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Synthesis and Structure of Poly-3,4-ethylenedioxythiophene Film with the Inclusions of Palladium Nanoparticles

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Abstract—By chemical deposition of ultrafine particles of metallic palladium on the polymer matrix of poly-3,4-ethylenedioxythiophene (PEDOT) composite PEDOT/Pd films were obtained. The conditions of synthesis of the composite films in dependence on the duration of exposure of the reduced form of PEDOT film in a solution of palladium chloride, its concentration and the film thickness were studied. By the methods of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) it was shown that in the process of the synthesis of the composite films the nanosized palladium particles of predominantly quasi-spherical shape precipitated on the globular structure of the polymer. The size of the palladium nanoparticles in the composite PEDOT film and the nature of their distribution over the film bulk were revealed. An increase in the duration of deposition of the palladium nanoparticles on the film was shown to lead to an increase in their size and in the density of particles in the film.

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Inclusion of dispersed metal particles in conducting polymers has attracted attention as a way for obtaining new conductive porous materials with a distribution of metals in the material volume, the important catalysts of some important electrochemical reactions [1–15]. Such metal–polymer composite materials are promising for the development of new electrocatalytic systems used to create fuel cells and chemical sensors. The key parameters affecting the properties of the materials are the size and the nature of distribution of the metal particles, as well as the conductivity and transport properties of the composite materials, which are largely determined by their morphology.

In this paper we present the results of the synthesis of metal–polymer films based on a conducting polymer poly-3,4-ethylenedioxythiophene (PEDOT) with inclusions of particles of palladium, and the results of examination of their structural characteristics. Palladium belongs to the group of noble metals that show the catalytic properties in many reactions of organic compounds and the sorption properties toward hydrogen. The catalysts based on palladium are widely used in the studies aimed at developing fuel cells, hydrogen energetics, and chemical sensors. Therefore the systems of conducting polymer PEDOT matrix that includes ultrafine particles of a metal like palladium are, in addition to scientific value, of practical interest in connection with the possibility of obtaining the electrode materials with the pronounced catalytic and sorption properties.

For the synthesis of metal–polymer PEDOT/Pd composite films we used a method of chemical deposition of palladium on the film of conductive polymer poly-3,4-ethylenedioxythiophene. The PEDOT film was synthesized electrochemically in galvanostatic conditions, then it was reduced (by maintaining at the potential of –0.2 V) and placed in a solution containing palladium chloride (5×10^{-3} to 2.5×10^{-4} M $PdCl_2$ in 0.1 M H_2SO_4). At the contact of the reduced form of PEDOT film with a solution of $PdCl_2$ a spontaneous redox process occurs leading to reducing the palladium ions to metallic palladium and oxidizing a part of the polymer. The corresponding reaction can be represented schematically by the following equation:

$$Pd^{2+} + 2PEDOT^0 \xrightarrow{+2A^-} Pd^0(Pedot^{+\bullet})_2 2A^-, \qquad (1)$$

where PEDOT is a redox fragment of the polymer chain, consisting of four monomer units. The reaction (1) can be carried out with involvement of different anion-dopants: sulfate ions and chloride ions, introduced by immersing the film in a solution of

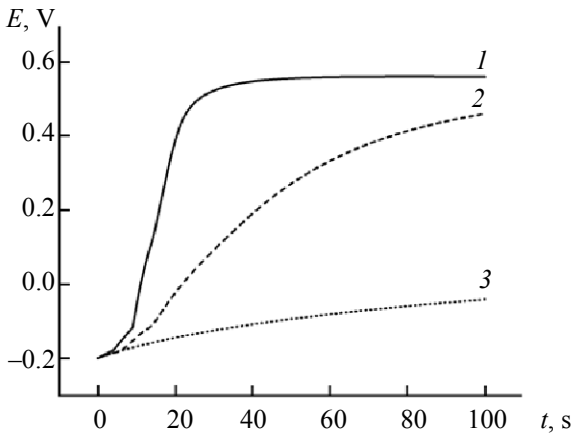


Fig. 1. Changes in the potential of carbon glass electrode with PEDOT film in the course of deposition of palladium from solutions: (*1*) 5×10^{-3} M $PdCl_2$, (*2*) 5×10^{-4} M $PdCl_2$, and (*3*) the background curve, 0.1 M H_2SO_4.

palladium chloride. The formal electrode potential pairs of Pd^{2+}/Pd is +0.85 V (in 0.5 M H_2SO_4) [5], so palladium ions can act as an effective oxidizer of the reduced form of the PEDOT film. The direction of oxidation–reduction reaction (1) is determined by the following conditions: a system with a more positive potential acts as the electron acceptor (oxidized Pd^{2+} form), and the system with a more negative potential acts as an electron donor (reduced PEDOT form). Theoretically, the reaction continues to reach a ratio of component concentrations at which the equilibrium potentials of the two systems are identical. However, if the rate of the redox processes is low or the concentrations of interacting components are very low, there may be a violation of equilibrium, and the equilibrium potential system is not realized.

The occurrence of the process of palladium reduction and the simultaneous film oxidation is seen in the change of the film electrode potential depicted in Fig. 1. Registration of the *E–t* curve started 2–5 s after the moment of immersion in a solution of palladium chloride. This is associated with the transition of the electrode with the PEDOT film after its reduction into 0.1 M H_2SO_4. The highest rate of change of the electrode potential was observed at immersing in a solution with a higher concentration of palladium ions. In this case, the initial sharp change in the potential followed by a plateau with little variations in the potential value. Reducing the concentration of ions in the solution by an order of magnitude led to a slow change in the potential of the film resulted in the final value of the potential (Fig. 1, curves *1, 2*). Experimentally reached maximum potential of the electrode with the film (as seen from *E–t* curves) is about 0.1–0.2 V below the equilibrium potential of Pd^{2+}/Pd pair (for the given concentration of palladium ion). However, at such estimations a possible shift in the Pd^{2+}/Pd potential to more negative values due to possible complexation [16, 17] with chloride and sulfate ions available in the electrolyte solution should be taken into account. Stirring the solution at the concentration of palladium ions 5×10^{-4} M $PdCl_2$/0.1 M H_2SO_4 did not significantly affect the rate of change of the potential. This indicates the absence of diffusion limitations on mass transfer of palladium ions in solution, and allows us to assume that the rate of potential change, apparently, is defined by other stages, such as chemical reactions or the formation of nuclei of metallic palladium. Background curve *3* (Fig. 1) shows the change in the potential of the electrode with film after switching off the cells in the absence of palladium ions in solution. The observed slow changes in the system potential in the absence of palladium ions in solution apparently is due to the gradual oxidation of the film by dissolved oxygen. Passing inert gas through the solution decreases the rate of background potential drift, but even long deaeration of the solution does not eliminate this process completely.

The presence of palladium in the composite film was confirmed by the energy dispersive X-ray spectroscopy (EDRS). In the spectrum intense peaks were observed of Pd Lα = 2.84 keV, Pd Kα = 21 keV, and a number of less strong peaks, Kβ = 23.8 keV, Lβ1 = 2.9 keV, Lι = 2.5 keV and LIab = 3.6 keV. At reducing the time of loading palladium from the solution of the concentration $5\cdot10^{-3}$ M $PdCl_2$ from 60 to 15 s a decrease in the intensity of all lines was observed. In the EDRS spectrum of the initial PEDOT film these peaks were not observed.

Figure 2 shows *E–t* plots in the process of deposition of palladium in PEDOT films of different thickness. For a thin film (~0.4 μm) a faster change in the potential toward positive values was observed than for thick films (~1.5 μm). The increase in the film thickness leads to a larger consumption of electricity for the oxidation of the film to a certain value of potential that is seen as a slow change in the potential over time.

Thus, it follows from the data obtained that by changing the concentration of palladium ion in the solution (5×10^{-4}–5×10^{-3} M $PdCl_2$) and the loading

time the amount of palladium in the film can be controlled. Changing these parameters at the synthesis of composite film, in principle, allows to vary widely the conditions of obtaining particles of palladium and, perhaps, to influence purposefully the degree of dispersion and the density of the particles distribution in the polymer matrix. Earlier [4–7], studying various ways of introducing metals into polymer films we showed that we may consider all three main features of the nucleation of metal particles: on the surface of the polymer films, in the pores in the bulk of the film, and on the border of the electron-carrier substrate with the film. A preferred mechanism for the formation of dispersed sediment should depend on the microporous structure of the polymer film, concentration of the metal ions, and the polymer conductivity. To clarify these issues, we carried out a study of surface morphology of the polymer and the effect of duration of chemical deposition on the palladium particles size of and the nature of their distribution in the polymer film.

Figure 3 shows a typical image obtained by scanning electron microscope of the surface of the reduced form of PEDOT film. As shown in Fig. 3, the spatial structure is an irregular net of the globular type with the pores of different size. The most common pore size is about 50–200 nm. In Fig. 3 the separate fused globular structures on the surface of the main polymer net are clearly visible. The polymer apparently is formed as a result of accretion on the surface of the individual globules to form irregular spatial structures resembling a sponge. Thus, the data of scanning electron microscopy confirmed highly porous structure of the polymer, which is characterized by a developed surface.

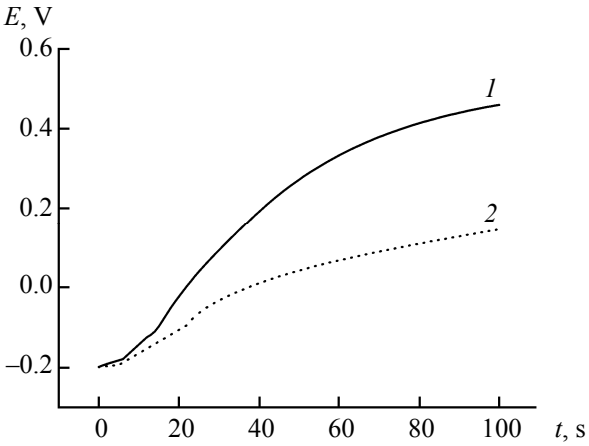


Fig. 2. Changes in time in the potential of carbon glass electrode with PEDOT films of different thickness in the course of the palladium deposition from 5×10^{-4} M solution of $PdCl_2$, μm: (*1*) 0.4 and (*2*) 1.5.

In the image of composite film (Fig. 3b) registered after the deposition of metallic palladium particles the globular structures can be seen covered with nanosized palladium particles mainly of spherical shape. The particles of palladium are close enough in size (the size of most particles is in the range of 10–20 nm) and are relatively evenly distributed on the polymer surface. It can be assumed that the deposition of particles of palladium also occurs in the pores available for the electrolyte in the bulk polymer. However, the images obtained by scanning electron spectroscopy do not give direct evidence of such distribution.

More precise estimates of the size of palladium particles deposited in the polymer film and the nature of their distribution were made using the method of

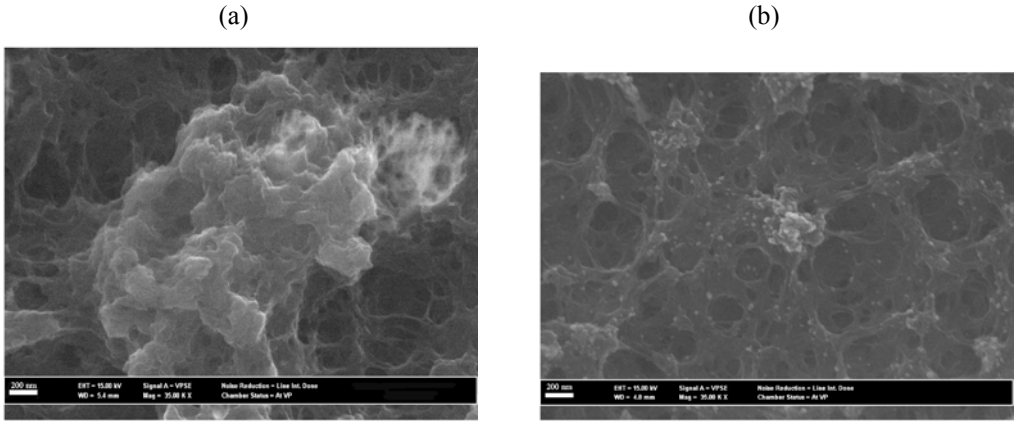


Fig. 3. (a) SEM image of a fragment of the surface of PEDOT film and (b) SEM image of a fragment of the surface of PEDOT/Pd film (palladium deposition duration 60 s from 5×10^{-3} M solution of $PdCl_2$ in H_2SO_4).

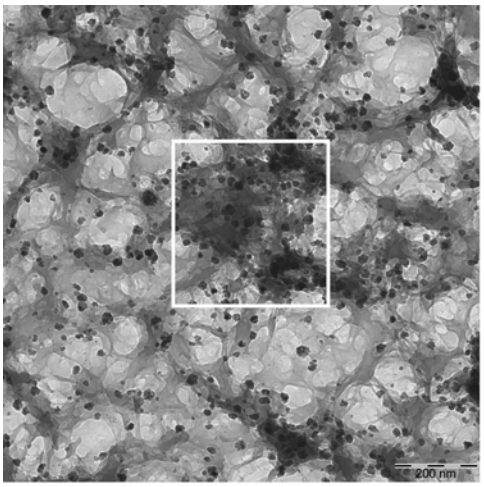


Fig. 4. Bright-field TEM image of PEDOT/Pd (duration of palladium deposition 120 s from 5×10^{-3} M $PdCl_2$ solution). In the square is shown agglomeration of palladium particles.

transmission electron microscopy (TEM) (Figs. 4–6). In Fig. 4 is seen a bright-field TEM image of the composite PEDOT/Pd film obtained at the duration of the palladium deposition 120 s from 5×10^{-3} M solution of $PdCl_2$. In this mode of registration the location of palladium particles appear as dark dots. It is seen from Fig. 4 that the average palladium particle size increased markedly being in the range from 15 to 30 nm, and the palladium particles are distributed also relatively evenly on the polymer film surface. In addition, note that for samples with longer deposition of palladium in some areas of the film appear clusters of palladium nanoparticles. Note also that the observed dark areas on the TEM image of the composite (e.g., the area marked in Fig. 4) are associated not with the large-sized particles of metal, but rather with the accumulation of nanoparticles of approximately the same size as in the main sectors of the film. This is especially evident when such sections of the film are shown with higher zoom level. The observed agglomeration of the nanoparticles is associated with their distribution on the surface of relatively large globules in the PEDOT film, mainly on the ridges of the latter. This can be explained by the deposition of palladium particles on those parts of the PEDOT, where the current density is much higher, namely on the "rough" surfaces: in the globules and the bridges between the globules, while on the smooth sections the deposition is less probable.

The change in the palladium particles size at the increase in the duration of their deposition on the polymer film is particularly well illustrated by Fig. 5b, where the images of films with different palladium loading duration are given with the same zoom level. At the deposition of palladium for 30 s (Fig. 5a) the average particle size of Pd is about 6–10 nm. With increasing deposition time to 120 s the average size of the dominant palladium particles increases appreciably, reaching ~15–30 nm (Fig. 5b).

Thus, it is seen from analysis of films images in Figs. 4–6 presented in different scales that the increase in the time of the exposure of the reduced film in a solution of palladium chloride leads to an increase in the palladium particle size.

Figure 6 shows the image of one of the palladium nanoparticles in the PEDOT film at a higher zoom

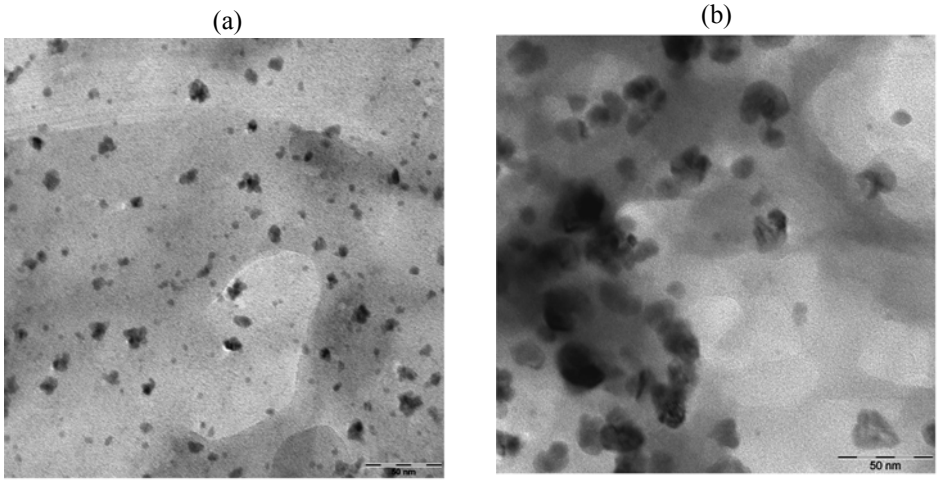
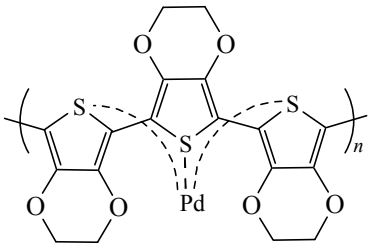


Fig. 5. Bright-field TEM image of PEDOT/Pd from 5×10^{-3} M $PdCl_2$ solution in 0.1 M H_2SO_4. The paladium deposition duration, s: (a) 30 and (b) 120.

level. As seen, the particle is an agglomerate of individual clusters. Every single cluster in the agglomerate is a nano-sized single crystal about 15×20 nm size oriented randomly to the neighbors. The diffraction pattern of the whole particle, as well as the Fourier transform of its individual sections confirms the existence of clusters of cubic phase oriented in random directions.

Based on the results obtained, it can be assumed that, as in the case of other metals such as gold [9], the sulfur atoms in the ring of the thiophene polymer molecules may interact primarily with the palladium ions, and then with the palladium atoms formed on the surface and in the pores of the polymer [see Eq. (1)]. These interactions may contribute to the stabilization of nanosized palladium clusters, and in conjunction with limited pore size should prevent their aggregation. Thus, the polymer film acts as a stabilizer of both the formed ultrafine palladium particles and the conductive matrix with a sufficiently high electronic conductivity, providing electrical contact between the metal particles and the current passing clamp in an integrated electrode.



Formation of the palladium nanostructures in the film can be represented as follows. At the first stage the formation occurs of individual palladium atoms, which are stabilized by sulfur atoms of the thiophene ring in the polymer molecule. Their interaction with sulfur is weak, and they can migrate along the polymer chain. The gain in energy at the interaction with similar palladium atoms leads to self-organization into larger structures to form crystalline nano-sized nucleations, which are fixed in the polymer structure near the accessible for the interaction sulfur atoms of one or more rings. The size of the forming palladium particle (nucleation) is determined on the one hand by its ability to move in the polymer, on the other hand, by the electrical conductivity of the polymer and its transport properties with respect to the diffusion of palladium ions on the surface and in the pores of the polymer. Since, according to the data obtained, the increase in the synthesis duration leads to an increase

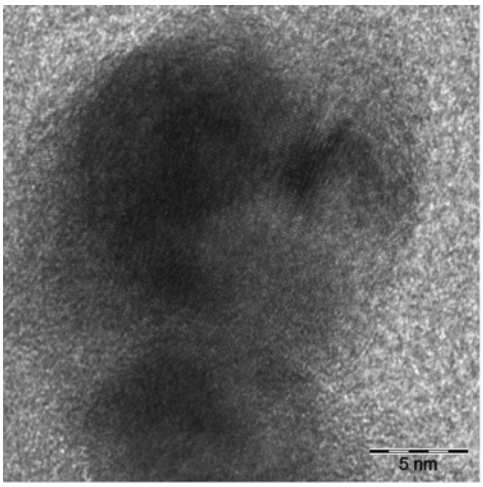


Fig. 6. Bright-field TEM image of individual Pd nanoparticles (palladium deposition time 30 s, from 5×10^{-3} M $PdCl_2$ solution in 0.1 M H_2SO_4).

in the palladium particle size, we can assume that the major influencing factor in the growth of particles becomes diffusion of palladium ions to the nucleations of the metal precipitate.

Thus, our data indicate a possibility of formation of nanocomposite metal-polymer structures based on the spontaneous reduction of palladium ions on the surface and in the film bulk of the conductive polymer poly-3,4-ethylendioxythiopene. By the method of energy dispersive X-ray analysis (EDX) a direct evidence is obtained of the presence of palladium particles in the polymer films; the number of the particles increases regularly with increasing duration of the synthesis of the composite films. Using the scanning electron microscopy we studied the morphology of the film PEDOT. We found that it has irregular net porous structure based on the interlocked polymer globules, with widely varied pore size (the main pore size is 50–200 nm). Highly porous structure of the polymer makes it easy to capture electrolyte by the polymer in a significant amount. Using scanning electron microscopy and transmission electron microscopy we showed that at the synthesis of the composite films the fibrillar-globular structure of the polymer is covered with nanosized palladium mostly of quasi-spherical shape. We revealed the size of palladium nanoparticles in the composite PEDOT film and their distribution. It is shown that the increase in the duration of deposition of palladium nanoparticles on the film leads to an increase in their size.

EXPERIMENTAL

Electrochemical synthesis of poly-3,4-ethylenedioxythiophene films was performed on an electrode of ITO-glass (the glass covered with a mixed oxide $SnO_2 \cdot In_2O_3$) under galvanostatic conditions at the current density $j \sim 1$ mA cm^{-2} . For the synthesis of the films were used solutions with concentration 0.05 M of 3,4-ethylenedioxythiophene (EDOT) and 0.1 M of $LiClO_4$ in acetonitrile [18, 19]. For preparation of solutions for the synthesis was used 2,3-dihydrothieno-[3,4-*b*]-1,4-dioxin (EDOT) (Aldrich), anhydrous lithium perchlorate (chemically pure grade), calcined in a drying oven until constant weight, and acetonitrile (extra pure grade, firm Kriokhrom, water content less than 0.008%).

Chemical deposition of palladium particles on the PEDOT film was carried out from the palladium chloride solutions with the concentrations from 5×10^{-3} to 2.5×10^{-4} M in 0.1 M H_2SO_4. Studies of the films by scanning electron microscopy were performed on a scanning electron microscope Zeiss SUPRA 40VP (Carl Zeiss, Germany). The secondary electrons images of surface morphology of the PEDOT and PEDOT/Pd films were obtained using accelerating voltage 15 kV at a high vacuum in the chamber. To study the elemental composition of films of PEDOT and PEDOT/Pd with a scanning electron microscope X-ray microanalysis was performed using an energy dispersive spectrometer Oxford Instruments X-act. The films were synthesized on the polished gold and platinum electrodes. These substrates are the most smooth, which is extremely important in the study of the surface.

Studies of the films by the method of transmission electron microscopy were performed on a LIBRA 200 FE microscope (Carl Zeiss, Germany). The samples for the TEM studies were prepared by transferring the films fragments on a copper grid.

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