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The modification of PETF-membranes by Langmuir-Blodgett films of Nafion

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Abstract. In this research, the surfaces of track PETF-membranes were modified by Langmuir-Blodgett (LB) films of Nafion. The changes of structure of modified membranes were studied by atomic force microscopy (AFM). The LB-film of Nafion monolayer was found to be 30-100 nm thick. The incorporation of SiO_2 nanoparticles in LB-layer in small quantities was structuring the monolayer. The performance of water of PET-200 membranes with a Nafion film was increased to 401.3 ml/(m^2·h) from the initial values of 342.1 ml/(m^2·h). The air performance was increased for all modified PETF-200 membranes. The maximum performance was achieved by modifying the membranes with pure Nafion; the productivity was 154.3 ml/min compared with 96.4 ml/min for the initial membrane. It was shown that LB-films were stable during monitoring filtration characteristics.

1. Introduction

Membranes are used in various ways of water treatment [1], in micro-, ultra-, and nano-filtration and reverse osmosis, as well as in the processes of electro-deionization. Membranes hold up particles, bacteria, colloids, and solute (reverse osmosis and desalination processes). The development of an advanced technology for effective water treatment is an actual problem. The track membranes (TM) are the most interesting since they are characterized by a through pores system in a film with a thickness from 10 to 25 μm, of a uniform size, an identical shape, and a flat, smooth surface.

Due to these characteristics, TM have special properties and advantages over known polymer, metal, and ceramic membranes [2] used in microfiltration processes in medicine, biotechnology, microbiology, and virology [3]. PETF membranes are a commercial product with a well-developed production technology [4].

Their modification provides the principle possibilities to regulate TM properties, such as high throughput, selectivity, hydrophilicity, hydrophobicity, bactericidal activity, and allows enhancing the application area. One of the promising methods of surface modification is the sol-gel method. Organo-silicon compounds of various compositions [5] do not close the pores, but form a thin waterproof film on the membrane surface. The modified membranes are dried at room temperature and then in an oven for fixation of applied layer. If the modifier concentration in the solution increases, then the adsorption capacity of the TM decreases; that is explained by the formation of a hydrophobic layer on the membrane surface and leads to a decrease in throughput of the modified membrane in the water. In this case, the air performance of the TM after modification does not change, which is explained by the preservation of the pore space of the membrane. The Langmuir-Blodgett (LB) method makes it possible to incorporate various molecules and molecular complexes, including biologically active ones, into the monolayer [6]. Using this method, it is possible to change the surface properties of the monolayer and, as a result, to form the high-quality film coatings due to precise control of the thickness of the resulting film, uniformity of coating, low roughness, and high adhesion of the film to the surface [7]. The properties of the films can also be easily varied by changing the structure of polar head of amphiphilic molecule, composition of monolayer, and also conditions of release – composition of subphase and surface pressure. The formation of thin nanometre-thick coatings allows providing the surface of macroobjects with the required hydrophilic properties. The LB method is used to form the ion-exchange membranes, e.g., based on Nafion [8], which can be used as ion-selective electrodes, sensors, in electrodialysis, and in water treatment systems [9]. Nafion-modified membranes are also used in the development of fuel cells [10]. It was shown [11] that incorporation of silicon oxide nanoparticles in the Nafion structure allowed improving current-voltage characteristics, increasing thermal stability of the material, and decreasing the coefficient of thermal expansion.

The aim of this work is to modify the surface of PETF-membranes by LB-films of Nafion and nanostructured films with silicon dioxide nanoparticles to increase their water and gas throughput.

2. Experimental

In the experiment, track PETF-membranes with pores diameters 100 and 200 nm were modified. PETF-membranes were prepared in Kazakhstan by method described in article [12]. The initial material for production of TM was a 12 μm thick PET film irradiated with 1.75 MeV / nucleon of Kr-ion beams with a fluency of $1\cdot10^{6}$ cm^{-2} on a DC-60 cyclotron. All samples were additionally sensitized with a UV-lamp for 12 h on one side to accelerate etching of the irradiated material. UV-radiation led to photooxidation of the surface layer of the polymer. Transformation of highly defective regions (latent tracks) formed as a result of irradiation into pores was carried out by two-sided chemical etching in a 2.2 mol/l solution of NaOH at a temperature of 85 ± 1°C.

Nafion layers on the water sub phase were formed by horizontal LB method using device LB-Trough (Belarus). Nafion films were formed from initial Nafion suspension in low aliphatic alcohol (Nafion 1100 EW, Sigma-Aldrich) and diluted in two times with ethanol. The incorporation nanoparticles were provided by mix suspension of Nafion and suspension of silicon dioxide nanoparticles (d=10-20 nm, Sigma-Aldrich) in ethanol with concentration 1 mg/ml. Final suspension was kept in ultrasonic bath for 30 min to ensure that nanoparticles have uniform distribution. The ratio of the components in suspension is 1 g of Nafion to $3.9\cdot10^{-4}$ mol of SiO_2 nanoparticles. The pressure of thin films formation was defined on the base of isotherm of monolayer compression and presented in the Table 1. Thickness of Nafion films is 100 nm, thickness of films of diluted Nafion and nanostructured with silicon dioxide nanoparticles is 30 nm.

The structure of samples was investigated by atomic force microscopy (AFM) method using device NT-206 (Belarus) with NSC 11 A silicon cantilevers (Mikromasch, Estonia). The stiffness of cantilevers is 3 N/m, curvature radius is 10 nm. The contact angle of thin films was measured by sessile drop method using device DSA 100E (KRUSS, Germany). For this purpose, the drop of water with volume 2 μl was formed using automatically system of dosing.

Table 1. The pressure of films formation.

The type of film	(π +/-1), mN/m
Nafion	43
Nafion diluted (1 : 1 V)	33
Nafion + SiO_2 (1 g : $3,9\cdot10^{-4}$mol)	24

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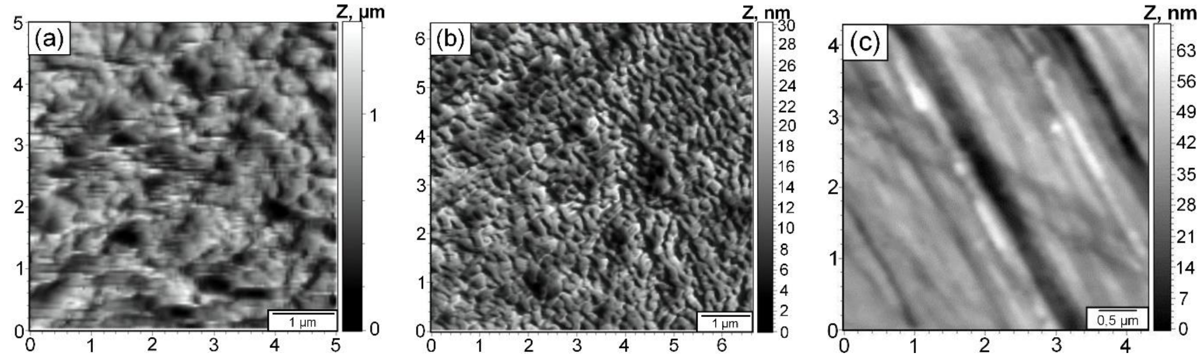

Figure 1. AFM-structure of LB-films: (a) Nafion, (b) diluted Nafion, and (c) Nafion with nanoparticles on silicon substrate.

The air throughput of initial and modified membranes was defined at a pressure drop of 0.02 MPa. The size of sample is 1 cm^2. The effective pore diameter was calculated by the gas performance, according to the formula:

$$r^3 = \frac{Q \cdot 3l}{\sqrt{\frac{2\pi}{R \cdot T \cdot M}} \cdot \Delta p \cdot 4n}, \tag{1}$$

where r – the radius of pores; Q – air performance; l – thickness of film; Δp – pressure; R – universal gas constant; M – molecular mass of air; n – radiation density; T – temperature.

The water performance was determined using deionized water (18 MΩ) and the pressure difference of 0.4 MPa. The size of samples is 2.54 cm^2. Performance was calculated using the Hagen-Poiseuille equation:

$$Q = \frac{n \cdot \pi \cdot r^4}{8\mu \cdot l} \cdot \Delta p, \tag{2}$$

where r – the radius of pores; l – thickness of film; Δp – pressure; n – radiation density; T – temperature, μ – dynamic fluid viscosity.

To identify the strength properties of the samples, we used the method of checking the tensile strength by increasing the flow of passing air through the membrane.

3. Results and discussion

As a result of studies of the structure of LB-films on the silicon substrates by AFM, it was shown that Nafion formed a dense and reticulate layer. The nanostructured films with nanoparticles had a directed structure determined by silicon dioxide nanoparticles (Fig. 1).

These surfaces were characterized by water contact angle of 70°. Free surface energy was 44 mJ/m^2 with prevailing polar component.

According to AFM-data, for track PETF-membranes a system of through pores with a diameter of 100 nm (Fig. 2a) and 200 nm (Fig. 3a) prevailed. In addition, interwoven fibres of the polymer were also visible on the surface. The surface of PETF membranes demonstrated the hydrophobic properties; the contact angle did not depend on pores diameter and was about 90°.

The structure of the modified membranes was similar to the initial surface. A dense layer of polyelectrolyte enveloped pores of the original membrane, thereby reducing their diameter by 10-20 nm. Wherein, the mean-square roughness values corresponded to those for the initial membranes. In comparison with the initial samples, the presence of thickened formations around the pores of the modified membrane was established. The Nafion monolayer obtained from a dilute suspension was less dense than the initial Nafion. As a result of modifying TM with Nafion films, the contact angle increased to 94°, thereby increasing the hydrophobic properties of the sample surface.

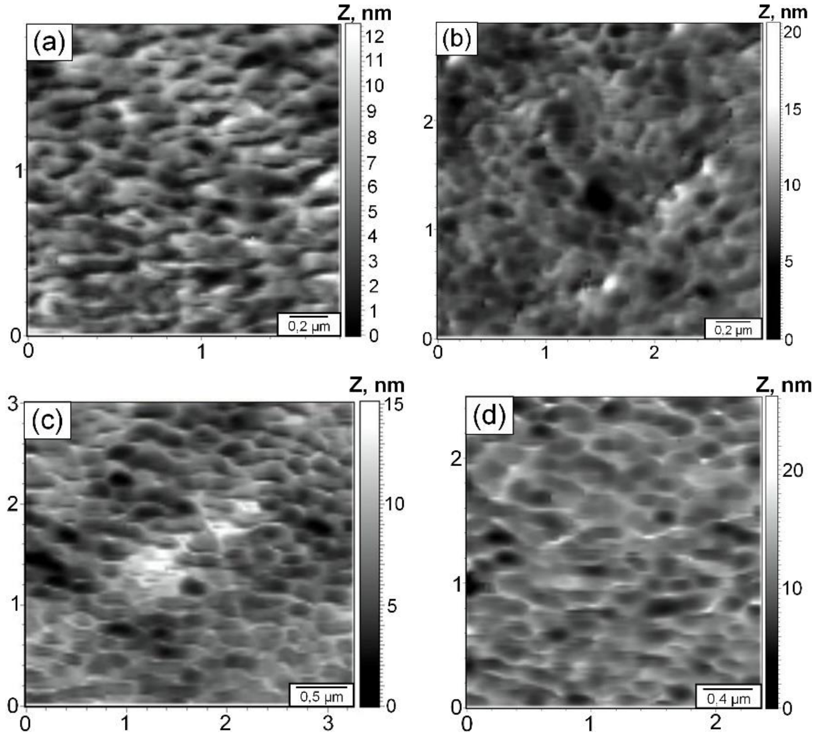

Figure 2. AFM images of the samples: (a) PETF-100; (b) PETF-100/Nafion; (c) PETF-100/Nafion$_{dil.}$; (d) PETF-100/(Nafion + npSiO$_2$).

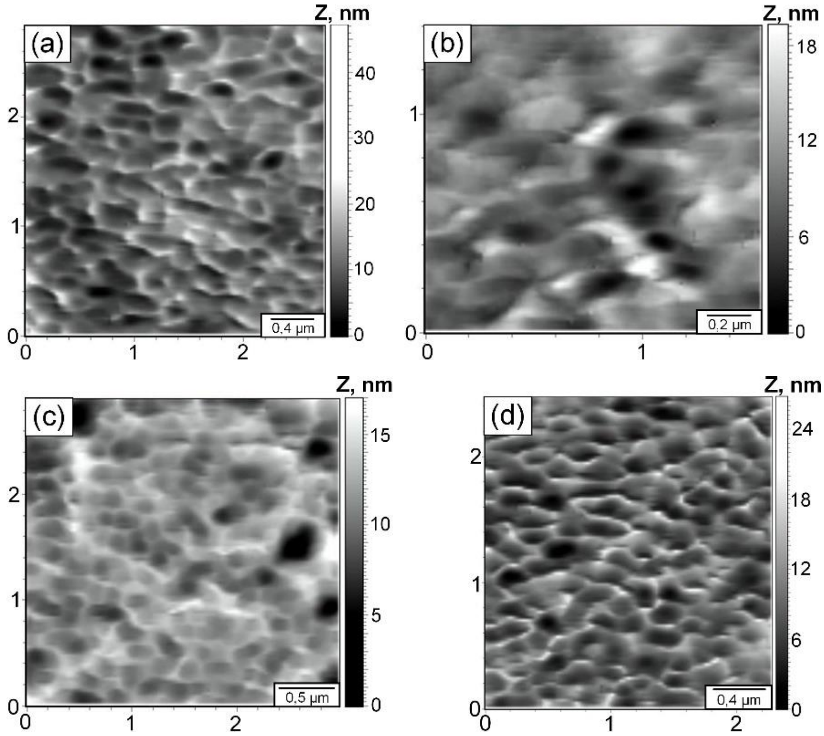

Figure 3. AFM images of the samples: (a) PETF-200; (b) PETF-200/Nafion; (c) PETF-200/Nafion$_{dil.}$; (d) PETF-200/(Nafion + npSiO$_2$).

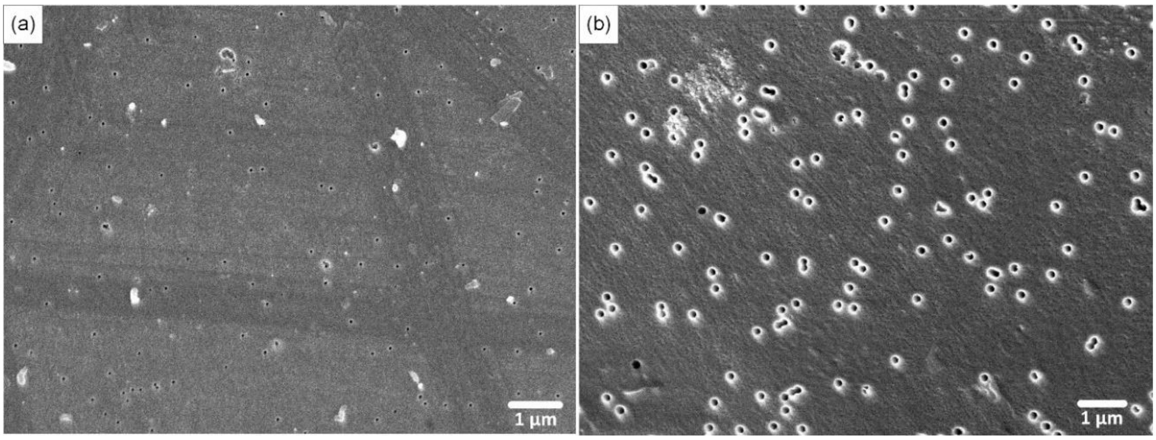

Figure 4. SEM-images of structure of surfaces PETF-membranes with diameter of pores of (a) 100 nm and (b) 200 nm, modified by layer of Nafion with SiO_2 nanoparticles.

In the case of the formation of composition structures (Nafion +SiO_2 np) on the surface of hydrophobic TM with dimensions of 100 nm, two regions of films were formed – island non-uniform films of Nafion and a homogeneous film with characteristic conglomerates of nanoparticles (Fig. 4a). This result can be explained by the high pressure of the film deposition near collapse of monolayer. When a film is formed on a TM with a pore diameter of 200 nm, silicon dioxide nanoparticles are structured around the pores of the membrane, forming characteristic rings (Fig. 4b).

After modification, the filtration properties of PETF100 membranes did not change (Table 2). However, the tensile strength of modified samples slightly increased. The modification of PET-200 membranes with a Nafion film showed the best results. The performance of water increased to 401.3 ml/·(m^2·h) from the initial values of 342.1 ml/(m^2·h). The air performance was increased for all modified PETF-200 membranes. The maximum performance was achieved by modifying with pure Nafion, the productivity was 154.3 ml/min compared with the initial membrane of 96.4 ml/min. These changes are due to an increase in the root mean square surface roughness by 1.2 times. The modification of PETF 200 membranes by a composite Nafion film with silicon dioxide nanoparticles led to the formation of characteristic ring-shaped structures along the membrane pore contour, which increased the adsorption of water on the surface. The LB-film not only modified the working surface of the membranes, but also could penetrate deep into the pores from 2 nm and more. As a result, hydrophilicity of the surface inside the pores increased; thereby, the water performance of the membranes also increased, despite the data obtained on the increase in surface hydrophobicity as a result of modification. The gas penetration changed as a result increasing air adsorption to modified surface of membrane.

Table 2. Flux parameters of initial PETF membranes and modified by Nafion films.

Samples	**Q_{air}, ml/min**	**Q_{water}, ml/·(m^2·h)**	**Tensile strength, MPa**
PETF 100	121.1	364.7	0.316
PETF 100 / Nafion	101.2	354.6	0.320
PETF 100 / $Nafion_{dil}$	122.2	376.7	0.356
PETF 100 / (Nafion+SiO_2)	103.4	359.6	0.388
PETF 200	96.4	342.0	0.224
PETF 200 / Nafion	**154.3**	**401.3**	**0.460**
PETF 200 / $Nafion_{dil}$	**132.1**	**397.5**	0.268
PETF 200 / (Nafion+SiO_2)	123.1	276.7	0.340

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Moreover, LB-films were stable during the experiment of monitoring filtration characteristic. The stability of the filtrate flow over time was also controlled. The values did not change, indicating the stability of the applied layers.

It should be noted that tensile strength increased significantly after modification of thin Nafion layer from 0.22 to 0.46 MPa.

4. Conclusion

The modification of LB-film of Nafion monolayer with thickness from 30 to 100 nm allowed improving both penetration properties of PETF-membranes and their strength characteristics. The incorporation of nanoparticles in LB-layer in small quantities was structuring the monolayer. It was shown that modification of only one monolayer significantly changed the properties of membranes.

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