Composite membranes with the hydrophobic and hydrophilic layers

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Abstract. The synthesis and characterization of polymer composite membranes with hydrophilic porous substrate and hydrophobic top layer were studied. To prepare the composite membranes a polytetrafluoroethylene thin film has been applied by the technique of electron-beam sputtering deposition in vacuum on one side of a poly(ethylene terephthalate) track-etched membrane used as a porous substrate. It was found that polymer deposition on the membrane surface results in the creation of composite membranes that possess asymmetric conductivity in electrolyte solutions – a rectification effect similar to that of a p-n junction in semiconductors. This effect is caused by decreasing the pore diameter in the deposited polymer layer that results in change of the pore geometry, as well as existence in the pores of an interface between two layers with different nature.

1. Introduction

The research on the properties of composite membranes, in particular two-layered ones, which are characterized by the presence of two layers with different 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 two-layered membranes concern the biological membranes, membranes with the modified surface, ion-exchange membranes consisting of two cationite or two anionite layers of different nature as well as bipolar membranes consisting of two layers with antipolar conductivity. The main distinctive feature of two-layered membranes is the anisotropy of their structure and physicochemical properties. The diffusion flow of the salt through them and the forming diffusion potential differ from one another depending on the orientation of layers relative to the diffusion flow direction. When the membrane simultaneously is under the effect of both gradients of concentration and electric fields, the value of electric current passing through a membrane also depends on a disposition of the layers. These phenomena, which are typical for two-layered membranes, make transport properties asymmetric.

For example, studying the electrotransport properties of track-etched membrane (TM) from poly(ethylene terephthalate) (PET) modified by thiophene [1] and pyrrole [2] plasmas has been shown that such treatment leads to formation of composite membranes that possess asymmetry of conductivity in electrolyte solution – a rectification effect similar to that of a p-n junction in semiconductors. It is explained by a specific structure due to the presence of two layers with functional groups differing in chemical structure and properties. Indeed, the original membrane surface bears cation-exchange carboxyl groups [3], whereas the layer synthesized by plasma...
polymerization of pyrrole or thiophene contains anion-exchange nitrogen- or sulfur-containing groups, respectively. The contact of such layers with the support membranes gives rise to the unique property of conduction asymmetry. It is due to the presence of functional groups on the surfaces of both the base membrane and the plasma-deposited polymer layers, which determine the appearance of electric charge on them in electrolyte solutions, which leads to the asymmetry of conductivity.

At the same time, it is of great interest to develop methods for producing two-layered composite membranes in which one layer is hydrophobic and investigate the electrical transport properties of such systems. In this respect in some papers were investigated the properties of PET TM modified by plasmas of acetylene [2] and 1,1,1,2-tetrafluoroethane [4], which do not contain functional groups. However, it was found that the treatment by plasma of these compounds leads to the formation of composite membranes whose plasma-deposited layers bear carboxyl groups on the surface. The formation of oxygen-containing functional groups, such as COOH, in the polymers obtained by plasma is associated with both the presence of residual oxygen in the vacuum reaction chamber and oxidation of the samples during their exposure to air. The resulting effect of asymmetry in two-layered composite membranes of this type is primarily due to the contact of two layers having different concentrations of carboxyl groups in the surface layer.

In the present paper, we describe the synthesis and characterization of polymer composite membranes with hydrophilic porous substrate and hydrophobic top layer. To prepare the composite membranes a polytetrafluoroethylene (PTFE) thin film has been applied by the technique of electron-beam sputtering deposition in vacuum on one side of a poly(ethylene terephthalate) track-etched membrane used as a porous substrate.

2. Experimental details

In the present experiments, PET TM samples with a thickness of 9.5 μm and an effective pore diameter of 250 nm (pore density 2×10^5 cm^−2) were used. To produce the membrane, poly(ethylene terephthalate) film with a thickness of 10.0 μm (Lavsan, Russia) was irradiated by krypton positive ions, accelerated to ~3 MeV/nucleon at the cyclotron. 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.

PTFE layers were applied onto membrane surface by physical vapor deposition using electron-beam sputtering of the polymer in vacuum. 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)×10^4 m^2. The initial pressure of residual gases in the vacuum chamber was ~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 PTFE deposition rate was about 35 nm/min.

The characteristics of the original 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. 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 5×5 μm. The main parameter to be determine a surface roughness was root-mean-square deviation of the surface profile (Rq), calculated over all scan points. For each sample, scans of the surface at five different points were obtained and the Rq value was then averaged. The surface properties were characterized by values of the contact angle 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 ±1°). 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 concentration of KCl was varied in the range of $10^{-4}$ to $10^{-1}$ mol/L.

The chemical composition of the deposited PTFE layer was studied by X-ray photoelectron spectroscopy (XPS) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. 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 (AlKα = 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). The FTIR reflection spectra were measured on a Thermo Nicolet Nexus 6700 infrared spectrometer in the range of 400-2000 cm$^{-1}$ with an optical resolution of 4 cm$^{-1}$ (digital resolution of 1 cm$^{-1}$), by averaging 32 scans. The assignment of absorption bands was carried out according to published data [5]. In order to record the XPS and FTIR-spectra of the PTFE obtained by electron-beam dispersion, the polymer was deposited on a silicon plate of 10×15 mm size.

3. Results and discussion

The characteristics measured for the original PET TM and the membranes prepared by applying a polymer layer using electron-beam sputter deposition of PTFE are shown in the table 1, where all results are expressed as means standard deviations of values from triplicate experiments. From these data, it follows that the deposition of the PTFE layer on the PET TM surface leads to a gradual increase in mass of the sample with the increasing time of the process. The thickness of the membrane increases and the effective pore diameter decreases in this case. Thus, during its deposition for 4.5 min, the thickness of applied PTFE layer reaches 150 nm and the effective pore diameter decreases by 55 nm. In the case of membrane treatment for 7 min, the thickness of the deposited PTFE layer is 250 nm and the effective pore diameter decreases by 75 nm. 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 that of the original PET TM.

| Parameters                                    | Original membrane | Modified membrane (min) |
|-----------------------------------------------|-------------------|-------------------------|
| Relative increase in the mass (%)             | –                 | 2.9 ± 0.1               |
| Thickness of deposited layer (nm)             | –                 | 150 ± 5                 |
| Air flow rate at $\Delta P=2\times10^4$ Pa (ml/min cm$^2$) | 300 ± 5           | 125 ± 3                 |
| Effective pore diameter (nm)                  | 250 ± 7           | 195 ± 5                 |
| Water contact angle (deg)                     | 65 ± 1            | 115 ± 1                 |
| Roughness, $R_q$ (nm)                         | 2.1 ± 0.2         | 13.1 ± 1.2              |

Figure 1. 3D AFM-images of the surface of the original PET TM (a) and the membranes after deposition the polymer layer by electron-beam sputtering of PTFE for 4.5 (b) and 7 min (c).
Examination of the surface of the modified membranes using AFM (figure 1) shows that the polymer deposition occurs mainly on the sample surface. For a membrane treated for 4.5 min, only an insignificant reduction of the pore diameter on the membrane surface is observed (figure 1b). The membrane pores are open in this case. In contrast, for a membrane treated for 7 min a PTFE layer on the treated side covers the membrane pores (figure 1c). Moreover, from the AFM data it follows that the deposited surface PTFE layer has 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. Characterization of the surface topography of the modified membranes using AFM shows a changing of the surface relief upon treatment. For the original membrane, the root-mean-square deviation of the surface profile \( R_s \) is equal to 2.1 ± 0.2 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 \( R_q \) for the modified membrane for 4.5 min is estimated at 13.1 ± 2 nm. A polymer layer formed on the PET TM surface during the deposition for 7 min has the \( R_q \) value of 30.5 ± 2.3 nm. In addition, according to the AFM data, the pore diameter on the backside of the modified membrane remains unchanged. This means that the polymer is deposited only of a part of the pore surface.

### Table 2. Atomic compositions of the membrane layers.

| Sample               | Atomic concentration (at.%) | Atomic ratio       |
|----------------------|-----------------------------|--------------------|
|                      | C   | O   | F   | C/O | F/C |
| Original PET TM      | 74.5 | 25.5 | –   | 2.9 | –   |
| Deposited PTFE layer | 35.5 | –   | 64.5 | –   | 1.8 |

![Figure 2](attachment:image.png)

**Figure 2.** Carbon (C1s) spectra of the polymer obtained by electron-beam sputter deposition of PTFE in vacuum (a) and the original PET TM (b).

The study of the surface properties of the membranes has shown that the deposition of the PTFE film leads to substantial hydrophobization. The original membrane has the water contact angle (\( \theta \)) of 65°, whereas the PET TM with a PTFE layer on the surface has \( \theta = 115° \) for the membrane treated for 4.5 min and 140° for the membrane treated for 7 min. An increase of contact angle can be explained by increasing the roughness in this case [6]. To chemical structure of the polymer obtained by the electron-beam sputter deposition of PTFE in vacuum was determined using XPS spectroscopic measurements. Analysis of the XPS spectrum of the PTFE layer shows the presence of the peaks due to carbon and fluorine atoms (table 2). Unlike the material obtained by plasma polymerization of 1,1,1,2-tetrafluoroethane, this polymer does not contain oxygen atoms. It is due to the formation of a certain amount of polar oxygen-containing groups during the plasma polymerization of 1,1,1,2-tetrafluoroethane that is responsible for a lower value of \( \theta_{\text{water}} = 88° \) [4]. Theoretically, the fluorine to
carbon atomic ratio in PTFE is equal to 2. In the polymer layer obtained by sputter deposition of PTFE, this ratio is 1.8, indicating the detachment of a certain amount of fluorine atoms during the deposition. A detailed analysis of the C1s spectrum (figure 2a) shows that it has a complex pattern due to the presence of C–C bonds (284.8 eV), C–F2 (292.1 eV), C*–CF (287.5 eV), C*F–CF (289.8 eV) and C–F3 (293.9 eV). Presence of the last testifies to presence in the polymer of macromolecules with short chains.

Examination by FTIR spectroscopy of the chemical structure of the polymer obtained by the electron-beam sputtering of PTFE in vacuum has shown resemblance of its IR spectrum (figure 3) to the well documented spectrum of starting PTFE [7]. The IR spectrum of PTFE displays the most intense bands at 1154 and 1210 cm\(^{-1}\) due to symmetric and asymmetric stretching vibrations of CF\(_2\) groups and a shoulder at 1233 cm\(^{-1}\) due to C–C stretching. In the low-frequency range, there are a 634 cm\(^{-1}\) band due to wagging vibrations of CF\(_2\) groups and bands at 551 and 520 cm\(^{-1}\) due to CF\(_2\) bending and rocking vibrations, respectively. All of the these bands are observed in the IR spectrum of the polymer sample prepared by the electron-beam sputter deposition of PTFE, indicating similarity in structure of the polymers in question. It is known that the PTFE molecule is a zigzag chain made of CF\(_2\) units and folded into a helix with an angle of deviation from the plane of 17°. The presence of dextro- and levorotatory helices in the polymer structure is manifested by bands at 640 and 622 cm\(^{-1}\), and an intense band at 502 cm\(^{-1}\) indicates a substantial degree of crystallinity of the sample. Similar absorption bands are observed in the spectrum of the polymer obtained by the electron-beam sputter deposition of PTFE, but their intensity is much lower. Thus, it may be assumed that the degree of crystallinity of the polymer structure is lower than that of the original PTFE. In addition, the most significant differences in spectra between the test polymers are the differences in intensity between the bands at 985 and 1786 cm\(^{-1}\), which are due to symmetric stretching vibrations of –CF\(_3\) groups (985 cm\(^{-1}\)) and stretching vibrations of –CF=CF\(_2\) groups (1786 cm\(^{-1}\)). A measurable intensity of these bands in the spectrum of the deposited polymer indicates the presence of macromolecules with short chains in the sample. Thus, the PTFE layer deposited on the PET TM surface is mainly made from polymer chains composed of –CF\(_2\)– units as the initial polytetrafluoroethylene. There are also macromolecules with substantially shorter chains, as evidenced by noticeable concentrations of the –CF\(_3\) and –CF=CF\(_2\) end groups.

![Figure 3. FTIR spectra of the polymer obtained by electron-beam sputter deposition of PTFE in vacuum (1) and the polymer used for sputter deposition (2).](image_url)

To characterization of the chemical structure of porous substrate, the XPS spectrum was recorded also. The surface composition of the original PET TM is shown in table 2. We can see the presence of the peaks due to carbon and oxygen atoms in the XPS spectrum. Figure 2b shows the detailed structure of the carbon C1s peak for the original PET TM. The peak consists of three sub-peaks belonging to the C–C and C–H bonds (284.6 eV), to the C–O bond (286.3 eV) and to the O=C–O bond from the ester
group (288.7 eV). Thus, the deposition of the PTFE layer onto the PET TM surface leads to the formation of the composite membrane consisting of two layers, one of which is the original 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 electron-beam sputtering of PTFE does not contain ionizable functional groups and has hydrophobic properties.

![Figure 4](image.png)

**Figure 4.** Current-voltage characteristics of the PET TM with the PTFE layers various thickness (L) in KCl solution with concentrations of \(10^{-1}\) (a) and \(10^{-2}\) mol/L (b).

The results of measurement of current-voltage characteristics for the test composite membranes show that its conductivity depends upon the current direction (figure 4). At the same time, as shows our results [1, 2] the conductivity of the original PET TM is independent of the direction of current. This means that the deposition of a hydrophobic polymer layer on the surface of the PET track-etched membrane imparts conduction asymmetry, 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 membrane with the PTFE layer thickness of 150 nm in KCl solution with a concentration of \(10^{-1}\) mol/L equals 1.8, and in the solution with a concentration \(10^{-2}\) mol/L it is 4.4. For the membrane with the PTFE layer thickness of 250 nm these values are 2.3 and 4.7 accordingly.

According to our earlier studies of the properties of track-etched membranes modified by pyrrole and acetylene plasmas [2], the asymmetry effect is caused by a significant reduction in the diameter of pores in the deposited polymer layer, resulting in a change of the pore geometry. The appearance of the conduction asymmetry for these membranes can also be associated with the existence of the interface between the original membrane and the deposited polymer layer. The interface is due to the presence of functional groups of different polarities in the surface layer in the case of plasma polymerization of pyrrole or different concentrations of carboxyl groups in the case of acetylene plasma polymerization. The PTFE layer in the composite membrane based on PET TM, as our results show, does not contain functional groups. Apparently, the main cause of the conduction asymmetry in this case is a decrease in pore diameter in the polymer layer deposited in the pores and resulting in a change in their geometry: the cylindrical PET TM pores acquire an asymmetrical shape during the deposition of the PTFE layer. In our opinion, for the description of the electrochemical properties of composite membranes with hydrophobic top layer should also be taken into account the phenomenon of slippage of the electrolyte solution on the hydrophobic surface [6]. Latest experiments led to the conclusion that water can slide on a hydrophobic surface [8] thereby increasing the flow velocity in hydrophobic nanochannels. The increase is because hydrophobic surfaces have a rather complex relief and can stabilize gas bubbles in cavities of the relief. Therefore, the appearance of conduction asymmetry for PET TM with a surface layer of the polymer having hydrophobic properties can be
interpreted as follows. When exposing the composite membrane in a solution of electrolyte to negative potentials under the action of the direct electric current (when the membrane surface on which the PTFE layer was deposited, was turned to the anode), a significant decrease in the resistance of the system is observed. It is caused by changing the number of the ions transferred in each layer of the membrane and appearing of a concentration polarization effect. So, $K^+$ ions in this case, due to the slippage, easily pass the hydrophilic layer of PTFE. The number of the $K^+$ ions transferred in the pores of the initial membrane, apparently, is a little bit less than the number of these ions transfers in the PTFE layer, because in the case of a smooth hydrophilic surface no slippage effect takes place. This leads to accumulation of ions in the pore volume on the boundary of the PTFE layer and PET TM. $Cl^-$ ions moving in the opposite direction are also accumulated in the pore volume on the boundary of this layer and PET TM, since the number of anions transferred through the gel phase with the anion parts is lower than in a solution of electrolyte. Increase of the local $KCl$ concentration on the boundary of the PTFE layer and the polymer matrix of PET TM promotes a current transfer.

When exposing the composite membrane in the electrolyte solution to positive potentials (the membrane surface on which PTFE was deposited is turned to the cathode in this case) under action of direct electric current, an increase of the resistance of the system is observed. At such orientation of the composite membrane, there is a fast transfer of $K^+$ ions through the PTFE layer from the pore volume into the solution. This leads to decreasing their local concentration on the boundary of this layer and PET TM. Compensation of ions from the volume of the electrolyte solution looks difficult, since the number of $K^+$ ions in the pores of the initial membrane, apparently, is less than the number of the ions transferred in the PTFE layer in view of slippage along the hydrophobic surface. The motion of $Cl^-$ ions to the anode also leads to decreasing their concentration in the membranes pore volume on the boundary of the PTFE layer and PET TM. It causes decreasing the local concentration of $Cl^-$ ions on the boundary of PTFE layer and polymer matrix PET TM thus leading to reduction of current in the system.

4. Conclusion
In summary, the formation of a hydrophobic polymer layer on one side of a track-etched PET membrane by electron-beam sputter deposition of PTFE results in a composite membrane exhibiting asymmetry of conduction in an electrolyte solution, the rectification 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 substrate membrane and the polymer layer, which have different wettability. In description of the electrochemical properties of membranes of this kind, the phenomenon of slippage of an electrolyte solution on the hydrophobic surface should be taken into account along with the electrostatic interactions between the electrolyte ions and the charge existing on the pore walls.

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