

DEPOSITION OF FLUORINATED POLYMER FILMS ONTO TRACK-ETCHED MEMBRANE SURFACE

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Abstract. The synthesis and characterization of polymer composite membranes with hydrophobic top layer were studied. To prepare the composite membranes the fluorinated polymer films have been deposited on one side of the poly(ethylene terephthalate) and polypropylene track-etched membranes. RF-magnetron and electron-beam sputter deposition of polytetrafluoroethylene were used as synthesis techniques to obtain polymer films onto membrane surface. It was found that polymer deposition on the membrane surface results in the creation of composite membranes that possess asymmetric conductivity in electrolyte solutions (diode-like effect), which manifests itself at various orientations of the electric field in respect to the membrane. It has been shown that the resulting effect of conductivity asymmetry is due to not only a significant decrease of the pore diameter and a change in their geometry in the deposited polytetrafluoroethylene layer, but also the existence of an interface in the pores between the initial membranes and the hydrophobic polymer layer.

Key words: bilayer composite membranes, hydrophilic and hydrophobic layers, diode-like effect.

1. INTRODUCTION

The research on the properties of composite membranes, in particular bilayered membranes, which are characterized by the presence of two layers with functional groups that differ in both chemical structure and properties, has become a subject of essential effort. It is caused by a wide expansion of such systems. So, to bilayered membranes concern membranes with the modified surface, ion-exchange membranes consisting from two cationic or two anionic layers of different nature as well as bipolar membranes [1, 2]. The major distinction of bilayered membranes is the anisotropy of their structure and physicochemical properties. The diffusion

flow of salt through these membranes and the forming diffusion potential differ from one another depending on the orientation of layers relative to the diffusion flow direction. When the membrane is simultaneously under the effect of both gradients of concentration and electric fields, the value of electric current passing through a membrane also depends on the disposition of the layers. These phenomena, which are typical for bilayered membranes, make transport properties asymmetric.

To producing the bilayered membranes the application of thin, including nanoscale, layers of polymers with different chemical nature on porous substrates (membranes) is used. For this purpose, the method of plasma polymerization of some organic compounds has been applied very often [3]. The use of plasma provides a number of essential advantages, such as the control of the thickness of the polymer layer deposited on the membrane surface, the high adhesion of the obtained layer, the short treatment time and the opportunity to use a large number of organic and element-organic compounds for the polymer layer formation. Besides, this method allows to change the contact properties of polymer membranes (hydrophilicity or hydrophobicity), as well as adhesion characteristics [4, 5].

In the last decade, the deposition of thin polymer layers has known the utilization of some new technological and environmentally friendly methods, such as magnetron and electron-beam sputter deposition of polymers in vacuum [6-10]. The most informative method to study the chemical composition and structure of nanoscale layers of polymers deposited on the porous substrates is X-ray photoelectron spectroscopy (XPS) [11]. Unlike other analytical methods, XPS provides information about the surface and near-surface layers, not distorted by the signal from the underlying layers. The high resolution of modern XPS devices using X-ray monochromators allows to confidently separate electron peaks within 1 eV. This allows us to determine the chemical state of atoms and to identify the functional groups consisting of ones. When the core levels are ionized by soft X-ray radiation ($AlK\alpha$ or $MgK\alpha$), the kinetic energy of the knocked-out electrons is about 1 keV, and the free electron path is about 10 Å.

In this paper, the chemical structure of nanoscale polytetrafluoroethylene (PTFE) films deposited on the surface of poly(ethylene terephthalate) (PET) and polypropylene (PP) track-etched membranes by RF-magnetron (MSD) and electron-beam sputter deposition (EBD) in vacuum was studied using the XPS method. The surface and electrotransport properties of the composite membranes produced by these methods are also studied.

2. EXPERIMENTAL

In the present experiments, poly(ethylene terephthalate) track-etched membrane (PET TM) with an effective pore diameter of 95 nm and pore density of $1.3 \times 10^9 \text{ cm}^{-2}$

were used. To produce the membrane, PET foil with a thickness of 10.0 μm (Lavsan, Russia) was irradiated by krypton positive ions, accelerated to energy of 3 MeV/nucleon at the cyclotron of the Flerov Laboratory of Nuclear Reactions. Then the ion-irradiated film was additionally sensitized with ultraviolet irradiation with a maximum emission intensity at 310 nm. The chemical etching process was performed in an alkaline (NaOH) aqueous solution (3.0 mol/L) at 75°C for up to 7 min according to a standard procedure [12]. In experiments, we also used a track-etched polypropylene membrane (PP TM) having an effective pore diameter of 300 nm, which was made on the basis of a Torayfan T2372 PP foil with a thickness of 10.0 μm as manufactured by Toray (Japan). To prepare the PP membrane, the foil was irradiated in a cyclotron by xenon positive ions, accelerated to energy of 1 MeV/nucleon at an ion fluence of 10^8 cm^{-2} . Chemical etching of the exposed foil to obtain through pores was performed at 80°C in an aqueous solution of chromic anhydride with a concentration of 1000 g/L according to the procedure described in [13]. The membrane samples were cut in circular form with diameter of 10 cm prior the experiments.

The nanoscale layers of polytetrafluoroethylene (PTFE-like) films were deposited on the surface of track-etched membranes from an active gas phase by RF-magnetron and electron-beam sputter deposition of the polymer in a vacuum. PTFE-like layers deposition onto PET TM support by the magnetron sputtering discharge (MSD) method was conducted in a spherical stainless steel vacuum chamber evacuated by a turbomolecular/rotary pumping system down to a base pressure of 10^{-2} Pa. The pressure in the chamber was monitored by a Pfeiffer gauge and the gas flow rates are controlled by electronic mass flow controllers (Bronkhorst Instruments). The chamber is equipped with a magnetron sputtering source (Kurt J. Lesker) mounted at 45° and of 6 cm distance in respect to the substrate holder, which serves also as grounded electrode. The substrate holder is rotating during the deposition in order to insure thickness uniformity over large area. The PTFE target mounted in the magnetron is sputtered by igniting a discharge in argon flow (100 sccm) at RF power of 50 W and working on a pressure of 6.8×10^{-1} Pa. In order to insure various thicknesses of the PTFE-like layers, the deposition time was varied from 10 to 35 min.

PTFE-like layers deposition onto PP TM support was applied by the electron-beam sputter deposition (EBD) of the polymer. The electron source was a filament electron gun, which could produce beams with a current density of 5–100 A/m^2 , an electron energy of 0.5–2 keV, and a cross-sectional area of $(5 - 10) \times 10^{-4} \text{ m}^2$. The initial pressure of residual gases in the reaction chamber was $\sim 10^{-3}$ Pa; the substrate surface temperature ~ 300 K; the emission current, 60 mA; and the electron energy, 1.2 keV. The target was a PTFE plate of 10 mm in thickness and 35 mm in diameter (Plastopolymer, St. Petersburg). The sputter deposition time was varied. The schematic of the setup and the treatment procedure detail are described in [14].

The chemical composition of the deposited PTFE-like layer was studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded using Thermo Scientific K-Alpha (USA) instrument with a hemispherical analyzer. For the excitation of photoelectrons, X-ray radiation of an aluminum anode ($AlK\alpha = 1486.6$ eV) generated at a tube voltage of 12 kV and at an emission current of 3 mA was used. The peaks positions (the binding energy values) were calibrated to the C1s standard peak (284.6 eV) given in [15]. In order to record the XPS spectra of the PTFE-like films obtained by magnetron and electron-beam sputter deposition, the polymer was deposited on a silicon plate of 10×15 mm size.

The characteristics of the initial membrane and of membranes with the deposited polymer layer were determined by different procedures. The amount of the deposited polymer on the membrane surface was defined by the gravimetric method. The gas flow rate through the membranes was determined at an adjusted pressure drop. Gas consumption was measured by a float-type flow meter. From the obtained data, the effective pore diameter was calculated using the Hagen-Poiseuille equation [16]. Surface topography of the membranes was studied using a NTEGRA Spectra (NT-MDT, Russia) atomic force microscope (AFM). Measurements were made in the dynamic mode to obtain a three-dimensional image; the scan area for each sample was $5 \times 5 \mu\text{m}^2$. The main determined parameter was the surface roughness – a root-mean-square deviation of the surface profile (R_{ms}), calculated over all scan points. For each sample, scans of the surface at five different points were obtained and the R_{ms} value was then averaged. The surface properties were characterized by values of the contact angle (Θ) measured with an Easy Drop DSA100 instrument (KRUSS, Germany) and the software Drop Shape Analysis V.1.90.0.14 using deionized water as a test liquid (error $\pm 1^\circ$). Measurements of the current-voltage characteristics of the membranes were carried out in direct current regime, in the voltage range of -1 to $+1$ V, using a PC-controlled potentiostat Elins P-8S (Russia) with a scan rate of 50 mV/s. A two-chambered cell with Ag/AgCl electrodes, containing a water solution of potassium chloride (KCl) of identical concentration on both sides of the membrane was used for this purpose. The volume of each compartment was 2.5 mL, and the active membrane area was 0.5 cm^2 . The electrodes were immersed in an electrolyte solution of each compartment at a distance of 7 mm from the membrane surface. To suppress the electrode polarization effect, large-area ($\sim 3 \text{ cm}^2$) electrodes were used. The concentration of KCl was varied in the range of 10^{-3} to 10^{-1} mol/L. Prior to measurements, the samples were held in the electrolyte solution for 30 min.

3. RESULTS AND DISCUSSION

The characteristics measured for the initial PET TM and PP TM and the membranes prepared by applying a polymer layer by MSD and EBD of PTFE are

shown in the Tables 1 and 2. From these data, it follows that the deposition of the PTFE-like layer on the TM surface leads to a gradual increase in mass of the sample with the increasing of the time of the processes. The thickness of the both membranes increases and the effective pore diameter decreases in this case. A decrease in the effective pore diameter of the composite membranes means that the pore diameter in the deposited polymer layer is much smaller than one of the initial membranes.

Table 1

Change of the PET TM characteristics after deposition a PTFE-like layer

Parameters	Initial membrane	Deposition time [min]		
		10	20	35
Thickness of deposited layer [nm]	—	60	120	210
Relative increase in the mass [%]	—	1.6	2.2	3.3
Air flow rate at $\Delta P = 2 \times 10^4$ Pa [ml/min cm ²]	155	140	110	45
Effective pore diameter [nm]	95	90	80	65
Water contact angle [deg]	65	112	112	110
Roughness, R_{ms} [nm]	7.9	9.9	4.6	3.1

Table 2

Change of the PP TM characteristics after deposition a PTFE-like layer

Parameters	Initial membrane	Deposition time [min]			
		2	4	10	40
Thickness of deposited layer [nm]	—	60	120	300	1400
Relative increase in the mass [%]	—	1.1	2.4	5.6	11.3
Air flow rate at $\Delta P = 10^4$ Pa [ml/min cm ²]	280	210	115	60	25
Effective pore diameter [nm]	300	275	230	190	150
Water contact angle [deg]	120	110	110	115	154
Roughness, R_{ms} [nm]	34.7	23.2	30.6	36.8	56.8

Examination of the surface of the modified membranes by AFM (Figs. 1 and 2) shows that the polymer deposition occurs mainly on the sample surface. For the membranes treated for a short time, only an insignificant reduction of the pore diameter on the membrane surface is observed (Figs. 1b and 2b). The membrane pores are open in this case. In contrast, for a membrane treated for a long time a PTFE-like layer on the treated side covers the membrane pores (Figs. 1d and 2d). The essential reduction in the effective pore diameter for this membrane suggests that PTFE-like polymer is deposited not only on the membrane surface, but on the pore surface too with the pore shape being altered. According to the AFM data, the pore diameter on the back side of the membranes remains practically unchanged in our experiments. This means that the polymer is not deposited on

the surface of a part of the pore channel. Thus, the magnetron and electron-beam sputter deposition of the PTFE-like layer onto the PET TM and PP TM surfaces leads to a change in the pore geometry, namely, the pores acquire an asymmetric shape. The formation of membranes with asymmetric pores was observed in the case of deposition on the PET TM surface of the polymer obtained by plasma polymerization of 1,1,1,2-tetrafluoroethane. A significant decrease in the pore diameter on the surface of the composite membrane occurred in that case too [17].

The surface morphology and topography of the PTFE-like films deposited by the methods of MSD and EBD have some difference. The morphological properties of the PET TM surface after deposition PTFE-like film formed by MSD method vary drastically with increasing the deposition time, namely the surface aspect changes from the initial porous one (Fig. 1a), with rounded shape typical for track-etched membrane, to a completely coated membrane, with a film having a granular structure (Fig. 1d). The apparent pore diameter significantly decreases until the surface seems completely covered by the deposited PTFE-like film and their shape at surface changes from round to irregular. The surface roughness for the initial PET membrane is ~ 8 nm and increases slightly to ~ 10 nm for the lowest deposition time (10 min), due to the combination of deposition and pores presence. The lowest $R_{ms} \approx 3$ nm is determined for the longest deposition time (35 min), for which there are no pores on the membrane surface and thus the surface roughness is determined mostly by the deposition process and the membrane surface is smoothest. As comparison, the roughness of a PTFE-like film deposited on a silicon plate under the same experimental conditions is 1.3 nm.

Unlike MSD, polymer formed by EBD of PTFE results in formation of a polymer film with more advanced relief of a surface. We can easily appreciate that the surface topography of PP track-etched membranes covered by PTFE-like film varies significantly with the deposition time (Fig. 2). The observed difference can be associated with the size of polymer particles to be deposited. In the case of EBD, the polymer particles can be substantially bigger; therefore, the PTFE-like layer deposited by this method has more globular character. The globules, constituting the porous system of the layer, are polymer nanoclusters with an irregular shape and a size ranging from 100 to 400 nm. The micro-relief of the membrane surface is changed significantly. Characterization of the surface topography of the modified membranes using AFM shows a changing of the surface relief upon treatment. For the initial PP membrane, the root-mean-square deviation of the surface profile R_{ms} is equal to 34.7 nm. In order to remove the pore influence in the determination of surface roughness, smaller areas without pores, was measured in this case. The standard deviation of the surface profile R_{ms} for the modified membrane for 2 min is estimated at 23.2 nm. A polymer layer formed on the PP TM surface during the

deposition for 4 and 10 min has the R_{ms} value of 30.6 and 36.8 nm accordingly. More long deposition time leads to rise of R_{ms} value to 56.8 nm.

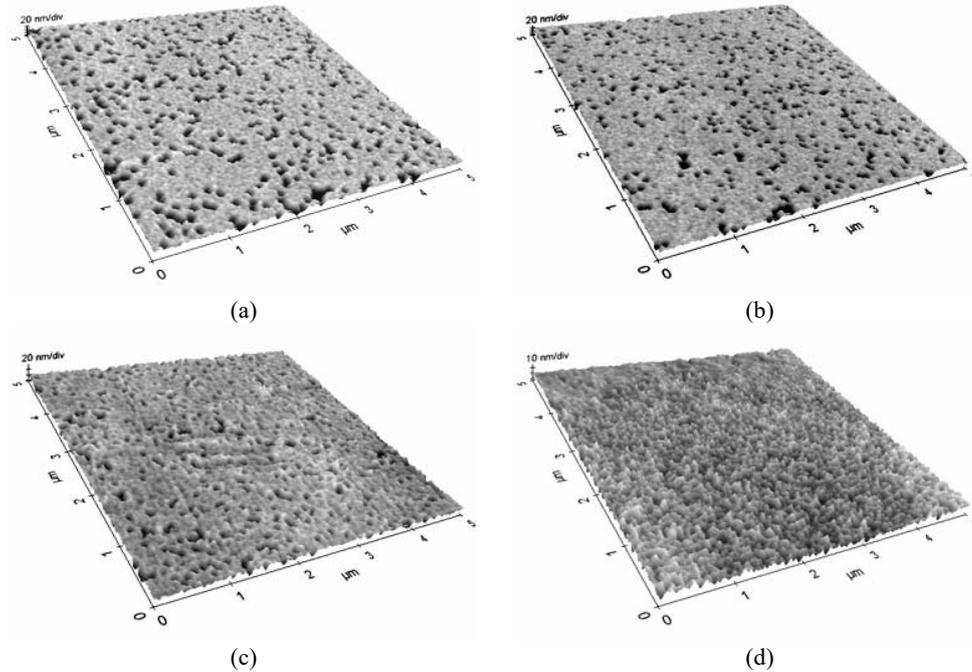


Fig. 1 – AFM images of the surface of the initial PET TM (a) and the membranes after deposition the polymer layer by magnetron sputtering of PTFE for 10 (b), 20 (c) and 35 min (d).

Research on the surface properties of initial track-etched membranes has shown that PET TM is characterized by an average level hydrophilicity. A water contact angle (Θ) for the membrane surface is 65° . For initial PP TM $\Theta = 120^\circ$, *i.e.* this membrane has hydrophobic properties. Note that this value was calculated by Young's equation [18], which is applicable to the case of a perfectly smooth surface that is chemically inert with respect to the test liquid. In the case of pronounced roughness or porosity of a solid surface, the contact angle observed is not the true angle characterizing the adhesion between the solid and the liquid, but it is rather an apparent angle. The roughness or porosity of solid surface increases the apparent contact angle relative to the true angle if the latter is greater than 90° . Otherwise, the apparent contact angle becomes less than the true angle [19]. A track-etched membrane has a porous surface, which means that the true value of the contact angle on PP TM is different from the value given above. For the virgin PP film, $\Theta = 97^\circ$. This means that it is the membrane structure and the presence of pores that are responsible for the increase of the contact angle to 120° .

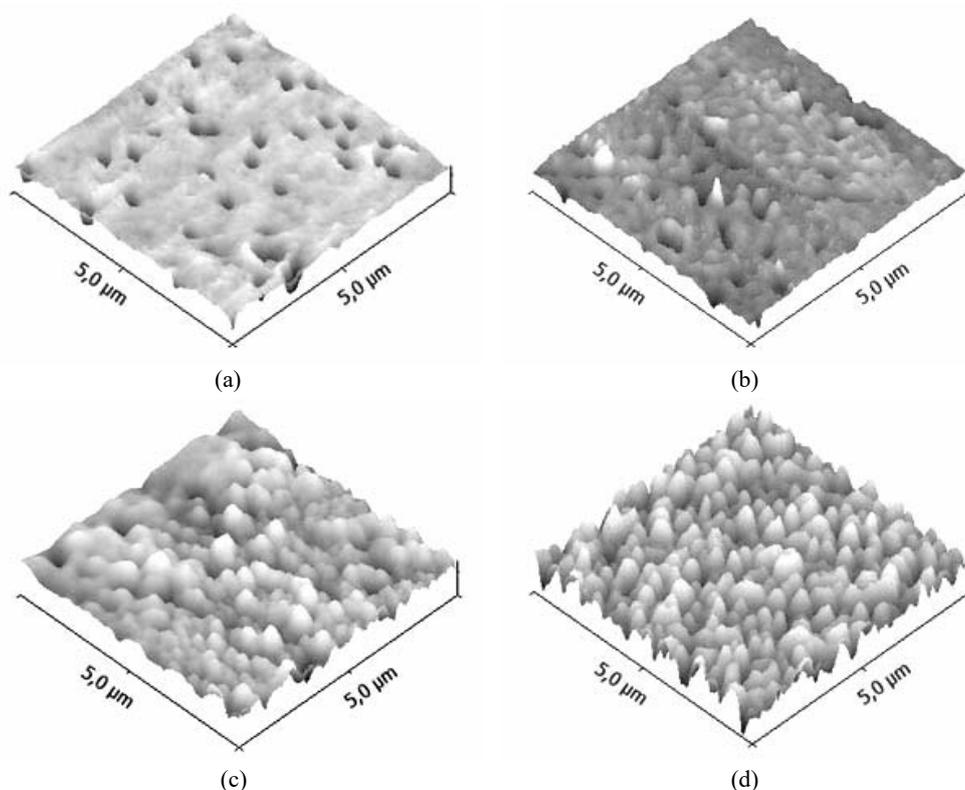


Fig. 2 – AFM images of the initial PP TM (a) and membranes after deposition onto its surface of polymer layer by electron-beam sputter deposition of PTFE for 2 (b), 4 (c) and 10 min (d).

In order to perform the characterization of the chemical structure of porous substrates, the XPS spectra were recorded. The surface composition of the initial membranes is shown in Table 3. For PET TM we can see the presence of the peaks due to carbon and oxygen atoms in the XPS spectrum. The XPS spectrum of the surface layer of the initial PP TM shows the presence of peaks associated not only with carbon, but also with oxygen and a minor amount of nitrogen. Chromium atoms were also detected on the surface of the unmodified membrane. The presence of oxygen atoms in the composition of the initial membrane is apparently due to the chemical oxidation of the polymer surface layer with a strong oxidant, the solution containing hexavalent chromium compounds, which was used as an etchant in membrane fabrication [13]. The presence of chromium atoms is also associated with chemical etching, which leads to chemisorption of chromium compounds on the membrane surface. The presence of nitrogen atoms is probably due to the presence of antioxidants (*e.g.*, hindered amines) as additives in the PP film used for preparing the track-etched membrane.

Table 3

XPS data for initial track-etched membranes

Membrane	Concentration of atoms [at %]			
	C	O	N	Cr
PET TM	74.5	25.5	—	—
PP TM	93.2	5.7	0.8	0.3

To elucidate the nature of the functional groups on the surface of the initial membranes, the associated C1s spectra were studied in detail. Deconvolution of C1s spectrum of PET TM (Fig. 3a) evidences the presence of the following bonds: C–C and C–H at 284.6 eV, which dominates the spectrum with an atomic percentage of the bond of almost 66%, C–O at 286.3 eV (18.3%), and C=O bonds from ester groups at 288.7 eV (15.7%). The deconvolution of the C1s spectrum of PP TM (Fig. 3b) shows that it has a complex pattern due to the presence of C–C and C–H bonds (284.5 eV) with a concentration of 98.4% and 1.6% of oxygen-containing O–C–O and C–OH functional groups (286.9 eV) in the surface layer. More significant concentration of oxygen-containing functional groups onto PET TM surface in comparison with PP TM surface defines the higher hydrophilicity of its surface.

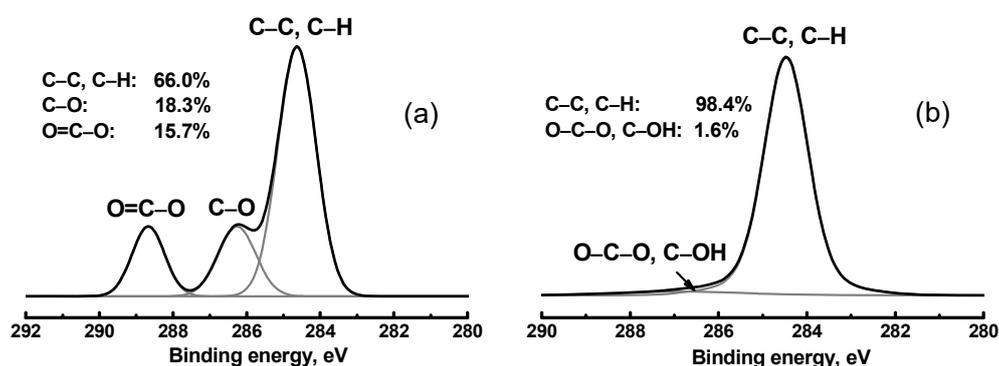


Fig. 3 – C1s spectra of initial PET TM (a) and PP TM (b).

The study of the surface properties of the composite membranes has shown that the deposition of the PTFE-like film onto PET TM surface leads to substantial hydrophobization. The water contact angle for the PET TM with a PTFE-like layer obtained by MSD method averages 111° (Table 1). The atomic composition of virgin PTFE and PTFE-like films with the 120 nm thickness obtained by MSD and EBD methods, as determined from the XPS survey spectra interpretation, is reported in Table 4, which includes as well the ratio between fluorine and carbon atomic concentration (F/C ratio). For the virgin PTFE, we found upon XPS measurements that F/C ratio is 2.16, while for magnetron deposited PTFE-like films the F/C ratio is not exceeding 1.1, even for long deposition times, as our

experimental results previously showed [10]. This lower value of F/C ratio for the deposited PTFE could be explained by two reasons. One is due to carbon contamination, which is unavoidable in the natural environment and thus causes a higher amount of detected carbon elements in the XPS spectra, especially for materials which are deposited by MSD due to the unsaturated chemical bonds from the surface. The second reason is referring to the MSD process, where the fluorine atoms ejected from the target can be pumped out from the deposition chamber, either in atomic form, or upon recombination in volatile compounds.

Table 4

XPS data for composition of PTFE-like films

Sample	Concentration of atoms [at %]				F/C ration
	F	C	O	N	
Virgin PTFE	68.4	31.6	—	—	2.16
PTFE-like obtained by MSD	49.8	45.7	3.4	1.1	1.1
PTFE-like obtained by EBD	64.5	35.5	—	—	1.8

The high resolution C1s spectra recorded for the virgin PTFE (Fig. 4a) was decomposed into two components (292.1 and 285.4 eV), corresponding to CF₂ groups and C–C bonds, suggesting the simple chemical structure of this material. The C1s spectrum of the PET TM covered by PTFE-like film obtained by MSD method for 10 min is displayed in Fig. 4b. In this case, the C1s spectrum was decomposed in five components, corresponding to the presence in the polymer of the following bonds: C–C (284.5 eV) with a concentration of 20.4%; C–CF (286.6 eV), 26.2%; C–F₂ (292.1 eV) with a concentration of 20.0%; C–F (288.9 eV), 23.4%; and respectively C–F₃ (293.3 eV) with 10.0% concentration. Such decomposition reveals the pronounced crosslinking for magnetron sputtered materials, which can be explained by the sputtering process itself; namely, upon polymer target bombardment with Ar⁺ ions, various atoms, ions and radicals based on C and F atoms from the PTFE target are present in the reaction chamber and once reaching the substrate the polymeric film growth is taking place. Note, presence of the peak answering to binding energy of 286.6 eV is caused, probably, to the presence at polymer oxygen-containing groups, such as C–OH and C–OR. It explains lower value of water contact angle in comparison with virgin PTFE.

Thus, the deposition of the PTFE-like layer onto PET TM surface leads to the formation of the composite membranes consisting of two layers, one of which is the initial PET matrix bearing terminal carboxyl groups on the surface and having an average level of hydrophilicity. The value of pK_{COOH} for PET is 3.6–3.7; *i.e.*, these groups undergo dissociation in a potassium chloride solution (pH 6.0). The dissociation leads to appearance of a negative charge on segments of the macromolecules, which facilitates the swelling of the membrane surface layer and the formation of a polyelectrolyte gel. The other layer deposited by magnetron sputtering of PTFE has hydrophobic properties. However, it contains a small amount of ionizable functional groups.

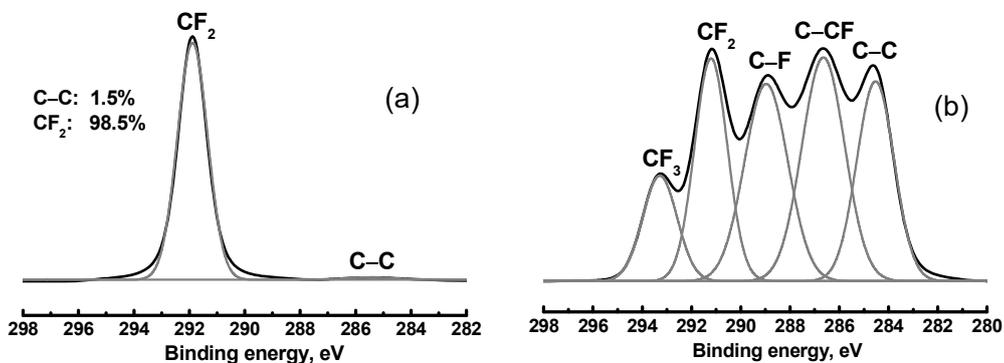


Fig. 4 – C1s spectra of virgin PTFE (a) and PTFE-like film deposited by magnetron sputtering of PTFE for 10 min (b).

Comparison of the contact properties of the initial PP TM and membranes modified by EBD method shows that there are no significant changes in the water contact angle if the PTFE-like film deposited on the surface has a thickness of 60–300 nm. Indeed, the initial PP TM has a value of $\Theta = 120^\circ$. For the composite membranes with a PTFE-like layer thickness of 60–120 nm, $\Theta = 110^\circ$; as the layer thickness increases to 300 nm, the value of Θ increases to 115° . This means that the deposition of the PTFE-like film by EBD method on the PP TM surface yields composite membranes containing two hydrophobic layers. The most interesting result is observed in the case of formation of an ordered, rough, textured PTFE-like film with a thickness of 1400 nm on the PP track-etched membrane surface. The contact angle significantly increases to become 154° . Thus, in this case, we observe the formation of a composite membrane with one of the layers having superhydrophobic properties [20, 21].

The XPS study of the chemical structure of the PTFE-like layer deposited on the PP TM surface by EBD method shows the presence of peaks associated with carbon and fluorine atoms (Table 4). This polymer does not contain oxygen atoms, unlike the one obtained *via* magnetron sputtering of PTFE. Theoretically, the ratio of fluorine to carbon atoms in PTFE is 2; however, this ratio for the polymer layer obtained via EBD of PTFE is 1.8, indicating the detachment of a number of fluorine atoms during the deposition. A detailed analysis of the C1s spectrum (Fig. 5) shows that it has a complex pattern due to the presence in the polymer of the following chemical bonds: C–C (284.8 eV) with a concentration of 2.8%; C–CF (287.5 eV), 6.4%; C–F₂ (292.1 eV), with a majority concentration of 69.8%; CF–CF (289.8 eV), 10.7%; and C–F₃ (293.9 eV), with a concentration of 10.3%, respectively. Comparison of these experimental data with the results obtained for the polymer layers deposited by the MSD method (Fig. 6) shows that the polymer obtained by the EBD method, is resembling more with respect to the chemical composition to virgin PTFE.

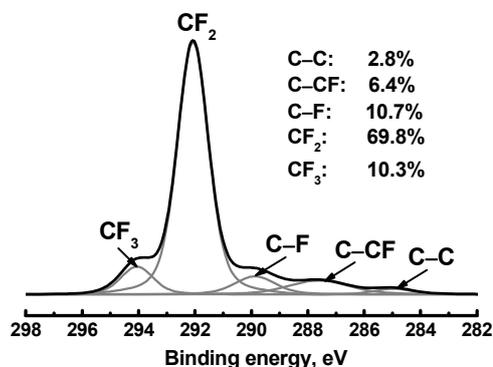


Fig. 5 – C1s spectrum of the PTFE-like film deposited by the method of EBD.

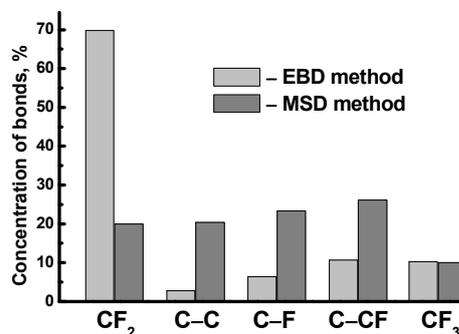


Fig. 6 – Concentration of carbon bonds in PTFE-like films obtained by the methods of EBD and MSD.

The results of measurement of current-voltage characteristics show that the conductivity of the initial membranes is independent of the direction of current (Fig. 7a). In contrast, the analysis of the current-voltage curves of the composite membranes show that its conductivity depends upon the current direction (Figs. 7 and 8). This means that the deposition of a hydrophobic polymer layer on the surface of the both PET and PP track-etched membranes imparts the asymmetry of conductivity, the rectifying effect. The magnitude of this effect is characterized by the coefficient of rectification (k_r), which is defined as the ratio of the current at potentials of +1 and -1 V. The research shows that the rectification coefficient for the composite membranes depends upon the concentration of the electrolyte. For example, for the PET TM with the PTFE-like layer thickness of 60 nm in KCl solution with a concentration of 10^{-1} mol/L a coefficient of rectification is equal to 2.1, and in the solution with a concentration of 10^{-2} mol/L it is 1.9 (Fig. 7b). For the PET membrane with the PTFE-like layer of 180 nm thickness these values are 3.8 and 3.6 accordingly (Fig. 7d).

The rectification coefficient for PP membrane with a PTFE-like layer of 60 nm thickness in a KCl solution with concentration of 10^{-2} mol/L is equal to 1.3, while for a solution with concentration of 10^{-3} mol/L it is 1.2 (Fig. 8a). The k_r value for a membrane with a PTFE-like layer of 120 nm thickness in a KCl solution with a concentration of 10^{-1} mol/L is equal to 1.8, and in a solution with a concentration of 10^{-2} mol/L it reaches 2.4 (Fig. 7b). The appearance of the asymmetry of conductivity for membranes of this type is apparently due to the existence of an interface between the initial membrane and the deposited polymer layer. This can be seen from experimental data on the electrochemical properties of a composite membrane with a 60 nm thickness PTFE-like layer, for which the pore diameter on the surface and the effective pore diameter do not change practically. However, the deposition of a PTFE-like layer of this thickness leads to a decrease

in the current value compared to the initial membrane, and also to the appearance of the asymmetry of conductivity. With the deposition of a 120 nm thickness PTFE-like layer, the formation of conical pores with the noticeable decrease in their diameter at the aperture of pore is observed. In this case, the reason for the asymmetry of conductivity (Fig. 8b) may be a change in the geometry of the pores and a substantial decrease in their diameter in the deposited polymer layer. The deposition of a thicker PTFE-like layer leads not only to a decrease in the current in the system, but also to an increase in the rectification coefficient for composite membranes (Figs. 8c and d). Thus, k_r for a membrane with a PTFE-like layer of 300 nm thickness in a KCl solution with a concentration of 10^{-2} mol/L is equal to 2.4, and in a solution with a concentration of 10^{-1} mol/L it is 3.6. For a membrane with a PTFE-like layer of 1400 nm thickness, k_r in a KCl solution with a concentration of 10^{-2} mol/L is equal to 9.1, and in a solution with a concentration of 10^{-1} mol/L it goes up to 11.0. From the data shown in Fig. 8, it follows also that in the region of positive potentials, composite membranes with a PTFE-like layer of 300 and 1400 nm thickness (the surface of the membranes with PTFE-like layer faces to the cathode) have practically the same electrical conductivity in electrolyte solutions.

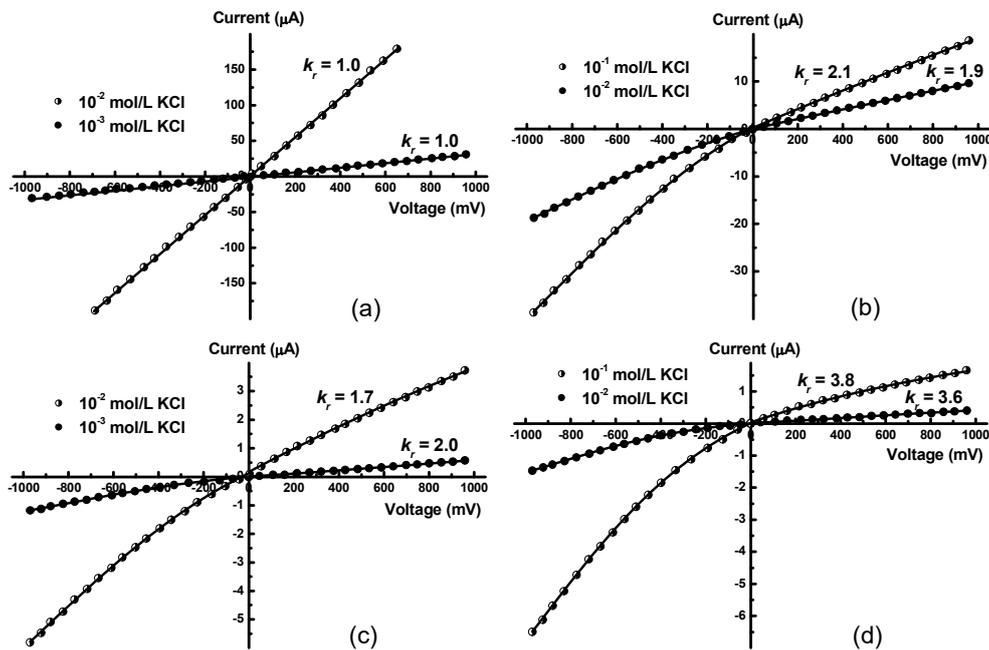


Fig. 7 – Current-voltage curves for initial PET TM (a) and membranes with deposited PTFE-like layer with the thickness of 60 (b), 120 (c) and 180 nm (d) in KCl solutions of different concentration.

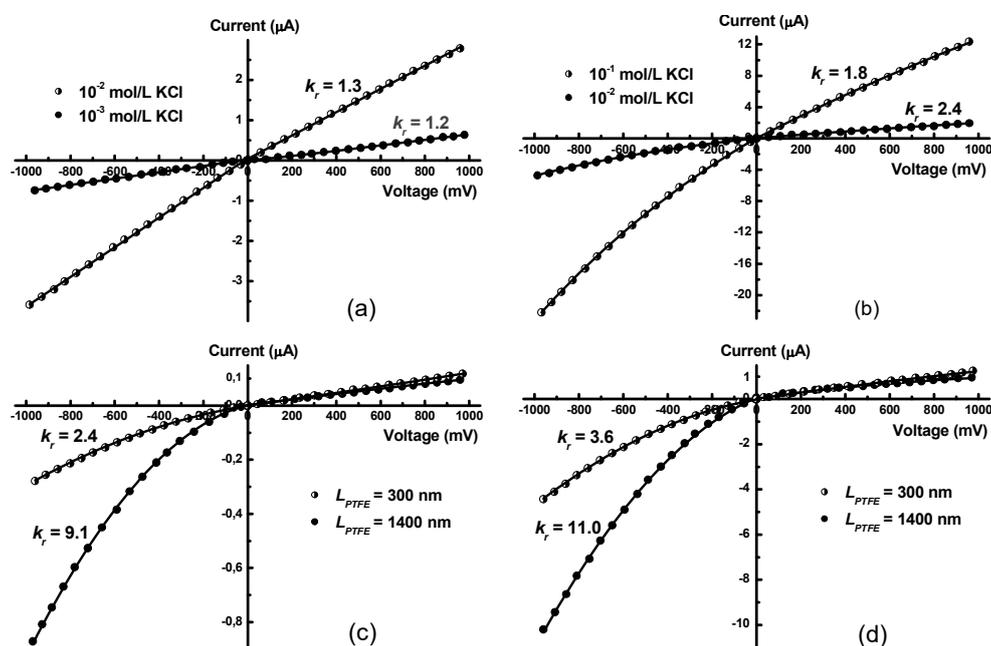


Fig. 8 – Current-voltage curves for PP TM after deposition of PTFE-like layer with the thickness of 60 (a) and 120 nm (b) in KCl solutions different concentration; PP TM after deposition PTFE-like layer with the thickness (L_{PTFE}) of 300 and 1400 nm in KCl solution with concentration of 10^{-2} (c) and 10^{-1} mol/L (d).

However, when negative potential is imposed to the composite membranes in the electrolyte solution under the action of a direct current (the surface of the membranes with PTFE-like layer is in this case facing to the anode) for a membrane with a PTFE-like layer of 1400 nm thickness, despite the smaller diameter pores compared to a membrane with a PTFE-like layer of 300 nm thickness, a higher electrical conductivity is observed. It should be noted that a membrane with a PTFE-like layer of 1400 nm thickness possess superhydrophobic properties. In this case, the increase of the conductivity of the composite membrane is due to the possibility of slipping of the electrolyte solution along the superhydrophobic surface [22, 23], which, as is known, has a significant effect on the transport phenomena near a solid surface [24, 25]. Experiments conducted using the latest techniques led to the conclusion that water can slide on a superhydrophobic surface [26, 27], thereby increasing the flow velocity in superhydrophobic nanochannels. This is due to the complex relief (topography) of the superhydrophobic surface, which can stabilize the bubbles of the gas phase inside the cavities of this relief. The presence of the gas phase, causing a decrease in the viscous resistance, allows the electrolyte solutions to slip on the areas of contact with the gas [28].

In this paper, we have considered only the qualitative effects in the change of electrotransport properties of a hydrophilic PET and hydrophobic PP track-etched

membranes by applying a hydrophobic PTFE-like layer on its surface on the basis of which it is impossible to judge the mechanism of charge transport across composite membranes containing hydrophobic layers. For decision of this question it is necessary to use additional electrochemical methods, in particular the impedance spectroscopy, allowing to investigate the processes of charge transport across membranes under electric current. Nonetheless, the observed effects may be a guide to designing of polymer composite membranes with asymmetry of conductivity, and are supposed to be the subject of further, more detailed studies.

4. CONCLUSION

In summary, the formation of a hydrophobic fluorinated polymer layer on one side of a track-etched PET and PP track-etched membranes by the methods of MSD and EBD of PTFE results in a composite membrane exhibiting asymmetric conduction in an electrolyte solution, the rectification or diode-like effect. This is due to both a reduction in the pore diameter in the deposited polymer layer, resulting in a change in the pore geometry, and the presence of an interface in the pores between the initial membranes and the deposited polymer layer.

Comparison of XPS data has shown that the PTFE-like polymers obtained by MSD and EBD methods present different chemical composition and size of recombination particles that is thought to result from the difference in types of particles sputtered from targets in each process. Polymer obtained by the MSD method conduct to a complex chemical composition with various CF_x bonds ($x = 1-3$), while EBD method presents a chemical composition more resembling to virgin PTFE. In this method case, a higher concentration of CF_2 chemical groups and significantly lower concentrations of the C-CF and CF_3 groups are observed compared to the polymer deposited by the magnetron sputtering. The AFM data showed a difference in the morphology of the films produced by these coating methods, which is connected to the size of the deposited polymer particles. Particles formed under the electron beam action of PTFE have noticeably larger size than those produced by magnetron sputtering of the polymer. This leads to an increase in the surface roughness of the deposited coating that allows forming a superhydrophobic polymer layer on the membrane surface.

These types of membranes can be used for creation of chemical and biochemical sensors. Besides, the composite membranes consisting from PET hydrophilic porous substrate and PTFE hydrophobic top layer can be employed in various separation processes, such as desalination of water, pervaporation, reverse osmosis, micro- and nanofiltration. On the other hand, the composite membranes on the basis of PP TM presenting hydrophobic behavior on both sides can be employed in separation processes of oxidant mixtures or harsh solvents mixtures and as separators in the production of alkaline and lithium-ion batteries.

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