PROPERTIES OF DIODE-LIKE MEMBRANES PRODUCED BY PLASMA MODIFICATION

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Abstract

A new type of single bipolar membranes was obtained by plasma polymerization that possess asymmetry of conductivity – the effect of the current rectification similar to *p-n* transition in semiconductors. To produce membranes with diode-like properties, polymer layers formed from aniline by plasma were deposited on one side of poly(ethylene terephthalate) track membranes. In order to increase the rectification effect, this polymeric layer was doped by iodine.

1. Introduction

Much attention has been recently paid to research of the properties of bipolar membranes (BM) involving a cation-exchange membrane joined to an anion-exchange membrane. It is connected to a number of their unique properties. So, at a certain orientation in the electric field BM generate ions H^+ and OH^- what determines an opportunity of their use for producing acids and alkalis and also for realization of other chemical transformations with participation of hydrogen and hydroxyl ions. The presence of rectifying properties leads to creation of semi-conductor devices on their basis. The ability of selective passing through ions depending on sign and size of their charge makes it possible to use them for creation of various chemical sensors. Therefore, the development of new methods of BM obtaining is of doubtless interest. In this connection in a number of recent publications, attempts were undertaken in the development of new methods of BM obtaining. Initially, bipolar membranes were prepared by placing the cation- and anion-exchange membranes together ("sandwich membrane") [1, 2]. During recent years, some new bipolar membranes ("single membranes") were obtained by modification of industrially produced membranes. For this purpose, various physicochemical methods were used: chemical [3] or radiation-chemical grafting of polymers [4], preliminary activation of the surface by plasma with a subsequent grafting of polymer from the solution [5] and so forth.

In this paper, a bipolar membrane was prepared from poly(ethylene terephthalate) track membrane (PET TM) as a substrate by plasma polymerization of aniline on one side. PET track membranes were used as the substrate because they have excellent material properties and they are characterized by presence of cation–exchange carboxylic groups on the surface. So, the pores of these membranes are cylindrical channels, their cross-sections being practically independent of depth, that is the main advantage of membranes of this type. Aniline has been chosen as a monomer due to opportunity of obtaining of a polymeric layer with nitrogen-containing functional groups. Besides, it is known that polyaniline is a conducting polymer, its conductivity can be changed in a wide interval by doping (oxidation). In this connection, the study considers the chemical oxidation process of the polymeric covering obtained by plasma polymerization of aniline by iodine and investigates the properties of the membrane formed in this case. For polymer deposition we selected a direct-current discharge, since the preliminary research showed that the highest concentration of functional groups playing a defining role in the process of mass transfer under action of the electric current is obtained in this case.

2. Experimental

In experiments PET TM with the thickness of 9.5 μm and an effective pore diameter of 0.215 μm (pore density 2×10^{8} cm^{-2}) were used. In order to produce the membranes, poly(ethylene terephthalate) film was irradiated with krypton ions, accelerated in a cyclotron with the energy ~ 3 MeV/nucleon and then subjected to chemical etching of the tracks of these particles up to obtaining of the pores of the required size using the standard procedure [6]. Deposition of the polymer from aniline vapors on the PET TM surface was carried out by direct current discharge at pressure of monomer vapors of 26.6 Pa and the discharge current density of 0.1 mA/cm^2 during 120 s by technique [7]. Introduction of iodine in the membrane samples after plasma modification was made by their keeping for 30 min in a desiccator in the presence of saturated iodine vapors at 20°C.

The characteristics of the initial membrane and membranes with deposited layer of polymeric composite were determined through a series of complementary procedures. The amount of the polymer obtained by plasma on the membrane surface, determined by the relation

$$Q_g = (m_g - m_o)\cdot 100/m_o,$$

where m_o is the mass of initial membrane and m_g is the mass of membrane with the polymer layer obtained by plasma. The changing of the surface properties of the membranes was conducted by measurement of the contact angle. For this purpose the sessile drop method using a horizontal microscope equipped with a goniometer was applied. Water (doubly distilled) was used as a test liquid. Six measurements were made at different places on the membrane surface and averaged. The change of the membrane thickness was measured with an electronic counter of thickness “Tesa Unit” (Austria), the precision of the measuring being ± 0.1μm. The gas flow rate through the membranes (a flow of gas (air) passing the membrane with a square $1cm^2$) was defined at a pressure drop of 10^4 Pa. Gas consumption was measured by float-type flow meter. On the basis of the values obtained according to these experiments the gas-dynamical pore diameter (an effective pore diameter) was determined as described in [8]. The study of the samples microstructure as well as the definition of the pore diameter on the membrane surface was carried out by SEM using the JSM-840 (JEOL) with the resolution of 10 nm. Before scanning, a thin layer of gold was deposited by thermal evaporation of metal in vacuum.

The structure of the aniline polymer obtained by plasma (PPA) was studied by ESCA and FTIR-spectroscopy. The ESCA spectra were recorded with the spectrometer Riber SIA-100 with MAC-2 analyzer (MgK_a, 100 W, 15 kV, 20 mA). FTIR-spectra were recorded with a Bruker Equinox 50S spectrometer in the range of 400-4000 cm^{-1}, working with 500-fold accumulation of data and a scanning step of 2 cm^{-1}. Measurements of the current-voltage characteristics of membranes were carried out on a direct current in a two-chambered cell with platinum electrodes, containing a water solution of potassium chloride (KCl) of identical concentration 10^{-3} N on both sides of the membrane. The volume of each chamber was 2.5 ml, the working area of the membrane – 1 cm^2. The current-voltage characteristics of the membranes were measured within the range of voltage from −1 up to +1 V, each point of the kept corresponding to the average value of the current for 5-10 s after its exit on the plateau. Before the measurements, the membrane samples were maintained in a corresponding solution of electrolyte during 24 h.

3. Results and discussion

The results of the research on measuring the current-voltage characteristics of membranes are given in Fig. 1. It is seen that electric conductivity of the initial PET TM (curve 1) in the solution of KCl of the chosen concentration does not depend upon the current direction due to the symmetry of the membrane structure. The treatment of PET TM by aniline plasma leads to formation of a membrane possessing asymmetry of conductivity (Fig. 1, curve 2). The obtained results can be interpreted as follows. The treatment of the initial membrane by plasma leads to deposition of the polymer obtained by polymerization of aniline (PPA), both on the surface of the membrane and on the walls of its pores. The increase in the thickness of the membrane and decrease of its effective pore diameter testifies to this (Table 1). The mass of the membrane sample thus increases. For the modified membrane with the PPA layer the thickness of the polymer layer deposited by plasma is equal to ~500 nm and the change of the effective pore diameter is ~15 nm. It allows one to make a conclusion that deposition of the polymer in the discharge occurs mainly on the membrane surface. Moreover, as data of SEM research on the sample show that the polymer is uniformly deposited on the surface of the membrane, not changing its relief.

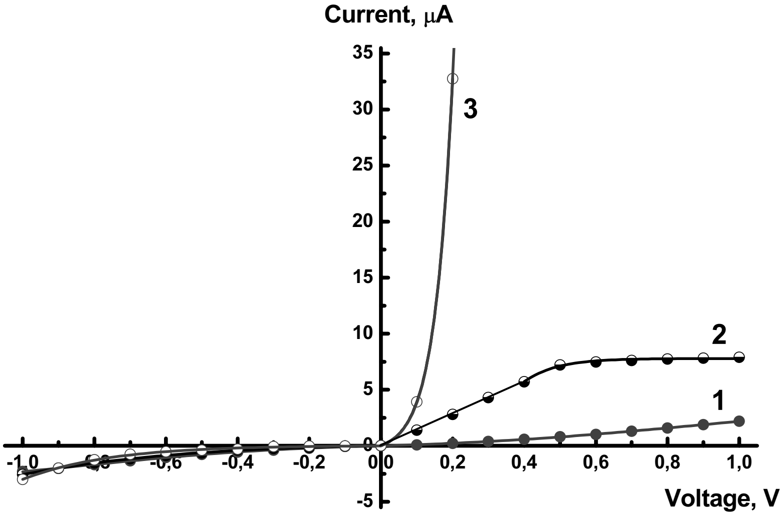

Fig. 1. Current-voltage characteristics of initial PET TM (1), modified by plasma of aniline (2) and doped with iodine after plasma treatment (3) using 10^{-3} N KCl as the electrolyte.

The analysis of the ESCA spectrum of PPA testifies to the presence of carbon, nitrogen atoms and a small content of oxygen. Thus the ratio of nitrogen to carbon atoms in the polymer is a little higher than in initial monomer. A small amount of oxygen in PPA can be explained by presence of residual oxygen in the working gas and also by subsequent oxidizing of PPA after plasma on air that is characteristic of polymers synthesized by plasma polymerization [9]. Research in the structure of PPA by FTIR-spectroscopy shows that absorption bands are characteristic at 3362 and 1633 cm^{-1}, which correspond to rocking and deformation oscillations of N–H groups. Absorption bands at 1600, 1500 and 1450 cm^{-1} corresponding to plane oscillations of aromatic rings, testify to their presence in structure of a polymeric circuit. Absorption bands at 830-840 cm^{-1} answer 1,4-disubstitution in a benzene ring; bands at 1316 and 1173 cm^{-1} correspond to bonds C–C and C=C and bands at 755 and 700 cm^{-1} – to bonds C–N in the diphenyl amine group. The latter are characteristic of completely restored leucoemeraldine form of polyaniline. Its chemical structure is presented in Fig. 2a. Thus, in the structure of the PPA obtained by plasma, there are nitrogen-containing groups which are capable to exchange mobile anions in solutions.

Table 1. Change of the membrane characteristics after treatment by plasma of aniline.

Type of membrane	Relative increase in the mass, %	Thickness, μm	Porosity, %	Effective pore diameter, μm	Contact angle by water, deg
Initial PET TM	–	9.5	7.25	0.215	65
PET TM with the PPA layer	5.5	10.0	6.30	0.200	82

On the basis of the presented data on FTIR-spectroscopy and ESCA one can see that the treatment of PET TM in the aniline plasma leads to formation of a composite membrane consisting of two layers with antipolar conductivity. Really, if the polymeric matrix of the initial membrane is characterized by presence of cation-exchange carboxyl groups on the surface, then the layer synthesized by plasma polymerization of aniline, as the research shows, contains anion-exchange nitrogen-containing groups. Besides, it has been shown above that deposition of the polymer occurs on the pore walls, too. For the modified membrane, the average thickness of the PPA layer deposited in pores is equal to ~ 7.5 nm. It is obvious that as a result of the chosen conditions for the modification carrying out, when only one membrane side is treated by plasma, a gradient of changing the deposited PPA layer thickness is formed in pores. Moreover, the thickness of the layer essentially decreases along pore channels and on the opposite side, which was not subjected to plasma treatment, becomes insignificantly small. Thus, in part of pore channels on the walls the content of surface carboxyl groups prevails over the content of nitrogen-containing groups. For we shall consider, however, that the place of the contact of cation-active COOH-groups and anion-active nitrogen-containing groups corresponds to the place of the contact of PET TM and the PPA layer.

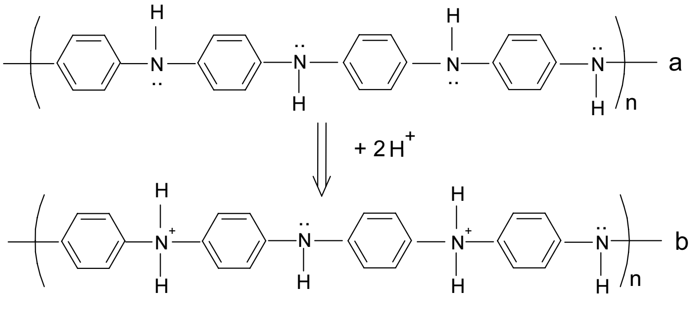

Fig. 2. Chemical structure of PPA in leucomeraldine form (a) and after its protonation in solution with ions H^{+} (b).

The dissociation of the surface COOH-groups in KCl water solution with pH=6.0 leads to appearing of anionic segments on the PET macromolecules (pK_{COOH} in PET is equal to 3.6-3.7). The forming protons join atoms of nitrogen in the PPA macromolecules thus causing formation of cationic segments. Thus, on the surface of pores of the modified membrane there are both polyanions and polycations that form polymeric hydrogels in the solution of potassium chloride. As a result of the microphase stratification in the pore channel there are two separate phases. One of them represents a polymeric hydrogel with negatively charged segments of PET containing anions COO^- and mobile counterions K^+, and the second – a PPA hydrogel having as a result of protonation of the nitrogen atoms positively charged segments, and counterions Cl^-. It is obvious, that in such a system the distribution of concentrating of the components of electrolyte (K^+ and Cl^-) will essentially depend upon the direction of the current, i.e. upon orientation of the membrane with respect to electrodes.

Under direct current (dc) forward bias the cations K^+ easily pass PET TM, meeting a potential barrier as a PPA layer for which they are co-ions. This effect is caused by reducing the number of transfer of the ions K^+ in the PPA layer. Thus in a place of contact of PET TM and the PPA layer the accumulation of ions K^+ occurs. A similar phenomenon is observed for anions Cl^- – they easily pass the PPA layer, but meet a potential barrier as PET TM since the transfer number for ions Cl^- is less, than in the layer of the initial membrane. At the predetermined current the accumulation of ions in the contact zone leads to their opposite diffusion flow. A stationary condition comes when sizes of the opposite diffusion flow of ions and a migratory current minus the current caused by co-ion movement, are leveled. For a binary symmetric electrolyte, concentration of ions increases linearly upon approaching the border of the layer dividing; the higher the current density, the faster the process. As a result, the transfer of co-ions and the conductivity of the composite membrane grow up. The diffusion flows of co-ions are directed outside the membrane. The origin of the limiting current on the right branch of the current-voltage characteristics (Fig. 1, curve 2) can be related to decreasing concentration of electrolyte in the boundary diffusion layers near the membrane due to the lack of hashing and with distinction of concentration of the fixed charges in PET TM and PPA layer. The latter testifies that we have an asymmetrical bipolar membrane. Measurements of the water contact angle (θ) confirm this conclusion. For PPA layer $\theta = 82^o$, i.e. it is more hydrophobic than PET TM. Hence, the concentration of anion-active nitrogen-containing groups in the PPA layer is lower than the concentration of cation-active COOH-groups in PET.

Under dc reverse bias the anion active layer of the membrane is inverted to the anode. At such orientation of the composite membrane there is a removal of ions of electrolyte from the contact zone. Their completions from an external solution do not occur, since ions K^+ and Cl^- meet a potential barrier as PPA and PET TM layer, accordingly. The concentration of ions here decreases with approaching PET TM border and PPA layer and is getting more considerable if the density of the current through the membrane is higher. The diffusion flows of co-ions in this case are directed inside the membrane. One could expect that decreasing of the concentration of co-ions down to zero will cause occurrence of a limiting current on the left branch of current-voltage characteristic of the modified membrane, however it does not occur. Apparently, in the range of potentials under study the concentration of co-ions in the contact zone of layers does not decrease down to zero, i.e. ion transfer takes place. It should be noted that the conductivity of the modified membrane in this case practically does not differ from the conductivity of the initial PET TM (Fig. 1). This can be caused by the fact that due to a significant pore diameter of this membrane the polyelectrolyte gel does not occupy the whole pore volume, i.e. it is located only on the pore walls.

The treatment of PET TM with PPA layer in iodine vapors leads to diffusion of the latter into the surface layers of membranes and into the pore volume too. The iodine contents in the composite membrane, according to ESCA data, is ~ 2×10^{18}см$^{-3}$. Introduction in PPA of iodine molecules, possessing high affinity to the electron, leads to the electron transferring from the nitrogen atom of the macromolecule of leucoemeraldine form of polyaniline to iodine [10]. Here a formation of ionic pairs occurs, each consists of a positively charged monomer segment and a counterion containing polyions of iodine of different types as J_3^-, J_5^-, etc. The presence of ionic pairs in the phase of the membrane causes changing of the electrotransport characteristics of the membrane. As experimental data show, under dc forward bias, the current in the system can grow up without limit (Fig. 1, curve 3). This is caused by the following reasons. First, introduction of iodine causes increase of a positive charge on the polymer macromolecules. Secondly, delocalization of the charge on the PPA macromolecules observed as a result of oxidation [10], leads to essential growth of the transfer number for anions Cl^- in this layer, i.e. the anion concentration in the place of contacting of PET TM and PPA layer sharply increases. Besides, the increase in the density of the positive charge on PPA causes decrease of the transfer number for ions K^+ in PPA layer, i.e. the cation concentration in the place of contacting of PET TM and PPA layer also grows. The opposite diffusion flows of counterions in each layer of the membrane in this case, apparently, are lower than for the modified membrane without doping. This is caused, probably, by formation at the interface of PET TM and PPA layer of associates – the ionic pairs. Such phenomena lead to decrease in the potential difference on the border of the phase dividing; therefore, the current caused by co-ions transfer, increases.

Under dc reverse bias in the modified membrane after doping that is in KCl solution, take places to exception iodine anions from the membrane phase. As a result, the conductivity of the modified membrane after the iodine doping, similar to the case of the modified membrane without doping, practically does not differ from the conductivity of the initial membrane.

4. Conclusion

Summing up the obtained results, we can make the following conclusions. The conductivity of the initial PET TM in KCl solution with concentration of 10^{-3} N does not depend on the direction of the current. Deposition of the PPA layer on its surface by plasma polymerization of aniline vapors in the direct current discharge leads to formation of a diode-like membrane that possesses asymmetry of conductivity – the rectification effect caused by presence of two layers with antipolar conductivity in it. Doping with iodine of the polymeric layer formed by plasma leads to an increase in the rectification effect what is caused by increasing of the positive charge density on the PPA macromolecules. This type membranes can be used for the development of chemical and biochemical sensors.

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