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The Properties of Cation-Exchange Membranes PTFE-PANI.

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ABSTRACT

We studied the physicochemical properties of modified PTFE membrane PANI permeability, degree of purification, exchange capacity, water capacity. Changes in the structure of the modified membranes were fixed with a scanning electron microscope. After the surface modification of PTFE membrane coated with a film in which a crack has a size 0.2-0.5 micrometers. Education on the surface of the PTFE membrane layer of the film proved PANI and a decrease in the permeability of the modified membrane. Analysis of the infrared absorption spectra of the initial and modified membranes showed the presence of polyaniline matrix membranes. Spectral changes in the modified membrane indicate the formation of electro conductive PANI form - emeraldina salt, which is a polycation radical.
Keywords: Membranes, Polyaniline, PTFE, Infrared spectrometry, Electron microscopy.

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INTRODUCTION

Polyaniline (PANI) attracted the attention of researchers because of their optical and electrochemical properties and high chemical stability. Some of the cation exchange material with a surface layer of PANI characterized by improved selectivity of transport [1]. For conducting form of PANI doped with its various acids. Interestingly the use of solutions of polyacids or films of them as a matrix for the polymerization of aniline [2].

The polymer chain is composed of electrically conductive PANI regularly alternating benzene rings and nitrogen-containing groups.

This circuit structure provides polyconjugated (regular alternation of single and double bonds). The polymer chain forming the zigzag lying in one plane, the π-electron cloud overlap above and below the plane of the chain. The charge carriers are formed in such a polymer during its oxidation. Centers oxidation of PANI are nitrogen atoms having not involved in the chemical bonds of the valence electron pair. In the oxidation, i.e. withdrawal of one of the electrons in the polymer chain there is a positive charge. Removing one electron pair is forming the unpaired spin. The presence of these spins in the material leads to the nontrivial magnetic properties of PANI. The most stable form is emeraldine PANI, where every second oxidized nitrogen.

The positive charge arising in the oxidation in the main circuit should be stabilized counterion. Best stabilizers carriers PANI is a strong acid. Anion of an acid associated with the Coulomb interaction of electron holes formed in the oxidation. Interaction PANI acid called reversible protonation. Removal of the stabilizing acid (deprotonation) reduces the electrical conductivity and the concentration of unpaired spins.

Oxidation-reduction and protonation-deprotonation PANI reversible. This creates a variety of forms of polymer with different properties [3].

A method of obtaining composite ion exchange membrane using predpodgotovki base sulfokationitovoy Nafion membranes by sequential boiling for 1 hour in a solution of hydrogen peroxide, water and sulfuric acid. The membrane was Nafion washed with water and equilibrated with a solution of sulfuric acid (from 15 minutes to 72 hours) and then polymerizing aniline in the matrix of the membrane Nafion by sorption from a solution of protonated aniline with subsequent polymerization in the presence of ammonium persulfate thereafter composite boiled water, sulfuric acid and again in water [4]. A disadvantage of the method of preparing such membranes is a multistage synthesis and the use of high concentrations of polymerizing solutions.

In [5] the membrane obtained by a process comprising the synthesis of polyaniline in a matrix by sequential exposure to a 1M solution of protonated aniline for 1 hour and the polymerization initiator 0.1M ammonium persulfate $(NH_4)_2S_2O_8$ for 1 h, taken as an initial matrix inert nonconductive film of copolymer of tetrafluoroethylene and perfluoro (3,6-dioxa-4-methyl-7-octene) sulfonyl fluoride, and subjected to a boiling solution of 10 % NaOH for 10-40 min to form a charged layer of the resulting sulfonated film, which is washed with distilled water, transferred to H^+ form, for the subsequent synthesis of the polyaniline in the charged sulphonated layer and then heated in aqueous ammonia.

METHODS

In this work as a template for polymerization of aniline was used ePTFE membranes with pore sizes of 0.45 microns. Membranes with such pore sizes are used for micro- and ultrafiltration processes, and are not ion-exchange. Modification of the membranes to form on the surface and in the pores layers PANI which is a cationic, ion-exchange membranes allows to obtain, is not inferior to the selectivity for a number of reverse osmosis cations.

As starting materials used PTFE microfiltration membrane (Phenex Filter Membranes. D = 0.45 microns), ammonium persulfate, aniline hydrochloride. The synthesis of membranes with surface distribution of PANI polymerization of aniline was performed directly in the matrix membranes. The membrane was preincubated for 2 h in a solution of aniline hydrochloride. Then, one surface of the membrane was treated with a solution of ammonium persulfate. The particles PANI formed directly in the matrix of the membrane, as evidenced by a color change to a dark green resin. Processing Time membranes ammonium persulfate was 10 min. The concentration of ammonium persulfate solution and aniline hydrochloride with 1 mol/dm^3. The resulting composite membrane was kept in the atmospheric air humidity of 90 % for 96 hours [6].

To study the exchange capacity of the starting and modified membranes, solutions passed through the membrane of ions of heavy metals. The results are shown in Table 2.

Specific permeability membranes (dm^3/h) was determined by passage through the membrane a certain volume of distilled water.

The microstructure of the prepared samples were examined by scanning electron microscope JEOL JSM 6390LA. Scanning Electron Microscope Jeol «JSM-6390 LA» (Japan) with energy dispersive system EX-230 ** BU is designed to study the elemental composition of the surface by X-ray fluorescence analysis.

To prove aniline hydrochloride modified membranes were removed IR spectra of initial PTFE membrane, and the membrane of the modified PTFE PANI. If the spectrum of the test sample contains all of the absorption band of the reference material, it can be assumed that the substance is actually contained in the sample. A study of the IR spectra of samples was performed on FT-IR spectrometer brand «BrukerVector 22» at 400-4000 cm^{-1}.

RESULTS

Physico-chemical properties of the membrane are shown in Table 1.

Table 1: Physical and chemical properties of the membranes in the swollen state

Membrane	Thickness, um	Exchange capacity, mmol/g	Moisture capacity, %
PTFE-PANI	117	0,17	3,6
PTFE Phenex AF0-0504	112	0	<0,1

Table 2: The average permeability of the membrane with distilled water

The membrane	The permeability, dm^3/h	Specific permeability, dm^3 / cm^2 • h
PTFE*	2,29	0,144
PTFE-PANI	1,93	0,121

* before filtration membrane wetting with acetone

Changes in the structure of the membrane were fixed with a scanning electron microscope JEOL «JSM-6390 LA», and the original images of the structure of the modified membranes are shown in Figures 1 and 2.

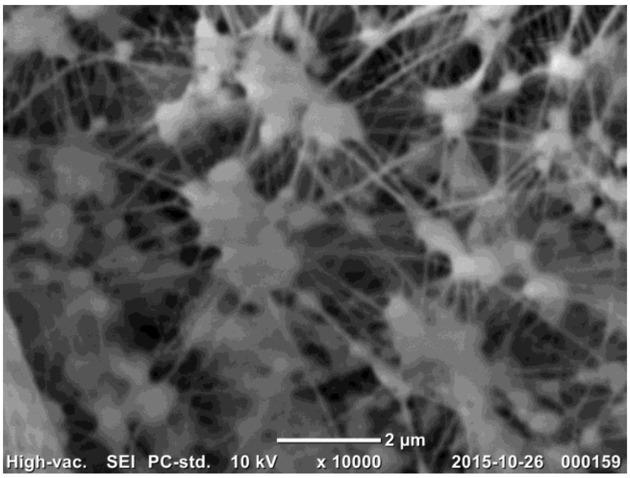

Figure 1: Snapshot of the original PTFE membrane.

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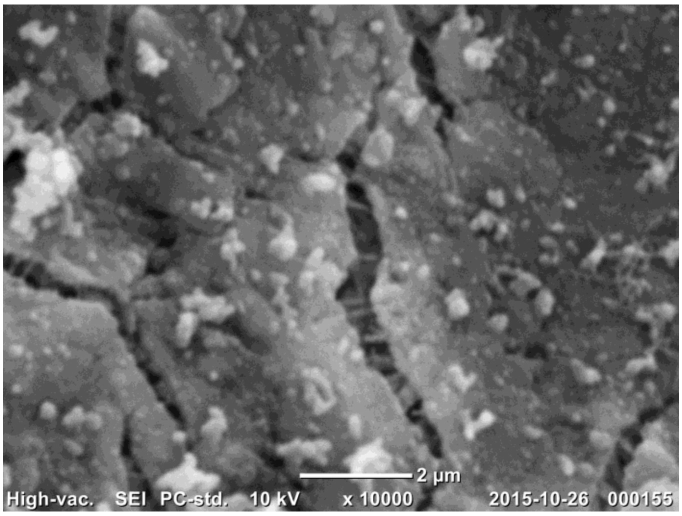

Figure 2: The picture is a modified PTFE membrane-PANI.

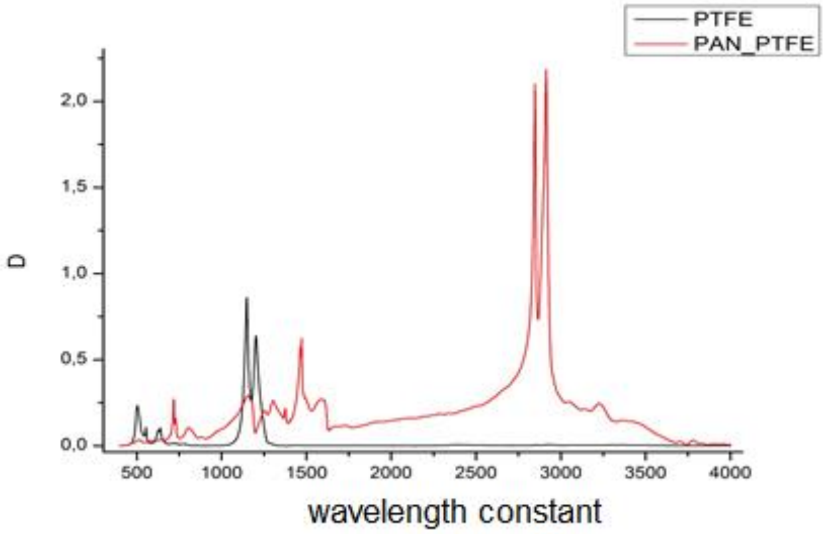

Figure 3: IR absorption spectra of PTFE: lower - PTFE top - membrane PTFE-PANI [7]

DISCUSSION

According to research [8,9] PANI modification leads to an increase in the conductivity of the entire temperature range. According to the model Gierke, ion exchange groups are formed in the membrane pore size of a few nanometers containing sorbed water. They may also be adsorbed ions fenilammoniya that during polymerization to form the particles of PANI. By implementing these particles there are additional transport centers. It is also possible for a change in the microstructure of the membrane, which helped to increase the conductivity.

Specific membrane permeability was determined by passage through the membrane a certain volume of distilled water. The permeability of the PTFE membrane (d = 0.45 mm) is equal to 0.144 $dm^3/cm^2 \cdot h$ from modified membrane PTFE -PANI is 0.121 $dm^3/cm^2 \cdot h$. Therefore, by applying a membrane layer on the initial PANI slightly alters the permeability of membranes.

The modified PTFE membrane PANI obtained by the inventive process has a selectivity of heavy metal ions, cation exchange capacity of the membrane is equal to 0.17 mmol/g. Background PTFE membrane has ion-exchange properties.

The original membrane (Figure 1) is a collection of woven strands of fluoroplastic. When comparing figures 1 and 2 that after the surface modification of PTFE membrane coated with a film in which there are cracks on the entire surface of the membrane with the size of 0.2-0.5 micrometers. Formation on the surface of the PTFE membrane layer PANI film explains the decrease in permeability of the modified membrane. Pore surface modified membranes coated with polyaniline. You can also notice that the pore size is smaller after modification.

Infrared spectroscopy is widely used for the analysis of mixtures of substances and identifying pure chemicals. The quantitative analysis is based on the law of Bouguer-Lambert, t. E., Depending on the intensity of the absorption bands of the concentration of analyte in the sample. As Figure 3 shows the infrared absorption spectra of the original and the modified PTFE membrane PTFE membrane-PANI. In comparison, the IR spectra of the original and modified PTFE membrane PTFE PANI observed differences. In the original PTFE membrane is observed in the absorption bands of frequencies: 720, 790 and 1154 cm^{-1} that correspond to the deformation and is planar vibrations of CF_2, and in the frequency of 1233 cm^{-1} - corresponds to the vibration (CC). A spectrum of the modified PTFE membrane PANI additional bands appeared with frequencies of 720, 790, 1313, 1490, 2823, 2900 cm^{-1} and there is change in the shape and the intensity ratio of the majority of bands. The reason for such changes may be the appearance of the spectrum in the field of new bands associated with the emergence of new groups. Since the band at 1313 cm^{-1} can be attributed to the symmetric stretching and bending vibrations of CN bonds in aromatic amines, and at 1490 cm^{-1} correspond to a planar stretching vibrations of C = C quinonediimine and C-C fenildiaminnyh fragments PANI.

Strong background absorption at higher wavenumbers 2000 cm^{-1} is characteristic of electroconductive PANI form - emeraldina salt, which is a polycation radical.

Thus, the results of IR spectroscopy, it is observed that in the modified membrane produced polyaniline salt form emeraldina comprising phenylamino quinonediimine fragments and [7].

CONCLUSIONS

Preparation of the cation exchange membrane by polymerizing aniline in the structure of the PTFE membrane. It proved selective membrane to ions of cations in model solutions of metal salts.

Based on the foregoing, it can be concluded that the composite membranes of PTFE and PANI obtained by the proposed method possess high electrical conductivity, permeability and selectivity.

After the surface modification of PTFE membrane coated with a film in which a crack has a size 0.2-0.5 micrometers. Education on the surface of the PTFE membrane layer of the film proved PANI and a decrease in the permeability of the modified membrane.

The analysis results obtained by infrared absorption spectrum of the original and the modified membrane reveal the presence of the polyaniline in the surface and structure of the membranes.

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