

Секция 3. Перспективные материалы и технологии

DEPOSITION OF NANOSIZED POLYMER FILMS BY ELECTRON-BEAM DISPERSION OF POLYTETRAFLUOROETHYLENE IN VACUUM ON THE TRACK MEMBRANE SURFACE

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ОСАЖДЕНИЕ НАНОРАЗМЕРНЫХ ПЛЕНОК ПОЛИМЕРА МЕТОДОМ ЭЛЕКТРОННО-ЛУЧЕВОГО ДИСПЕРГИРОВАНИЯ ПОЛИТЕТРАФТОРЭТИЛЕНА В ВАКУУМЕ НА ПОВЕРХНОСТЬ ТРЕКОВОЙ МЕМБРАНЫ

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***Аннотация.** Исследованы структурные и электрохимические свойства композитных мембран, образующихся при осаждении на поверхность полипропиленовой трековой мембраны слоя полимера, полученного электронно-лучевым диспергированием политетрафторэтилена в вакууме.*

In recent years great interest of the work, in which the questions of mass transfer under the action of electric current in track membranes from polyethylene terephthalate (PET TM) modified by plasma enhanced chemical polymerisation deposition on the surface of a thin film polymer of a different chemical nature [1, 2]. Thus, in [1] were investigated the properties of PET TM modified in the plasma pyrrole, and in [2] - in the plasma of thiophene. The initial PET TM is characterized by the presence on the surface of cation-exchange carboxyl groups [3], whereas in the layer obtained via polymerization of pyrrole in the plasma, contain anion-exchange nitrogen-containing groups [1] and in the layer obtained on the basis of the thiophene - sulfur-containing groups [2]. It is known that the contact ion-exchange membranes of opposite charges leads to asymmetry of conductivity - the effect of the current rectification similar to p-n junction in semiconductors [4].

With the aim of obtaining composite membranes containing hydrophobic layer, in [5] on one side of the membrane made of polypropylene (PP TM), which has a contact angle for water is $\theta = 120$ degree, applied a thin layer of hydrophilic polymer by polymerization in the plasma for vapour of pyrrole. In another case, on the surface of PET TM by method of electron beam dispersion of polytetrafluoroethylene (PTFE) in vacuum [6].

In the experiments used PP TM with an effective pore diameter of 300 nm obtained at the Joint Institute for nuclear research (Dubna) based on PP film Torayfan T2372 produced by "Toray" (Japan) with a nominal thickness of 10.0 μm . For membranes used PP film was irradiated at the cyclotron accelerated xenon ions (with an energy of 1 MeV/nucleon), ion fluence was 10^8 cm^{-2} . Chemical etching of the irradiated films to ob-

tain through pores was carried out at a temperature of 80 degrees in an aqueous solution of chromic anhydride with a concentration of 1000 g/l by the method of [7].

A thin layer of PTFE applied to the surface of PP TM deposition from the active gas phase by electron beam dispersing of polymer in vacuum. As the source of electrons used electron-beam gun with the direct channel cathode, which allows to form beams with a current density of 5-100 A/m², particle energy 0.5–2 Kev and cross-sectional area (5–10)×10⁻⁴ m². The initial pressure of the residual gases in the vacuum chamber was ~10⁻³ PA, the temperature of the substrate surface ~300 K, the emission current of 60 mA, the electron energy is 1.2 Kev.

As a target used a PTFE thickness of 10 mm and a diameter of 35 mm (JSC “Plast-polymer”, St.-Petersburg). The deposition rate of the coating PTFE was 10 nm/min, the time of the dispersion process varied. The scheme of installation and processing method described in detail by us in [7]. The characteristics of the initial and modified membranes were determined using a number of complementary techniques are described in detail in [1, 2]. When conducting the process within 6 min the thickness of the deposited layer of PTFE is 60 nm, and effectively pore diameter of the resulting composite membrane is reduced to 275 nm. The deposition of the polymer film thickness of 120 nm results in the decrease in pore diameter of the composite membrane to 230 nm.

Investigation of the surface of composite membranes with an electron microscope shows that the deposition of the polymer occurs predominantly at the surface of the samples (Fig. 1-3). For the membranes treated for 6 min, there is a slight decrease of pore diameter (Fig. 1б), whereas the membrane treated for 12 min, the decrease of the pore diameter is more significant (Fig. 1в). The study of the cross-cleavage of this membrane shows (Fig. 2в, 3) that the pores in the layer of deposited polymer is markedly narrowed, and the average pore diameter at the mouth is 50-60 nm.

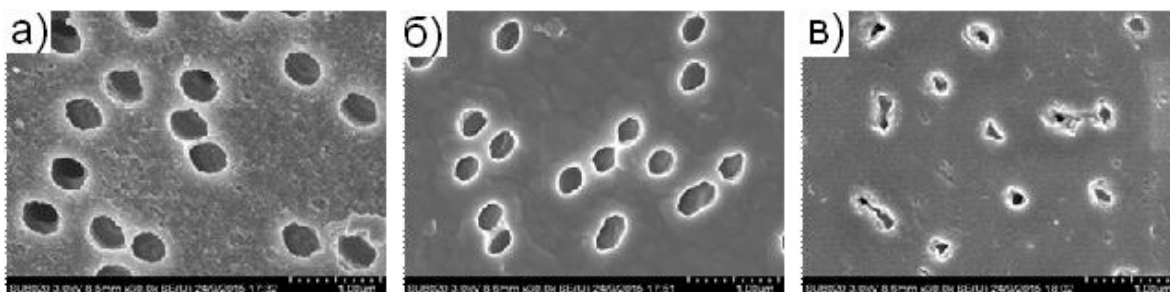


Figure 1 – Electronic micrograph of the surface of the original PP TM (a) and membranes with the deposited layer of PTFE with a thickness of 60 nm (б) and 120 nm (B); an increase 30000

The original PP TM is characterized by the magnitude of limiting wetting angle for water (θ) equal to 120 degrees. For composite membranes with a layer of PTFE value $\theta = 110$ degrees. This means that the deposition of a film of PTFE on the surface of PP TM leads to the formation of composite membranes containing two hydrophobic layers.

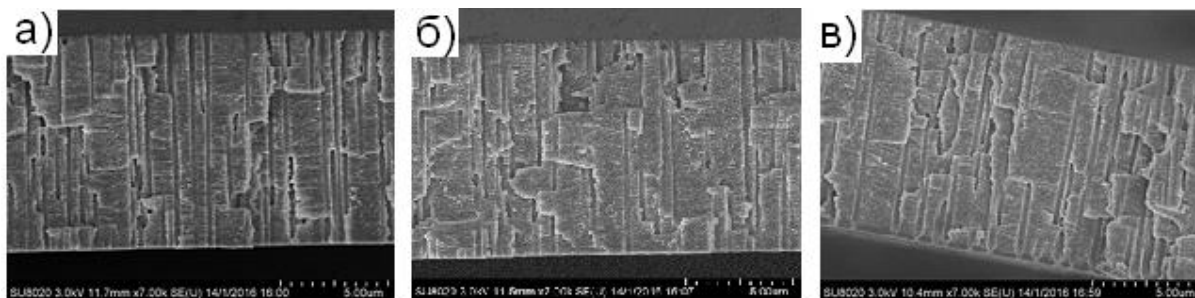


Figure 2 – Electronic micrograph of the transverse chips of the original PP TM (a) and membranes with the deposited layer of PTFE with a thickness of 60 nm (б) and 120 nm (в); an increase of 7,000

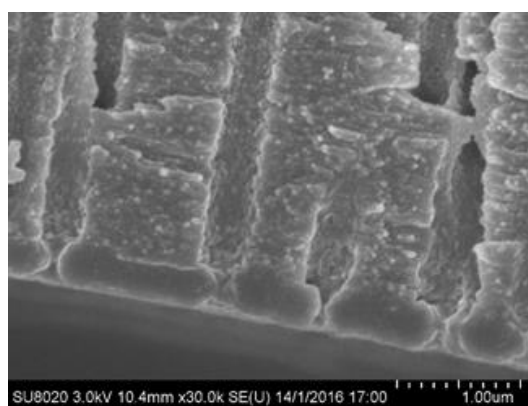


Figure 3 – Electron micrograph of transverse cleavage of the membrane with the deposited layer of PTFE with a thickness of 120 nm; an increase of 30000

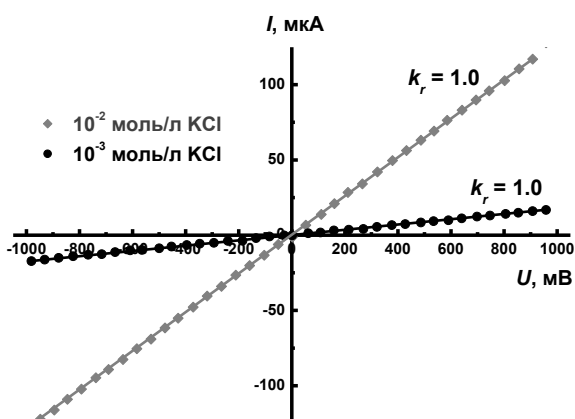


Figure 4 – Volt-ampere characteristics of the original PP TM in solutions of KCl with concentrations of 10^{-2} and 10^{-3} mol/l

The results of measuring current-voltage characteristics of the membranes show that the electrical conductivity of the source PP TM does not depend on the direction of the current (Fig. 4). In front of, the analysis of current-voltage characteristics of the modified membranes shows that their conductivity depends on the direction of the current (Fig. 5). The magnitude of this effect can be characterized by a coefficient straightening (k_r) calculated as the ratio of current in two opposite directions: the potentials of +1 and -1 V. The studies show that the coefficient straightening for the membrane with the layer of PTFE with a thickness of 60 nm in KCl solution with concentration 10^{-2} mol/l equal to 1.3, and in a solution with a concentration 10^{-3} mol/l – 1.2. The coefficient straightening for the membrane with the layer of PTFE with a thickness of 120 nm in KCl solution with a concentration of 10^{-1} mol/l is equal to 1.8, and in the solution with concentration 10^{-2} mol/l – 2.4.

This is indicated by the experimental data of the research of electrochemical properties of composite membranes with a layer of PTFE of a thickness of 60 nm, for which the diameter of the pores on the surface and the effective pore diameter remains almost unchanged. The deposition of the layer of PTFE with a thickness of 120 nm induces the

formation of conical pores. The diameter of the pores in the estuary of the composite membranes markedly reduced.

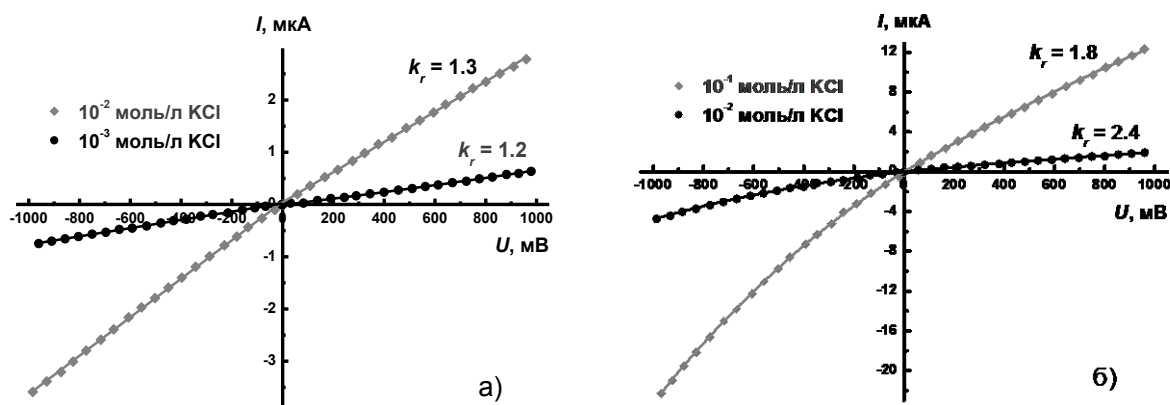


Figure 5 – Current-voltage characteristics PP TM membranes with the deposited layer of PTFE with a thickness of 60 nm (a) and 120 nm (б) in solutions of KCl with different concentrations

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