present on the substrate after overoxidation remains electroactive. At the electrode potential of  $E = 0.4$  V vs. SSCE the readsorption of the polymer chains (polymer chain ends) becomes possible, i.e. the number of the polymer chains directly contacted with (adsorbed on) the substrate surface is increasing with the passing time. In other words, during overoxidation the “effective” coverage of the substrate by the polymer decreases, and at less positive potentials the coverage starts to increase again, leading to the decrease of the charge transfer resistance.

The reasoning above leads us to the conclusion that in the case of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode the number of irreversibly oxidized (desorbed or deactivated) polymer chains (or polymer chain ends) per unit area is greater than in the case of the Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode. However, this fact does not explain the apparent difference in the relative rates of decay of  $R_{ct}$  in the two systems.

A plausible mechanistic explanation of this behavior is based on the differences in the chemical states of the substrate surfaces. In the case of Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> after the last overoxidation CV (at  $E = 0.4$  V vs. SSCE, the electrode potential was kept at this value during the impedance spec-

troscopy measurements, as well) the whole of the oxide is completely reduced, as is evident from the appearance of the reduction peak in Fig. 1a (and is well known from the electrochemistry of gold [36,37]). On the other hand, it is quite clear from Fig. 4 that immediately after an oxidation cycle up to a positive potential limit of  $E = 1.4$  V vs. SSCE, the electrochemical reduction of the surface of glassy carbon at 0.4 V vs. SSCE is incomplete. This means, that in the case of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode two processes may occur simultaneously during the impedance measurements: (a) reduction of the oxidized surface of the GC substrate, including the reduction of oxygen-containing surface functionalities and (b) readsorption of the polymer chains (polymer chain ends) on the surface. The extent of the first process will clearly influence the rate at which the other can proceed, manifesting in the increase in the rate of decay of the charge transfer resistance.

Nevertheless, it should be noted here, that other processes may also occur during the overoxidation process, *i.e.* chemical changes in the polymer chains that affect the extent of charging and the conjugation of the PEDOT chains and slow conformational relaxation phenomena of the polymer structure that may not be necessarily influenced by the substrate.

## Conclusions

The 4-dimensional analysis method, originally proposed by Stoynov, was successfully applied for the determination of the charge transfer resistance of a glassy carbon|PEDOT|0.1 mol·dm<sup>-3</sup> sulfuric acid (aq.) electrode corresponding to different time instants after overoxidation. During the impedance measurements carried out almost immediately after the overoxidation procedure the electrode potential was held in the “stability region” of the system (at  $E = 0.4$  V vs. SSCE in the present case). The post-experimental mathematical/analytical procedure could be used also for the estimation of the charge transfer resistance corresponding to the time instant just after overoxidation of the PEDOT film. The decreasing capacitance and the increasing 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. During the impedance measurements the charge transfer resistance decreased continuously with experiment time, the “starting” (calculated)  $R_{ct}$  value was approximately 1391  $\Omega\cdot\text{cm}^2$ . After 50 seconds this value fell to about 1222  $\Omega\cdot\text{cm}^2$ , *i.e.* it decreased by ~12 % in the first minute after the overoxidation procedure.

By comparing the properties of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> and the Au|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrodes a possible mechanistic explanation for the observed behavior has been proposed. This is based on the assumption that in the case of the GC|PEDOT|0.1 M H<sub>2</sub>SO<sub>4</sub> electrode two processes may occur simultaneously during the impedance measurements: (a) reduction of the oxidized surface of the GC substrate (including the reduction of oxygen-containing surface functionalities), and (b) readsorption of the polymer chains (polymer chain ends) on the surface.

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