Structure and electrochemical properties of track membranes with a polymer layer obtained by plasma polymerization of acetylene

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Abstract. The structure and electrochemical properties of poly(ethylene terephthalate) track membrane modified by acetylene plasma were studied. It was found that polymer deposition on the surface of a track membrane by plasma polymerization of acetylene results in the creation of composite membranes that, in the case of formation of a thin semipermeable layer, possess an asymmetry of conductivity in electrolyte solutions – a rectification effect. It is caused by the reduction of the pores diameter due to the plasma polymer that results in changing the pore geometry, and as well due to the existence of an interface between the initial membrane and the polymer layer which have various concentrations of carboxyl groups.

1. Introduction
Membrane processes have found wide application in many areas of science and technology, such as gas separation, desalination of water, pervaporation, separation and isolation of individual solutes, and purification and concentration of biologically active substances [1]. Prominent among the variety of the membranes used in these processes are polymer membranes. However, the properties of existing membranes are frequently inconsistent with the requirements of industrial processing technologies, since the range of polymers suitable for the manufacture of membranes is limited. To extend the application area of commercial membranes, research works on the modification of their properties are performed. The most popular technique used for this purpose is the treatment of membranes in low-temperature plasma [2]; an important advantage offered by this process is the possibility of modifying a thin surface layer, which alters membrane properties, namely, the adsorption, transport, and selectivity properties. This possibility substantially extends the application area of membranes. The bulk of the membrane matrix remains intact in this case, which is undoubtedly very important from the viewpoint of retention of its mechanical and physicochemical properties.

The low-temperature plasma treatment entails a number of physicochemical processes, depending of the discharge type (frequency) and the nature of the plasma gas, which makes it possible to control in a desired mode the structure and the chemical composition of the surface of polymer membranes [3]. Chemical processes that occur during modification in the surface membrane layers are largely determined by the gas-phase composition of plasma. Two kinds of plasma are used, the plasmas of simple gases that do not result in the formation of polymers (non-polymerizing gases) and the plasma produced by discharge in vapors of any organic or organoelement compound that leads to polymer
formation [4]. When various organic vapors are used for the plasma treatment of membranes, a thin polymer film is deposited on their surface as a result of polymerization. In this case, composite membranes consisting of the porous substrate and a plasma deposited polymer layer are produced. Depending on the plasma treatment time and the pore diameter of the parent membrane, composite ultra- and nanofiltration membranes and reverse osmosis membranes can be obtained [4]. In the latter case, a thin semipermeable layer, which completely covers the pores, is deposited on the surface. The possibility for controlling the thickness of the plasma deposited layer, which determines the selective properties of membranes, and a wide choice of organic compounds suitable for this process make this method especially promising. The surface properties of composite membranes obtained via plasma modification depend on the chemical compound used.

In this paper the structure and electrochemical properties of the membranes composed of a porous substrate and a polymer layer deposited by plasma polymerization of acetylene were studied, where the substrate was a poly(ethylene terephthalate) track membrane (PET TM).

2. Experimental details

In the present experiments, PET TM samples with a thickness of 9.5 μm and an effective pore diameter of 65 nm (pore density 3×10^9 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 maximum emission intensity at 310 nm. Chemical etching was performed in an alkaline (NaOH) aqueous solution (1.0 mol/L) at 75 °C for up to 4 min.

Acetylene was used as a monomer to obtain a polymer film by the plasma polymerization method. The deposition of the polymer thin film on the membrane surface from the acetylene was done in a plasma-chemical reactor using a RF-discharge in parallel plate configuration at the frequency of 13.56 MHz, gas pressure of 12 Pa, discharge power of 20 W, and treatment duration of 300 and 600 s. Before treatment, the chamber was vacuumed down to a residual pressure of 6.5 Pa. The acetylene vapors were carried into the reaction chamber by an argon gas flow. Disk-shaped membrane samples, with an area of 56 cm^2, were positioned on the grounded electrode at a 4-cm distance from the powered electrode. The treatment procedure and the scheme of this installation were described previously in [5]. Only one side of the membrane was subjected to the plasma treatment.

The characteristics of the initial membrane and of membranes with the deposited layer of plasma polymer were determined by different procedures. The amount of the polymer obtained by plasma on the membrane surface was defined by the gravimetric method. The thickness of the plasma polymer on the membrane surface was measured with an electronic counter of thickness Tesa Unit (Austria). 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 Knudsen equation. The study of the samples microstructure and the determination of the pore diameter at the membrane surface were conducted by SEM using a JSM-840 (JEOL). The changing of the wettability of the membrane was evaluated by measurement of the water contact angle. For this purpose the sessile drop method with a horizontal microscope equipped with a goniometer was applied. 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 with a scan rate of 100 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 procedure of the measurements is detailed elsewhere [5].

The chemical composition of the polymer obtained by plasma polymerization of acetylene was studied with ESCA and FTIR-spectroscopy. The ESCA spectra were recorded with a Riber SIA-100 spectrometer using the MAC-2 analyzer (MgKα, 100 W). The peaks’ positions (the binding energy values) were calibrated to the C1s standard peak (284.6 eV). FTIR reflection spectra were measured on a Bruker Equinox 50S Fourier-transform IR spectrometer with a MIRacle™ single reflection horizontal ATR attachment, using a ZnSe crystal, over the range of 400–4000 cm^-1; the data of 500
scans were collected with a scanning step size of 2 cm⁻¹. In order to record the ESCA and FTIR-spectra of the plasma polyacetylene, the polymer was deposited on a 10×15-mm silicon plate.

3. Results and discussion

The parameters of the membrane subjected to the acetylene plasma are presented in the table 1. The results show an increase of sample mass during plasma treatment on the PET TM surface. This increase is explained by the deposition of the layer of plasma polymerized acetylene (PPAc). The thickness of the membrane increases, and the effective pore diameter in this process decreases. The increasing thickness and decreasing effective pore diameter indicate that the deposition of polymer takes place both on the surface of the membrane and on the walls of its pores. Electron-microscopic research of the modified membranes (figure 1) shows that deposition of the polymer at the chosen gas pressure and discharge power occurs mainly on the sample surface. For a membrane treated for 300 s, only an insignificant reduction of the pore diameter on the membrane surface is observed (figure 1b). The membrane pores are open in this case, and the thickness of the deposited polymer layer on the surface is 70 nm (table 1). An increase in the plasma treatment time up to 600 s leads to an increase in the thickness of the deposited polymer layer to 150 nm. The membrane pores on the plasma treated side are covered by a PPAc layer in this case (figure 1c). SEM investigation of the cross-section of this membrane (figure 2c) shows that a thin PPAc layer is formed on its surface that blocks the pores. From the electron microscopy data, it also follows that for the modified membranes the pore diameter on the untreated side remains unchanged. Moreover, results of the parameters’ testing of modified membranes show that an effective pore diameter of the membrane formed at the plasma treatment time of 300 s decreases insignificant. On the contrary, the membrane formed at the plasma treatment time of 600 s has an effective pore diameter of 26 nm. It’s indicates that the pore diameter of a polymer layer deposited by plasma is much smaller than the ones of the initial membrane and pores get the asymmetric form.

Table 1. Change of the membrane characteristics during treatment by acetylene plasma.

| Parameters                          | Initial membrane | Plasma treatment time (s) |
|-------------------------------------|------------------|---------------------------|
|                                     |                  | 300 | 600 |
| Relative increase in the mass (%)   | –                | 3.7 | 8.2 |
| Thickness of deposited layer (nm)   | –                | 70  | 150 |
| Air flow rate at $\Delta P=3\times10^4$ Pa (ml/min cm²) | 165.0 | 95.0 | 10.0 |
| Effective pore diameter (nm)        | 65.0             | 54.5 | 26.0 |
| Water contact angle (deg)           | 65               | 67  | 65  |

From the SEM images of the membrane surface and cross-sections it was difficult to determine how the plasma polymer is deposited inside the PET TM pores. It was also difficult to present the pore geometry in the polymer layer. We can only suppose how the plasma polymer fills in the membrane pores. We suppose the plasma polymer coating tapers off quite rapidly in thickness as one descends into the pores from the pore entrances, but it was not possible to see this in the SEM images. Besides, we assume that short treatment time in plasma (300 s) leads to formation of a thin polymer film on the membrane surface and inside the pore entrances that does not cause significant decreasing the pore diameter. Increasing the deposition time to 600 s causes additional polymer growth on the surface that leads to significant reduction of the pore diameter in the plasma polymer layer. Probably, extended growth of the polymer film using longer deposition time may cover totally the pores on the membrane surface. Also, the research on the surface properties shows that for the modified TM no improvement of the wettability of the surface is observed. Indeed, if for the initial membrane the water contact angle is 65°, then for the modified membrane the value of the water contact angle is almost the same at 66°.
The analysis of the ESCA spectra of the PPAc film deposited directly on the silicon plate in the plasma reactor shows the presence of peaks related to atoms of carbon and insignificant contents of oxygen. The latter is possible due to the presence of residual oxygen in the vacuum reaction chamber and subsequent oxidation of PPAc on air that is characteristic for polymers synthesized by plasma [4]. A detailed analysis of C1s of the spectrum of PPAc samples shows that it has a complex character due to the presence in the polymer of C−C/C−H (284.4 eV) and −CH2− (283.5 eV) bonds as well as some bonds of C−O (286.1 eV) and O−C=O (288.9 eV). The presence of the last two groups means that part of the carbon atoms could be bound to oxygen. The deconvolution of the O1s peak indicates that the predominant groups are O=C (531.4 eV), C−O−C (532.8 eV) and −O−C− (534.6 eV). There is a small amount of ions O2− (529.9 eV) in the spectrum. It also means that part of carbon atoms is connected to oxygen. Apparently, these groups of atoms exist as functional end groups.

Figure 1. SEM photographs of the initial PET TM surface (a) and membranes treated by acetylene plasma for 300 (b) and 600 s (c).

Evaluation of the chemical composition of the plasma polymer by FTIR-spectroscopy shows absorptions compatible with the structure of ethylene. So, there are a band at 1600 cm−1 in the spectrum which corresponds to stretching vibrations of the bonds C=C in olefins, a band at 1300 cm−1, corresponding to in-plane bending of C−H in −CH=CH2, a band at 900 cm−1, corresponding to in-plane bending of the bond C−H in RCH=CH2. Besides, in the spectrum there are absorption bands which are characteristic for acetylene. So, the spectrum contains a band at 3300 cm−1 which corresponds to stretching vibrations of the bond C−H in H−C≡; bands at 2198 cm−1 and 2102 cm−1 corresponding to stretching vibrations of triple bond C=C in R′−C≡C−R and H−C≡C−R as well as a band at 609 cm−1 which can be related to in-plane bending of groups H−C≡C−. Apparently, these groups exist as end ones on the polymer macromolecules. Data of the FTIR-spectroscopy thus confirm that fact that olefin groups are the basic structural element of the polymer synthesized from acetylene plasma. In addition to that, in the spectrum one can observe an absorption band corresponding to stretching vibrations of bond C−H in satiated hydrocarbons: at 2953 cm−1 – asymmetric vibrations in CH3-groups, at 2928 cm−1 – asymmetric vibrations in CH2-groups and 2870 cm−1 – symmetric vibrations in CH2-groups. The spectrum also has the absorption bands corresponding to in-plane bending of CH3 and CH2-groups: 1452 cm−1 and 1376 cm−1, and a band at 750 cm−1 which answers rocking vibrations of CH2-groups. Apparently, these groups are formed as a result of cross-linking and recombination processes in the discharge. In the spectrum one can observe also an absorption band at 1020 cm−1 due to the stretching vibrations of groups C−O, a band at 1150 cm−1, corresponding to stretching vibrations of C−O−C and absorption at 1720 cm−1, corresponding to stretching vibrations bond C=O, most likely, of carboxyl groups. The presence of the carboxyl groups in the surface PPAc layer is proved also by the results of research by the ESCA method.

The deposition of polymer on the PET TM surface by plasma polymerization of acetylene thus leads to formation of composite membranes consisting of two layers. One of them, which corresponds to the initial membrane polymer matrix, has cation-exchange carboxyl groups on the surface [6]. In KCl solutions (pH of which is 6.0), dissociation of surface COOH-groups leads to formation of negatively-charged segments on the polymer macromolecules. The presence of a negative charge on
the macromolecular segment causes the surface layer to swell and a polyelectrolyte gel to form. The second layer synthesized by the plasma polymerization of acetylene also contains some cation-exchange carboxyl groups, as our results have shown. In the electrolyte solutions, dissociation of surface COOH-groups leads to formation of negatively-charged segments on the polymer chains too and formation of a polyelectrolyte gel. Certainly, the volume of the gel in this case is much less than the volume of the gel on the PET surface because the concentration of COOH-groups is lower on the plasma polymer surface.

![Figure 2](image1.png)

**Figure 2.** SEM photographs of the cross-sections taken at an angle 40° of the initial PET TM (a) and the membranes treated by acetylene plasma for 300 (b) and 600 s (c).

![Figure 3](image2.png)

**Figure 3.** Current-voltage characteristics of the initial PET TM and membrane treated by plasma for 300 s (a) and membrane treated by plasma for 600 s (b) in KCl solution with concentrations of $10^{-2}$ and $10^{-3}$ mol/L. On the inserts a membrane orientation is specified in the electric field.

The results of measuring the current-voltage characteristics of the membranes (figure 3) show that the conductivity of the initial track membrane does not depend on the current direction. The pores have symmetric (cylindrical) form in this case (figure 2a). The conductivity of the membrane treated by plasma for 300 s also does not depend on the current direction because the membrane structure does not change too much in this case – the pores also have practically a symmetric form. On the contrary, the analysis of current-voltage characteristics of the membrane treated by plasma for 600 s shows that its conductivity depends on the current direction. The size of rectifying effect can be characterized by a rectification coefficient ($k_r$) calculated as the ratio of values of the current in the opposite directions at a potential of 1 V. The research shows that the rectification coefficient for the membrane treated by plasma for 600 s in KCl solution with a concentration of $10^{-2}$ mol/L equals 2.5, and in the solution with a concentration $10^{-3}$ mol/L it is 2.0 (figure 3b). The obtained results can be explained as following. Firstly the pores of this membrane have asymmetric form. Besides, the pore diameter on the plasma treated side of membrane is much lower than the pore diameter of the initial membrane. Secondly in the composite membrane there is an interface between two layers – the initial membrane and the plasma polymer, which have various concentrations of carboxyl groups on their surface layer. Obviously, presence of this interface between layers may also be the reason of the
appearing of the conductivity asymmetry for track membranes with the layer of plasma polyacetylene on the surface. Therefore, appearing the asymmetry of conductivity for the composite membranes with a thin semipermeable PPAc layer on the surface can be interpreted as follows. Under a direct current (DC) reverse bias condition, when PPAc layer is inverted to the anode (figure 3b, lower insert), a significant decrease in the resistance of the system is observed. It is caused by the change of the transference number of counter ions in each layer of the membrane and appearance of the effect of concentration polarization. So, K⁺ ions in this case easily pass the gel phase of the PPAc layer as the transfer number for the cations in gel with anion segments is higher than in a solution. It leads to their accumulation in a wide area of pores of PPAc layer. Ions of Cl⁻ moving in an opposite direction also are accumulated in a wide part of the pores of this layer because the transfer number for the anions through the gel phase with anion segments is lower than in a solution of electrolyte. Increase of the local concentration of KCl in the left (wide) part of the pore channels of PPAc layer on the boundary of this layer and PET TM promotes the transfer of current.

Under the DC forward bias condition, when the PPAc layer is inverted to cathode (figure 3b, upper insert), one can observe increase of resistance of the system. It is caused by the following. At such orientation of the composite membrane there is a removal of K⁺ ions from the PPAc layer through gel phase that leads to decrease in the local concentration of these ions on the interface of this layer and PET TM. Their replenishment from the volume of electrolyte solution which is in the PET TM pores is complicated, since the transfer number of K⁺ ions in the pores of the initial membrane is a little bit lower than the transfer number of these ions in the gel phase of the PPAc layer. A similar phenomenon is observed for Cl⁻ ions – they are removed from pores, and their replenishment from the electrolyte solution through the gel phase of the PPAc layer is complicated. This also causes decrease of the local concentration of Cl⁻ ions in the wide part of the pore channels of the PPAc layer – on the boundary of this layer and the PET TM that leads to decreasing the current in the system.

4. Conclusion
Summarizing the obtained results, one can conclude that the conductivity of the initial PET track membrane in the electrolyte solutions does not depend on the current direction. The deposition of the polymer on its surface by the plasma polymerization of acetylene, resulting in formation of a thin semipermeable layer that blocks the pores, leads to the creation of a composite membrane possessing asymmetry of conductivity – a rectification effect. This effect is caused by an important reduction of the pore diameters in the plasma polymer that results in changing the pore geometry, as well as an existence of an interface between the initial membrane and the polymer layer, which separates regions with different concentrations of carboxyl groups. Membranes with such properties can be used to create chemical and biochemical sensors.

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