

Electrochemical Properties of Overoxidized Poly-3,4-Ethylenedioxythiophene

M. A. Kamensky^a, S. N. Eliseeva^{a, *}, G. Láng^b, M. Ujvári^b, and V. V. Kondratiev^a

^aSt. Petersburg State University, Institute of Chemistry, St. Petersburg, 199034 Russia

^bEötvös Loránd University, Institute of Chemistry, Budapest, 1117 Hungary

*e-mail: svetlana.eliseeva@spbu.ru

Received July 10, 2017; in final form, April 10, 2018

Abstract—The properties of poly(3,4-ethylenedioxythiophene) (PEDOT) films were studied electrochemically at high positive potentials (from -0.3 to 1.5 V relative to the Ag/AgCl electrode). A cyclic voltammetry (CV) study revealed the range of potentials (up to 1.3 – 1.5 V) where the cycling leads to significant changes in the electrochemical, structural, and morphological properties of the polymer film due to overoxidation. When the upper cycling potential E_{up} exceeded 1.4 V, the anodic current significantly increased during the first cycle and then decreased, which suggests a loss of the electroactivity of the polymer and degradation of its properties. In the high-frequency region of the impedance spectra of the PEDOT films, a semicircle appears after overoxidation, which indicates a notable increase of the charge transfer resistance in the system, in contrast to the films subjected to potentiodynamic processing in a limited range of potentials from -0.3 to 1.3 V. The effect of overoxidation on the polymer morphology was studied by scanning electron microscopy. The chemical state of elements in the structure of the polymer film was determined by X-ray photoelectron spectroscopy. The obtained data indicate that —S=O groups formed at the thiophene sulfur in the polymer.

Keywords: conducting polymers, poly-3,4-ethylenedioxythiophene, overoxidation, cyclic voltammetry, impedance spectroscopy, electrochemical properties, degradation

DOI: 10.1134/S1023193518130219

INTRODUCTION

The conductive organic polymers with conjugated bonds and composite materials based on them remain the subject of active fundamental and applied electrochemical research [1–8]. One of the problems discussed in studies on the electrochemical properties of conducting organic polymer films is the degradation of film properties, i.e., the gradual reduction of their electroactivity under certain conditions (for example, polymer synthesis conditions, varying the nature of electrolyte, the use of high positive potentials and definite pH values of aqueous electrolytes, etc.). The determination of the conditions of stable electrochemical activity of polymers is extremely important for their practical use in various electrochemical devices, in particular, for determining the range of potentials in which the electrochemical behavior of the polymer is stable.

Poly-3,4-ethylenedioxythiophene (PEDOT), which is a representative of conducting organic polymers with conjugated bonds, has attracted the attention of researchers because of its high chemical stability and electroactivity in organic and aqueous solutions of electrolytes [9]. In recent years, various

composite functional materials were obtained based on PEDOT, which have found application in energy storage devices (batteries and supercapacitors), in electrocatalysis and electrical analysis, solar cells, and many other applications [10–28]. The wide use of PEDOT in various electrochemical devices necessitates studies on the ranges of potentials for its stable electroactive behavior to reveal the factors that determine the degradation of its electrochemical properties under definite conditions. These studies will make it possible to further develop the materials and select conditions for their optimum use.

The electrochemical properties of the PEDOT polymer in neutral and acidic aqueous electrolytes are usually quite stable in the potential range from -0.3 to $+0.8$ V relative to the silver chloride reference electrode (SCE). In this range of potentials, reversible p doping of PEDOT occurs with the formation of positively charged fragments in the polymer structure with appreciable charge delocalization within a fragment of the polymer chain (polarons and bipolarons).

When a certain critical value (denoted as E_{up} for simplicity) of the positive potential of the electrode is exceeded, so-called “overoxidation” of the polymer

occurs, leading to a significant deterioration of its conductivity and electrochemical activity, i.e., to the electrochemical degradation of the properties of the material in general. Although many researchers encountered the problem of overoxidation of polymers, in particular, of PEDOT [29–32], the number of papers that reported on systematic studies of these processes for conducting polymers is very limited.

Previously, G. Láng and coauthors [30, 31, 33, 34] studied PEDOT films synthesized under galvanostatic conditions from aqueous solutions (7200 s, current 0.2 A/cm²) on gold and platinum substrates. The electrochemical properties of PEDOT and their degradation in the range of overoxidation potentials were studied in aqueous 0.1 M H₂SO₄ solutions. It was shown that overoxidation in 0.1 M H₂SO₄ starts at potentials above 0.8 V relative to the saturated calomel electrode, but the effect of degradation of the properties of the PEDOT film is small up to the potential of 1.2 V. When the electrode potential reaches 1.5 V, the electrochemical and morphological properties of the films change noticeably. As a result of overoxidation, the porous polymer film partially cracks, regions of the crystallinity appear in the structure, and the redox currents markedly decrease, which was attributed in [33] to the possible partial or complete peeling of the polymer surface from the substrate. The impedance spectra of the overoxidized film show that the charge transfer resistance considerably increased.

In general, it is expected that the critical value of the positive potential E_{up} during oxidation, which causes an appreciable degradation of the electrochemical properties of the polymer, may depend on the synthesis conditions of the polymer film, the nature and concentration of the electrolyte under study, the nature of the substrate, and other factors. Therefore, it is important to perform a comparative study of the stable electrochemical behavior of PEDOT on different substrates.

We performed an electrochemical study of the properties of poly-3,4-ethylenedioxythiophene films synthesized on glassy carbon (GC) from acetonitrile solutions. Glassy carbon is a representative of carbon materials that are widely used to create energy storage devices. In addition to the practical importance of these studies, it was of interest to compare the film degradation on different substrates, taking into account the results of previous studies on platinum and gold [31]. The studies were performed by cyclic voltammetry (CV) in the range of high positive potentials (from –0.3 to 1.5 V) and electrochemical impedance spectroscopy. The literature analysis did not reveal any data on overoxidation (electrochemical degradation) of PEDOT films synthesized from acetonitrile monomer solutions on glassy carbon substrates in a dilute (0.1 M) sulfuric acid solution. The choice of

electrolyte for the study was dictated by the use of PEDOT in composite materials with transition metal oxides for electrochemical capacitors [28, 35] and electrocatalysts with inclusions of noble metal nanoparticles in the polymer matrix [27, 36].

Along with the electrochemical studies, the film morphology at different potentials was monitored by scanning electron microscopy (SEM). The chemical state of the main elements of the polymer film structure was identified by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

The PEDOT films were synthesized by electrochemical deposition on a glassy carbon electrode ($S = 0.07 \text{ cm}^2$) in a galvanostatic mode from an acetonitrile solution of 0.05 M 3,4-ethylenedioxythiophene (EDOT) and 0.1 M LiClO₄. The synthesis was performed for 200 s at a current density of $i = 1 \text{ mA/cm}^2$. After the synthesis, the films were washed with deionized water. The resulting film was subjected to potentiodynamic processing in a 0.1 M H₂SO₄ aqueous solution in different potential ranges from –0.3 to +0.8 V with the upper limit of the potential increased to +1.5 V at a scan rate of 50 mV/s. After the recording of three current-voltage curves for each potential range, the electrochemical impedance spectra of the PEDOT film were recorded at potentials in the range of stable properties of the film (–0.3 to 0.8 V). All the spectra presented below were recorded at a potential of $E = -0.1 \text{ V}$. The recording conditions of the impedance spectra: frequency range 100 kHz–0.1 Hz, storage time 300 s, amplitude 5 mV.

The solutions for the synthesis were prepared from 3,4-ethylenedioxythiophene (Aldrich), anhydrous lithium perchlorate (reagent grade) calcinated in a desiccator to constant weight, and acetonitrile ((extra-pure), Cryochrome, 0.008% water). Sulfuric acid (reagent grade), density 1.84 g/mL and deionized water Millipore Direct-Q UV (Millipore, United States) were used in the electrochemical studies.

The electrochemical studies were performed in 0.1 M H₂SO₄ in a three-electrode cell. The reference electrode was a silver chloride electrode in a saturated sodium chloride solution. All the potentials are given relative to SCE, whose potential is 0.222 V relative to the standard hydrogen electrode. The measurements were performed at room temperature ($22 \pm 2^\circ\text{C}$).

For the electrochemical synthesis of the PEDOT film on electrodes and electrochemical measurements, an Autolab 30 potentiostat-galvanostat (Eco-Chemi, The Netherlands) was used. The films were studied by scanning electron microscopy using a Zeiss SUPRA 40VP scanning electron microscope (Carl Zeiss, Germany). The images of the surface morphol-

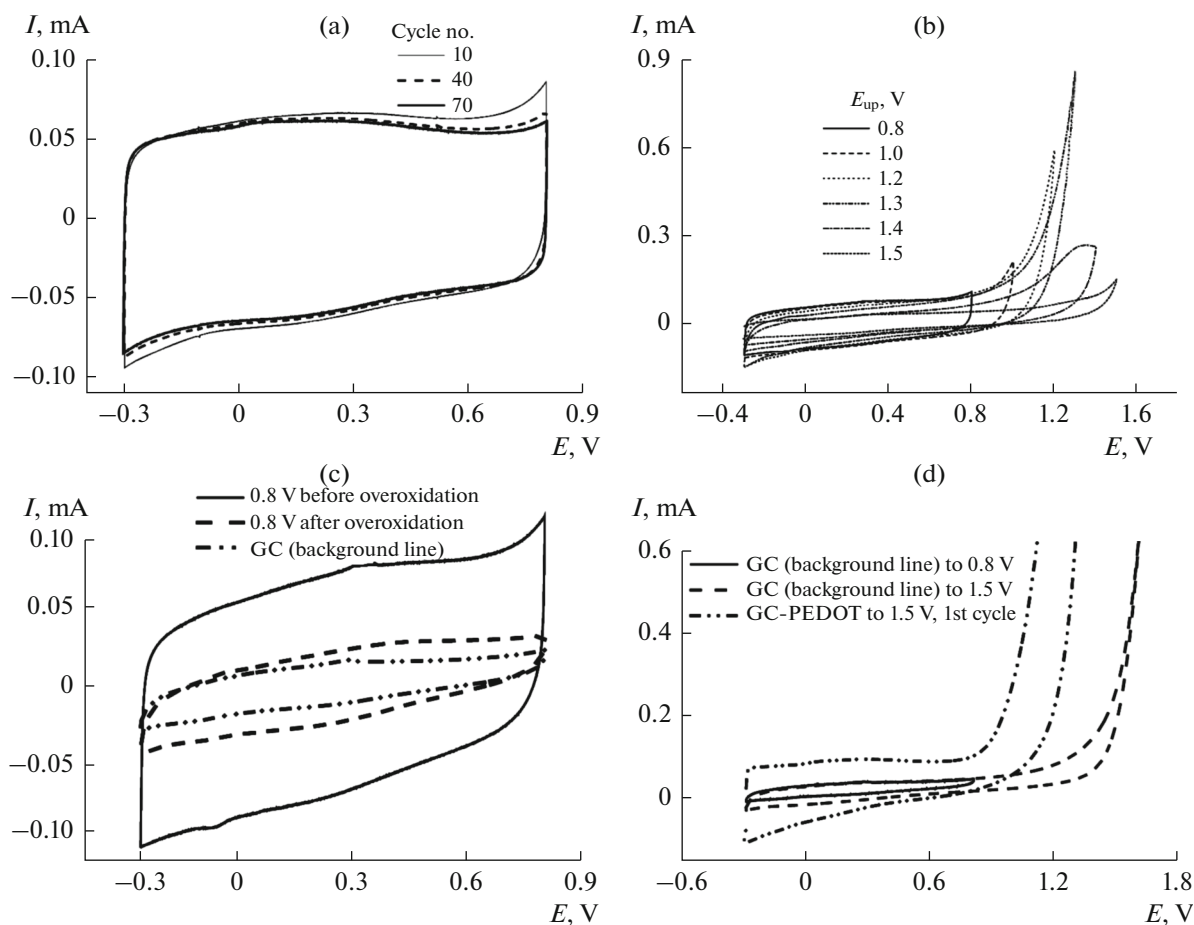


Fig. 1. Cyclic voltammograms of PEDOT in 0.1 M H_2SO_4 : (a) to $E_{\text{up}} = 0.8$ V depending on the cycle number; (b) depending on the upper limit of cycling (E_{up}), third cycle, for one film in sequence; (c) before and after overoxidation in the range from -0.3 to $+0.8$ V, third cycle; and (d) to 1.5 V, first cycle in comparison with background currents of GC when cycling to 0.8 and 1.5 V.

ogy of the PEDOT films were obtained before and after cycling in different potential ranges.

RESULTS AND DISCUSSION

Figure 1a shows the cyclic voltammograms of a PEDOT film in 0.1 M H_2SO_4 depending on the cycle number in the potential range from -0.3 to $+0.8$ V at a scan rate of 50 mV/s. The CV curve of PEDOT shows a typical pseudo-capacitive response of quasi-rectangular form. The film exhibited stable behavior during repeated cycling in the potential range from -0.3 to 0.8 V.

Figure 1b presents the CV curves of PEDOT films, which show an increase in the upper limit of the applied potential (E_{up}). The anodic currents increase with the positive limit of potential scan to 1.1 V in the first cycles of CV. The decrease in the total electrochemical activity of the film from cycle to cycle evaluated as a decrease in the charge under the anode

branch of the curve occurs slowly in this range of potentials. An increase in the anodic limit of potential scan to $+1.3$ V and higher leads to a more dramatic decrease in the electrochemical activity of the film, and the electrochemical degradation progresses. The rapid decrease in the anodic currents at the highest positive potentials E_{up} and the absence of the corresponding cathodic peak suggests that irreversible film oxidation takes place.

Figure 1c shows the CV curves of PEDOT recorded before and after overoxidation in the range of potentials from -0.3 to $+0.8$ V. The shape of the CV curve of PEDOT after overoxidation resembles that of the original curve. According to the values of currents, however, it is close to the shape of the background currents of glassy carbon, suggesting a decrease in the currents on the CV of PEDOT after its overoxidation. This suggests a decrease in the total number of electroactive fragments in the film. Figure 1d presents the background CV curves for the GC electrode and the

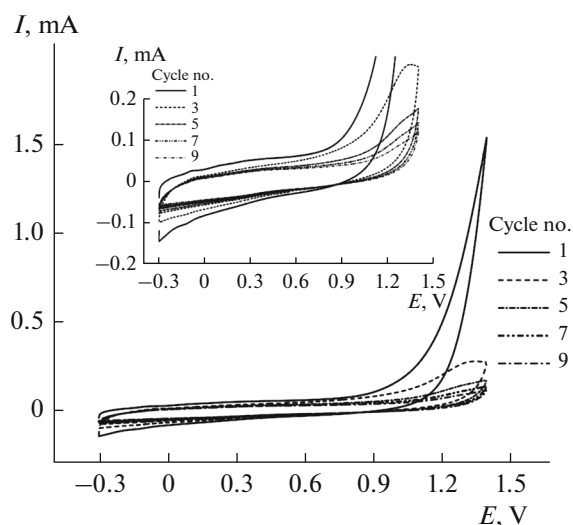


Fig. 2. CV of the PEDOT film in 0.1 M H₂SO₄ at the upper bound of potential of 1.4 V depending on the cycle number. Insert: current-voltage curves on an enlarged scale.

CV curves of the PEDOT film at the positive potential limit increased to $E_{up} = 1.5$ V (first cycle). The anode current drastically increases during the oxidation of the polymer at potentials above 1.0 V, while on the background curve of GC a noticeable rise in the anode current occurs around $E = 1.5$ V. This indicates that the anode currents in the potential range 1–1.5 V are mainly associated with the oxidation involving the polymer film itself, but not with the oxidation of water and oxygen release on the electrode.

According to Fig. 2, which shows the CV curve of PEDOT in the range of potentials from -0.3 to $+1.4$ V depending on the cycle number, the anode currents increase significantly at a potential of 1.2 V during the first cycle and markedly decrease within the whole range of cycling during the third and subsequent cycles (insert, Fig. 2). The currents gradually decrease in all the ranges of potentials under study during repeated cycling.

Figure 3 shows the ratio of the total charge under the CV curve to the charge of the first cycle depending on the cycle number during the constant film cycling in the potential range (for different positive limits of the potential E_{up}). Evaluation of the capacity of the polymer film depending on the cycling range of the electrode potential showed that after 70 cycles, the decrease in capacity (in %) was 2 (cycling limit 0.6 V), 10 (0.8 V), 62 (1.1 V), 85 (1.2 and 1.3 V), and 93% after 1.4 and 1.5 V. This is indirect indication that raising the upper limit of E_{up} to 1.2–1.5 V is not reasonable for practical purposes.

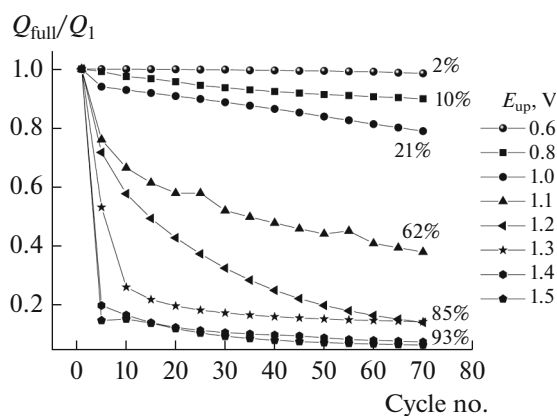


Fig. 3. Stability of PEDOT during 70 cycles of CV depending on the potential range.

After the recording of the CV curves in each potential range, the electrochemical impedance spectra of PEDOT were obtained at a potential of -0.1 V. Figures 4a and 4b show the electrochemical impedance spectra of PEDOT at $E = -0.1$ V. After the cycling of the potential of the modified electrode to E_{up} values shown in Fig. 4 (to 1.2 V) in the Nyquist coordinates $-Z''$ (Z'), the impedance spectra were similar. The spectra are dominated by the vertical curve, which suggests the pseudocapacitive response of the film. The observed form of the impedance response suggests that the electron and ion transfer at the interface between the film and solution and substrate occurs rapidly, under reversible conditions.

After the CV recording to $E_{up} = 1.4$ V, noticeable changes are observed in the impedance spectra of PEDOT. In the high-frequency region (up to 9.102 Hz), some part of a semicircle appears, which indicates that the resistance to charge transfer at one of the film/solution or electrode/film interfaces in the electrode/film/electrolyte system increased. The assignment of the observed semicircle to a particular interface for polythiophene films today provokes debate and diverse interpretations. Based on their studies of the effect of the concentration and nature of electrolyte, the authors of [37, 38] concluded that the charge transfer at the film/solution interface is slow. In [31, 33, 34], the substrate effect on the semicircle diameter was shown, and the corresponding resistance was attributed to the film/electrode interface. The latter assignment seems reasonable in view of the fact that the initial film overoxidation should occur exactly at this interface. The diameter of the semicircle on the impedance spectrum recorded after removing the CV of PEDOT increases for the film subjected to potentiodynamic processing at high positive potentials (up to 1.5 V).

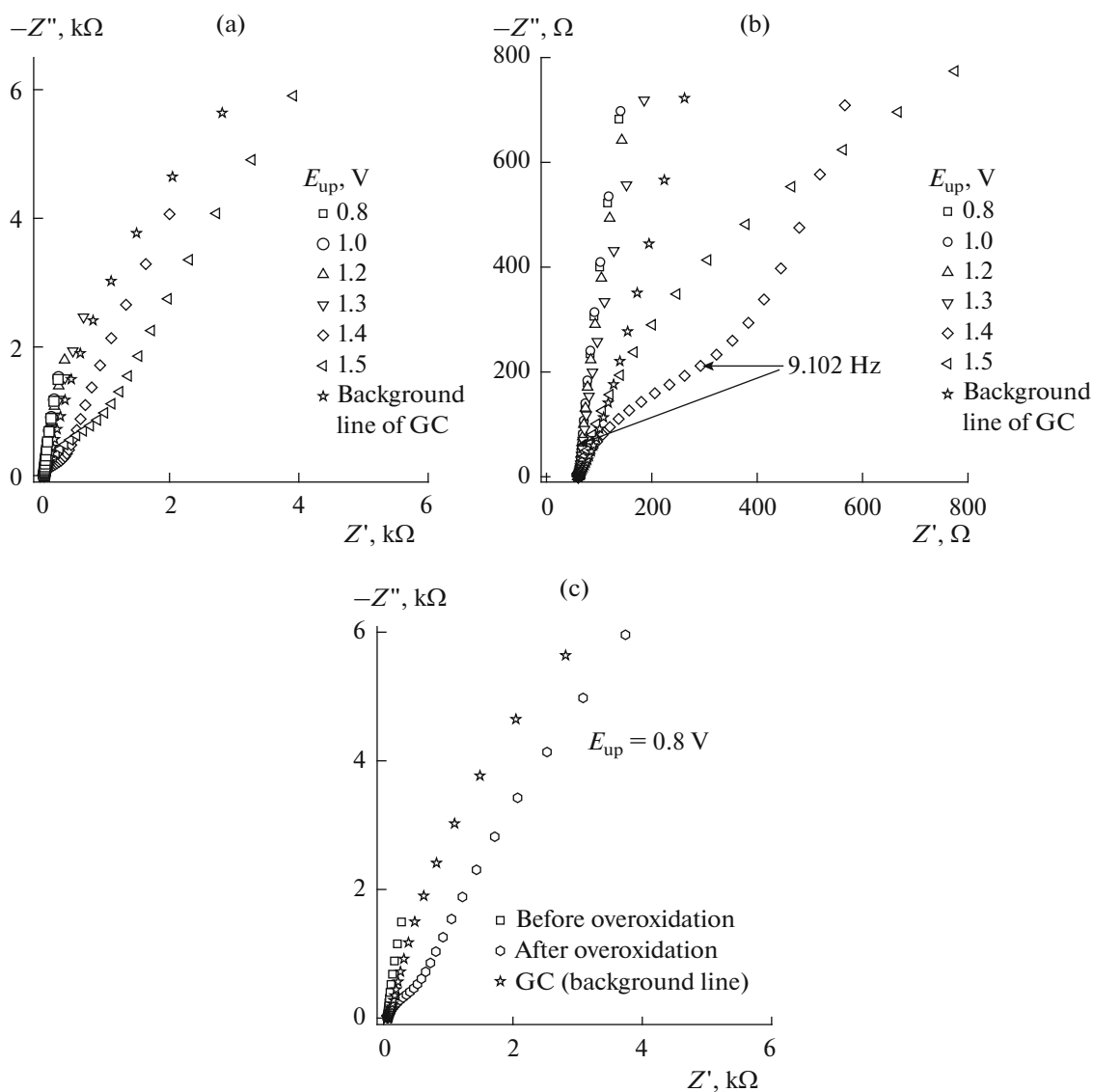


Fig. 4. (a) Electrochemical impedance spectra of a PEDOT film in 0.1 M H_2SO_4 at a potential of -0.1 V after the recording of three CV cycles to the different E_{up} values indicated in the legend, (b) increased high-frequency part of the spectra, and (c) impedance spectra of PEDOT after cycling to 0.8 V (before and after overoxidation) and impedance spectrum of GC without a PEDOT film.

Figure 4c shows the impedance spectra of PEDOT recorded after the cycling to 0.8 V (before and after overoxidation). Regarding the latter circumstance, note that after the CV recording for PEDOT to different E_{up} values, the recording was again performed in the range from -0.3 to $+0.8$ V and after that the impedance spectra of the PEDOT film were recorded after overoxidation without prolonged storage. The spectra do not coincide in shape and resistance. This indicates that the electrochemical properties of PEDOT changed after overoxidation, which is also consistent with the CV data (Fig. 1c).

Figure 5 shows the dependences of $-Z''(Z')$ recorded after CV to $E_{up} = 1.4$ V. After the first cycle,

the impedance spectrum coincides in its shape with the spectra recorded at lower potentials, and after a few consecutive cycles, there were noticeable changes in the spectrum shape and resistance values (Fig. 5b). This agrees with the previously observed changes in the spectra of the PEDOT film synthesized from aqueous solutions for 7200 s on a gold electrode [31].

Thus, when cycling the potential of a PEDOT film in the range of high potentials (1.2–1.5 V), the electrochemical properties of the film change, as can be seen from the drop in the currents on the current-voltage curves and the appearance of a semicircle in the electrochemical impedance spectra.

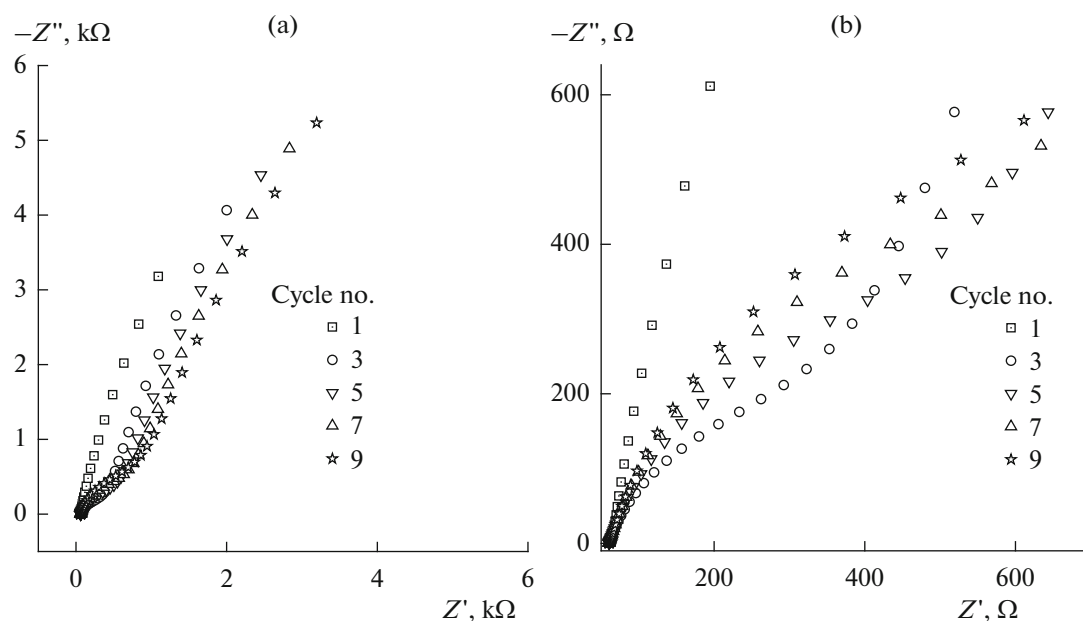


Fig. 5. (a) Electrochemical impedance spectra of a PEDOT film in 0.1 M H_2SO_4 at a potential of -0.1 V recorded after the cycling the electrode potential from -0.3 to 1.4 V ($v = 50$ mV s) depending on the cycle number and (b) part of the spectra in the high-frequency region.

The SEM images of the PEDOT films were obtained. Figure 6 clearly shows the porous structure of the PEDOT polymer film before CV recording in the range of high positive potentials. It was found that the same typical morphology of the polymer surface persists after the recording of several CV curves in the potential range from -0.3 to $+0.8$ V. After the cycling to the upper limit (1.4 and 1.5 V), appreciable changes in the structure of PEDOT were observed (Fig. 6). After the cycling to 1.4 V (Fig. 6b) and 1.5 V (Fig. 6c), the degree of porosity of the structure decreased. After the cycling to 1.5 V (Fig. 6c), the pores disappeared completely, some crystallite-like formations appeared, and the polymer did not cover the entire surface any more. Visualization also showed that the film on the electrode surface diminished relative to its size before overoxidation. A semicrystalline and crystalline structure was observed for the overoxidized PEDOT film on the gold electrode in [32, 33]. In contrast to the PEDOT films on the platinum and gold substrates [33], in the present study there were no cracks or disruptions of the PEDOT film on GC. One possible reason for the difference in the behavior of the films is the difference in the oxidation processes on the substrate. In the case of platinum and gold, the surface oxide layers form in the range of positive potentials, and molecular oxygen can appear at the highest potentials. The electrochemical side processes occurring on the metal substrates and not directly related to polymer film oxi-

dation may be the reason for film disruptions and peeling from the substrate.

The electronic structure of the surface groups of poly-3,4-ethylenedioxythiophene was investigated by X-ray photoelectron spectroscopy. The XP spectra in Fig. 7 show that the spin doublet $S2p_{1/2}$ and $S2p_{3/2}$ from thiophene sulfur in the doped form of PEDOT appears at binding energies of ~ 164.0 and 165.2 eV at an intensity ratio of spin-orbital splitting of peaks close to theoretical $1 : 2$, which agrees with the data of [39]. After the cycling of the PEDOT film at high positive potentials (1.4 and 1.5 V, curves 2 and 3), an additional peak appeared at ~ 169.0 eV, which may be indicative of sulfur oxidation in the thiophene ring of PEDOT [40]. During the overoxidation of thiophene sulfur, $S=O$ groups can form. Note that on passing to the upper limit of potential on cycling from 1.4 to 1.5 V, the signal intensity in the energy region of 169.0 eV decreases, although deeper oxidation of sulfur at increased potentials might be expected. One possible reason for this change in the signal may be a decrease in the porosity and specific surface area per geometric unit observed from the SEM data of the film surface (Fig. 6). Accordingly, the signal intensity probably decreases when photoelectron emission from the region of the surface at the focus of X-radiation decreases. The peak intensity ratio at 169.0 and 164.0 eV is preserved, which is evidence in favor of the proposed explanation.

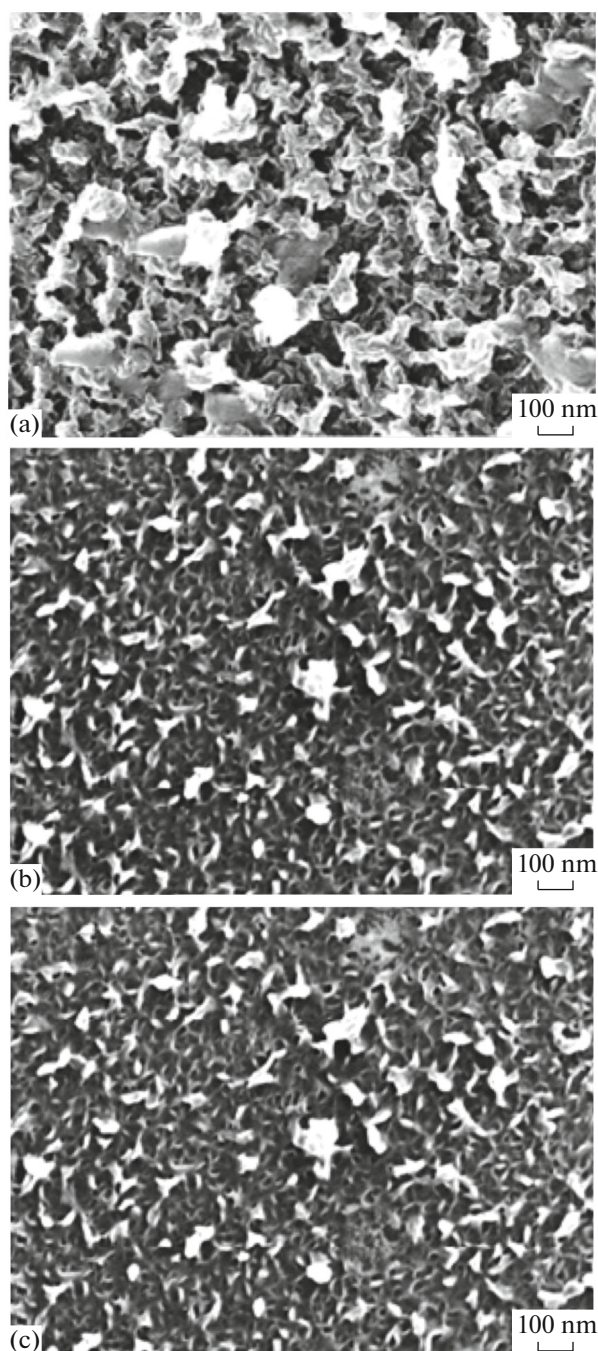


Fig. 6. SEM image of the PEDOT film on the GC electrode: (a) after the synthesis, not subjected to potentiodynamic processing; (b) and (c) after the cycling in the range of high potentials: (b) 3 cycles of CV to 1.4 V and (c) 10 cycles to 1.5 V.

CONCLUSIONS

The overoxidation of a PEDOT film on a glassy carbon electrode in a 0.1 M sulfuric acid solution was studied. The range of positive potentials was found (1.2–1.5 V) in which the cycling markedly changes the electrochemical properties of the film. The CV and

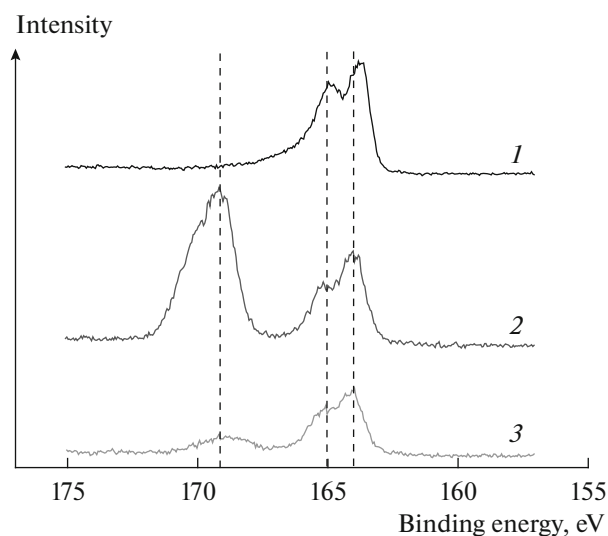


Fig. 7. XPS of the PEDOT film on a GC electrode: (1) after the synthesis, not subjected to potentiodynamic processing; (2) and (3) after the cycling in the range of high potentials: (2) 3 cycles of CV to 1.4 V and (3) 10 cycles to 1.5 V.

electrochemical impedance spectroscopy studies revealed a change in the shape and quantitative parameters of electrochemical response of the PEDOT film during the cycling in the range of high positive potentials. The effect of the value of the positive potential during the specific potentiodynamic processing of a film on its morphology was studied. It was shown that the degree of porosity of the polymer film structure appreciably decreased. The state of the main elements on the surface of the PEDOT film before and after the CV recording at high positive potentials was studied by photoelectron spectroscopy. It was found that after the cycling of the PEDOT film at high positive potentials (1.4 and 1.5 V), an additional peak with an energy of ~ 169.0 eV appeared in the region of the sulfur doublet ($S2p_{1/2}$ and $S2p_{3/2}$) in the X-ray photoelectron spectra, which was attributed to the appearance of S=O groups during the oxidation of thiophene sulfur.

ACKNOWLEDGMENTS

The scanning electron microscopy and X-ray photoelectron spectroscopy studies were performed using the equipment of the Resource Center of the Research Park of St. Petersburg State University (“Nanotechnologies” and “Physical methods of surface studies”). We are grateful to the Chemistry Educational Center for providing the equipment for use in our studies. This work was financially supported by St. Petersburg State University (grant no. 26455158).

REFERENCES

- Tourillon, G., in *Handbook of Conducting Polymers*, Skotheim, T.A., Ed., New York: Marcel Dekker, 1986.
- Heinze, J. Electronically Conducting Polymers, in *Top. Curr. Chem.*, vol. 152, Springer, 1990, p. 1.
- Roncali, J., *Conjugated Poly(Thiophenes): Synthesis, Functionalization, and Applications*, Chem. Rev. (Washington, DC, U.S.), 1992. doi 10.1021/Cr00012a009
- Inzelt, G., Pineri, M., Schultze, J.W., and Vorotyntsev, M.A., Electron and proton conducting polymers: recent developments and prospects, *Electrochim. Acta*, 2000, vol. 45, p. 1016. doi 10.1016/S0013-4686(00)00329-7
- Novak, P., Muller, K., Santhanam, K.S.V., and Haas, O., *Electrochemically active polymers for rechargeable batteries*, Chem. Rev. (Washington, DC, U.S.), 1997. doi 10.1021/Cr941181o
- Inzelt, G., *Conducting Polymers: A New Era in Electrochemistry*, Berlin: Springer, 2008.
- Inzelt, G., Rise and rise of conducting polymers, *J. Solid State Electrochem.*, 2011, vol. 15, p. 1007. doi 10.1007/s10008-011-1338-3
- Holze, R. and Wu, Y.P., Intrinsically conducting polymers in electrochemical energy technology: Trends and progress, *Electrochim. Acta*, 2014, vol. 122, p. 1016. doi 10.1016/j.electacta.2013.08.100
- Groenendaal, L., Jonas, F., Freitag, D., Pielartzik, H., and Reynolds, J.R., Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future, *Adv. Mater.*, 2000, vol. 12, p. 481. doi 10.1002/(sici)1521-4095(200004)12:7<481::aid-adma481>3.0.co;2-c
- Murugan, A.V., Kwon, C.W., Campet, G., Kale, B.B., Maddanimath, T., and Vijayamohan, K., Electrochemical lithium insertion into a poly(3,4-ethylenedioxythiophene)/PEDOT/V2O5 nanocomposite, *J. Power Sources*, 2002, vol. 105, p. 1. doi 10.1016/s0378-7753(01)00992-2
- Arbizzani, C., Balducci, A., Mastragostino, M., Rossi, M., and Soavi, F., Characterization and electrochemical performance of Li-rich manganese oxide spinel/poly(3,4-ethylenedioxythiophene) as the positive electrode for lithium-ion batteries, *J. Electroanal. Chem.*, 2003, vol. 553, p. 125. doi 10.1016/S0022-0728(03)00305-X
- Murugan, A.V., Viswanath, A.K., Campet, G., Gopinath, C.S., and Vijayamohan, K., Enhancement of double-layer capacitance behavior and its electrical conductivity in layered poly(3,4-ethylenedioxythiophene)-based nanocomposites, *Appl. Phys. Lett.*, 2005, vol. 87. doi 10.1063/1.2140468
- Murugan, A.V., Novel organic-inorganic poly(3,4-ethylenedioxythiophene) based nanohybrid materials for rechargeable lithium batteries and supercapacitors, *J. Power Sources*, 2006, vol. 159, p. 312. doi 10.1016/j.jpowsour.2006.04.033
- Zhan, L.Z., Song, Z.P., Zhang, J.Y., Tang, J., Zhan, H., Zhou, Y.H., and Zhan, C.M., PEDOT: Cathode active material with high specific capacity in novel electrolyte system, *Electrochim. Acta*, 2008, vol. 53, p. 1016. doi 10.1016/j.electacta.2008.06.053
- Lei, C.H., Wilson, P., and Lekakou, C., Effect of poly(3,4-ethylenedioxythiophene) (PEDOT) in carbon-based composite electrodes for electrochemical supercapacitors, *J. Power Sources*, 2011, vol. 196, p. 7823. doi 10.1016/j.jpowsour.2011.03.070
- Fabre-Francke, I., Aubert, P.H., Alfonsi, S., Vidal, F., Sauques, L., and Chevrot, C., Electropolymerization of 3,4-ethylenedioxythiophene within an insulating nitrile butadiene rubber network: Application to electroreflective surfaces and devices, *Sol. Energy Mater. Sol. Cells*, 2012, vol. 99, p. 109. doi 10.1016/j.solmat.2011.07.004
- Hong, S.F. and Chen, L.C., Nano-Prussian blue analogue/PEDOT:PSS composites for electrochromic windows, *Sol. Energy Mater. Sol. Cells*, 2012, vol. 104, p. 1016. doi 10.1016/j.solmat.2012.04.032
- Romyen, N., Thongyai, S., Prasertthadam, P., and Sotzing, G.A., Enhancement of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) properties by poly(vinyl alcohol) and doping agent as conductive nano-thin film for electronic application, *J. Mater. Sci.: Mater. Electron.*, 2013, vol. 24, p. 2897. doi 10.1007/s10854-013-1188-0
- Trinh, N.D., Saulnier, M., Lepage, D., and Schougaard, S.B., Conductive polymer film supporting LiFePO₄ as composite cathode for lithium ion batteries, *J. Power Sources*, 2013, vol. 221, p. 284. doi 10.1016/j.jpowsour.2012.08.006
- Kim, J., Park, H.S., Kim, T.H., Kim, S.Y., and Song, H.K., An inter-tangled network of redox-active and conducting polymers as a cathode for ultrafast rechargeable batteries, *Phys. Chem. Chem. Phys.*, 2014, vol. 16, p. 1039. doi 10.1039/C3cp54624a
- Wang, X., Shen, L., Li, H., Wang, J., Dou, H., and Zhang, X., PEDOT coated Li₄Ti₅O₁₂ nanorods: Soft chemistry approach synthesis and their lithium storage properties, *Electrochim. Acta*, 2014, vol. 129, p. 283. doi 10.1016/j.electacta.2014.02.112
- Cintora-Juarez, D., Perez-Vicente, C., Kazim, S., Ahmad, S., and Tirado, J.L., Judicious design of lithium iron phosphate electrodes using poly(3,4-ethylenedioxythiophene) for high performance batteries, *J. Mater. Chem. A*, 2015, vol. 3, p. 14254. doi 10.1039/c5ta03542b
- Das, P.R., Komsysiaka, L., Osters, O., and Wittstock, G., PEDOT: PSS as a Functional Binder for Cathodes in Lithium Ion Batteries, *J. Electrochem. Soc.*, 2015, vol. 162, p. 1149. doi 10.1149/2.0581504jes
- Eliseeva, S.N., Levin, O.V., Tolstopjatova, E.G., Alekseeva, E.V., Apraksin, R.V., and Kondratiev, V.V., New functional conducting poly-3,4-ethylenedioxythiophene: polystyrene sulfonate/carboxymethylcellulose binder for improvement of capacity of LiFePO₄-based cathode materials, *Mater. Lett.*, 2015, vol. 161, p. 117. doi 10.1016/j.matlet.2015.08.078
- Eliseeva, S.N., Levin, O.V., Tolstopyatova, E.G., Alekseeva, E.V., and Kondratiev, V.V., Effect of addition of a conducting polymer on the properties of the LiFePO₄-based cathode material for lithium-ion batteries, *Russ. J. Appl. Chem.*, 2015, vol. 88, p. 1146. doi 10.1134/S1070427215070071
- Lee, J. and Choi, W., Surface Modification of Overlithiated Layered Oxides with PEDOT:PSS Conducting Polymer in Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2015, vol. 162, p. 1149. doi 10.1149/2.0801504jes

27. Smolin, A.M., Novoselov, N.P., Babkova, T.A., Eliseeva, S.N., and Kondrat'ev, V.V., Use of composite films based on poly(3,4-ethylenedioxythiophene) with inclusions of palladium nanoparticles in voltammetric sensors for hydrogen peroxide, *J. Anal. Chem.*, 2015, vol. 70, p. 967. doi 10.1134/S1061934815080171
28. Tolstopjatova, E.G., Eliseeva, S.N., Nizhegorodova, A.O., and Kondratiev, V.V., Electrochemical Properties of Composite Electrodes, Prepared by Spontaneous Deposition of Manganese Oxide into Poly-3,4-ethylenedioxythiophene, *Electrochim. Acta*, 2015, vol. 173, p. 40. doi 10.1016/j.electacta/2015.05.033
29. Zykwincka, A., Domagala, W., Pilawa, B., and Lapkowski, M., Electrochemical overoxidation of poly(3,4-ethylenedioxythiophene)—PEDOT studied by means of in situ ESR spectroelectrochemistry, *Electrochim. Acta*, 2005, vol. 50, p. 1625. doi 10.1016/j.electacta.2004.10.026
30. Ujvári, M., Takacs, M., Vesztergom, S., Bazso, F., Ujhelyi, F., and Láng, G.G., Monitoring of the electrochemical degradation of PEDOT films on gold using the bending beam method, *J. Solid State Electrochem.*, 2011, vol. 15, p. 1007. doi 10.1007/s10008-011-1472-y
31. Láng, G.G., Ujvári, M., Bazso, F., Vesztergom, S., and Ujhelyi, F., In situ monitoring of the electrochemical degradation of polymer films on metals using the bending beam method and impedance spectroscopy, *Electrochim. Acta*, 2012, vol. 73, p. 1016. doi 10.1016/j.electacta.2012.01.068
32. Ujvári, M., Zalka, D., Vesztergom, S., Eliseeva, S., Kondratiev, V., and Láng, G.G., Electrochemical impedance measurements in non-stationary systems: application of the 4-dimensional analysis method for the impedance analysis of overoxidized poly(3,4-ethylenedioxythiophene)-modified electrodes, *Bulg. Chem. Commun.*, 2017, vol. 49, p. 106.
33. Ujvári, M., Gubicza, J., Kondratiev, V., Szekeres, K.J., and Láng, G.G., Morphological changes in electrochemically deposited poly(3,4-ethylenedioxythiophene) films during overoxidation, *J. Solid State Electrochem.*, 2015, vol. 19, p. 1247. doi 10.1007/s10008-015-2746-6
34. Láng, G.G., Ujvári, M., Vesztergom, S., Kondratiev, V., Gubicza, J., and Szekeres, K.J., The Electrochemical Degradation of Poly(3,4-ethylenedioxythiophene) Films Electrodeposited from Aqueous Solutions, *Z. Phys. Chem.*, 2016, vol. 230, p. 1281. doi 10.1515/zpch-2016-0752
35. Zhuzhel'skii, D.V., Yalda, K.D., Spiridonov, V.N., Eliseeva, S.N., and Kondratiev, V.V., Electrochemical deposition of molybdenum oxide into films of poly(3,4-ethylenedioxythiophene) conducting polymer on glassy carbon substrates, *Russ. J. Appl. Chem.*, 2016, vol. 89, p. 1252. doi 10.1134/s1070427216080061
36. Kondratiev, V.V., Malev, V.V., and Eliseeva, S.N., Composite electrode materials based on conducting polymers loaded with metal nanostructures, *Russ. Chem. Rev.*, 2016, vol. 85, p. 1070. doi 10.1070/rcr4509
37. Fall, M., Diagne, A.A., Dieng, M.M., Deflorian, F., Rossi, S., Bonora, P.L., Volpe, C.D., and Aaron, J.J., Electrochemical impedance spectroscopy of poly(3-methoxythiophene) thin films in aqueous LiClO₄ solutions, *Synth. Met.*, 2005, vol. 155, p. 569. doi 10.1016/j.synthmet.2005.09.043
38. Refaey, S.A.M., Electrochemical impedance studies on the electrochemical properties of poly(3-methylthiophene) in aqueous solutions, *Synth. Met.*, 2004, vol. 140, p. 87. doi 10.1016/s0379-6779(03)00357-6
39. Greczynski, G., Kugler, T., Keil, M., Osikowicz, W., and Fahlman, M., and Salaneck, W.R., Photoelectron spectroscopy of thin films of PEDOT-PSS conjugated polymer blend: a mini-review and some new results, *J. Electron Spectrosc. Relat. Phenom.*, 2001, vol. 121, p. 1016. doi 10.1016/s0368-2048(01)00323-1
40. King, Z.A., Shaw, C.M., Spanninga, S.A., and Martin, D.C., Structural, chemical and electrochemical characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) prepared with various counter-ions and heat treatments, *Polymer*, 2011, vol. 52, p. 1302. doi 10.1016/j.polymer.2011.01.042

Translated by L. Smolina