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POLARIZING PROPERTIES OF PERFLUOROSULFONIC MEMBRANES MODIFIED WITH TERBIUM

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Abstract. In order to determine the features of polarization and structural properties of perfluorosulfone membranes after their modification with Tb, MF-4SK membranes have been prepared and studied. The sorption properties of membranes were investigated by recording their optical absorption and transmission spectra in the visible and UV ranges in dynamics, as well as infrared reflection spectra. The temperature-frequency dependences of the main dielectric parameters of the objects under study, their spectra of complex conductivity were recorded and analyzed. As a result, it was found that the specific conductivity of terbium-modified perfluorosulfone membranes obeyed a power law. The presence of critical temperature of the system's transition from semiconductor conductivity to metallic one was revealed. A scheme for the ion-exchange mechanism of the sorption fixation of terbium ions in the membrane was put forward.

Keywords: composite material, perfluorosulfonic membrane, modification, sorption, polarization and structural properties

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Научная статья

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ПОЛЯРИЗАЦИОННЫЕ СВОЙСТВА ПЕРФТОРСУЛЬФОНОВЫХ МЕМБРАН, МОДИФИЦИРОВАННЫХ ТЕРБИЕМ

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Аннотация. Для определения особенностей поляризационных и структурных свойств пленок перфторсульфоновых мембран при их модифицировании Tb, были



подготовлены и исследованы мембраны MF-4SK. Сорбционные свойства мембран изучались путем динамической регистрации их спектров оптического поглощения и пропускания в видимой и ультрафиолетовой областях, а также инфракрасных спектров отражения. Регистрировались и анализировались температурно-частотные зависимости основных диэлектрических параметров указанных объектов, спектры комплексной проводимости. В итоге установлено, что удельная проводимость модифицированных перфторсульфоновых мембран подчиняется степенному закону. Выявлено наличие критической температуры перехода системы от полупроводниковой проводимости к металлической, и предложена схема ионно-обменного механизма сорбционного закрепления ионов тербия в мембране.

Ключевые слова: композитный материал, перфторсульфоновая мембрана, модификация, сорбция, структурные и поляризационные свойства

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Introduction

Composite materials based on ion-exchange perfluorosulfonic membranes (PFSM) are increasingly being used in various fields of science as a part of sensor devices, electrolyzers, and current sources. They are also used for energy generation and storage, catalysis, PD sensors (their signal is the Donnan Potential).

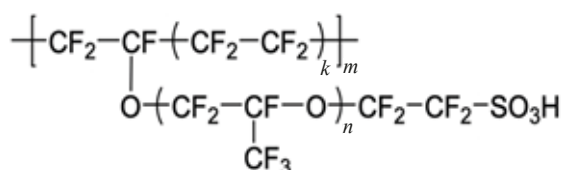
Such membranes have certain positive characteristics: a highly developed porous structure, a large surface area of about 130 m²/g, optical transparency in a wide spectral range and high sorption capacity. This combination of features determines the prospects for directed modification of membranes by substances of both inorganic and organic nature in order to obtain materials with ion-conducting, luminescent, sorption, sensory and catalytic properties. Nanoparticles, complex compounds of transition and rare earth elements, organic dyes, various dopants of inorganic nature, for example, silicon dioxide, zirconium dioxide, heteropoly acids, were all used as compounds introduced into the membrane matrix [1 – 4].

Depending on the method of membrane modification, the nature and concentration of the injected particles, their size and intrinsic characteristics, it is possible to obtain materials with different properties. Nevertheless, there is a limited number of research devoted to the study of sorption and luminescent, electrophysical properties of substances enclosed in the pore space of membranes as a result of sorption or their synthesis. The specificity of the substances' state in nanostructured pore space and the sorption, luminescence-spectral, dielectric properties determined by this distinctive nature of the state have not yet been revealed. At the same time, due to a wide selection of potentially suitable precursors, we are provided with opportunities for the obtainment of new optical and sorption film materials.

The aim of this work is to analyze the polarization and structural properties of perfluorosulfone membrane modified with terbium (III) chloride.

Research methods and materials

The objects of current studies were MF-4SK membranes (“PlastPolimer” LLC, St. Petersburg, Russia) being thin plates with a thickness of 220.0 ± 0.5 μm and an area of 1 – 2 cm. MF-4SK is the Russian equivalent of Nafion.



Chemical structure of the membrane of Nafion type

Previously, MF-4SK membranes were cleaned by boiling for 2 – 3 hours in concentrated nitric acid (65 % by mass) followed by washing with distilled water until there was no qualitative visual reaction to the residual nitrate ion. After that, the membranes were kept in a drying cabinet at a temperature of 90 °C until a constant mass was obtained. At a temperature of 90 °C, water was removed from the pore space but the porous structure was preserved.

The absorption spectra of the spent solutions and modified PFSM in the visible and UV ranges were taken in the transmission mode on the automatic spectrometer Shimadzu “UV-2550”.

The transmission spectra of the samples were obtained using a Fourier spectrometer “FSM 1202” with the prefix of multiple disturbed total internal reflection in the middle of IR range of 400 – 5000 cm⁻¹.

Measurements of dielectric spectra, such as temperature – frequency dependences of dielectric parameters, were carried out using a spectrometer “Concept-81” (Novocontrol Technologies GmbH & Co) over the frequency range $f = 1 - 10^7$ Hz and the temperature range $T = 293 - 403$ K (accuracy 0.5 K). The measuring voltage applied to the sample was 1.0 V.

The values of the imaginary and real parts of the impedance of the cell with the measured sample were collected as experimental data [9,10]:

$$Z^*(\omega) = R + \frac{1}{i\omega C} = Z' + iZ'' = \frac{U_0}{I^*(\omega)}, \quad (1)$$

where Z^* is the complex impedance; ω is the angle frequency; R is the resistance; C is the cell capacity; Z' , Z'' are real and imaginary parts of complex impedance; U_0 is the voltage amplitude; I^* is the complex current.

The complex conductivity spectra were calculated from the impedance spectra using the following formula:

$$\sigma^* = \sigma' - i\sigma'' = \frac{-i}{\omega Z^*(\omega)} \frac{S}{d}, \quad (2)$$

where σ^* is the complex conductivity; σ' , σ'' are real and imaginary parts of complex conductivity; S is the electrode area; d is the sample thickness.

Experimental results and discussion

To change the electrophysical properties of the membranes, ion-exchange modification of the initial samples with trivalent terbium salt was made by holding the samples for 1 h in the aqueous solution of 0.01 mole/L TbCl₃. The equilibrium state achievement time and the content of terbium cations in the membrane were determined by a decrease in the optical density of the water-salt solution at the maximum of the absorption band of terbium ions ($\lambda = 219$ nm).

The sorption was controlled by the spectrophotometric method based on the decrease in optical density D . Fig. 1,*a,b* shows the dynamics of the substance concentration decrease in solution (a decrease in the optical density D) and an increase in the amount-of-substance Q in the membrane over time.

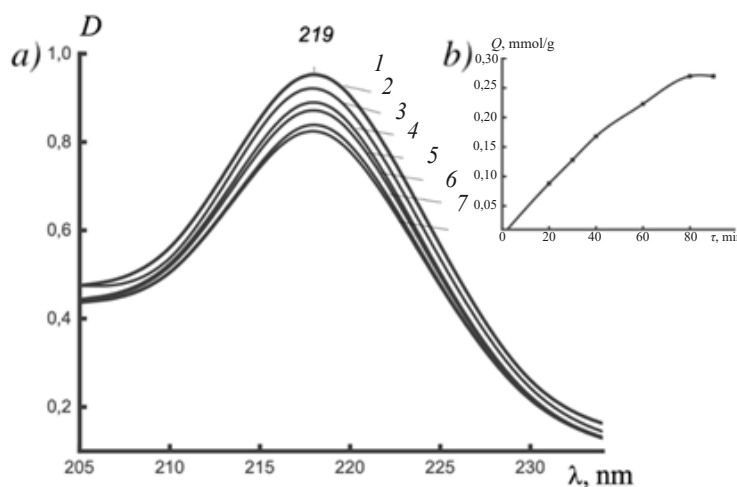


Fig. 1. Absorption spectra of TbCl_3 aqueous solution (30 ml ($1 \cdot 10^{-2}$ mol/L)) during membrane (0.06 g by weight) sorption (a) and a quantitative increase in the substance Q in the membrane over time (b).
The points of time, min: 10 (1), 20 (2), 30 (3), 40 (4), 50 (5), 60 (6), 70 (7) from the moment of membrane contact with salt solution

The sorption limit value ($Q = 0.27 \pm 0.05$ mmol/g) is steadily reproduced and corresponds to an almost ideal molar ratio $Q/[-\text{SO}_3\text{H}] \approx 1/3$.

The frequency dependence of the specific conductivity at different temperatures for samples modified with terbium is shown in Fig. 2, a. This is typical for many disordered systems [5, 6]. As follows from the figure, the variance σ' , in the studied frequency domain, obeys the power law:

$$\sigma'(\omega) \sim \omega^s, \quad (3)$$

where ω is the angle frequency, s is the exponent which decreases at low temperatures as the temperature increases (Fig. 2, b).

The relative error in determining the value of parameter s did not exceed 5 % for all temperatures.

The detected frequency dependence of conductivity, according to Eq. (3), and the decrease in the value of parameter s with an increase in temperature are probably due to the existence of a hopping conduction mechanism. According to the correlated barrier hopping model (CBH model) [7], electrons jump between energy states, overcoming a potential barrier. At the same time, to calculate the value of the specific conductivity at a certain temperature, the following equation can be applied [8]:

$$\sigma'(\omega) = \frac{\pi^3 N^2 \varepsilon \varepsilon_0 \omega R_\omega^6}{24}, \quad (4)$$

where N is the density of states between which charge carriers jump, ε is the dielectric permittivity, ε_0 is the dielectric constant, σ' , S/cm, is the real part of complex conductivity, R_ω is the hopping length.

According to the CBH model, the charge transfer mechanism can be described as follows: in the presence of an external electric field, charge carriers (electrons) make jumps while overcoming a potential barrier of height (W) between two localized states (equilibrium centers). The height of the potential barrier is contingent on the Coulomb interaction between neighboring defective states. Charged defects in the structure of the material, as well as other formations (impurities, etc.), can act as such states. In the former and the latter cases, the mentioned states form a dipole (quasi-dipole).

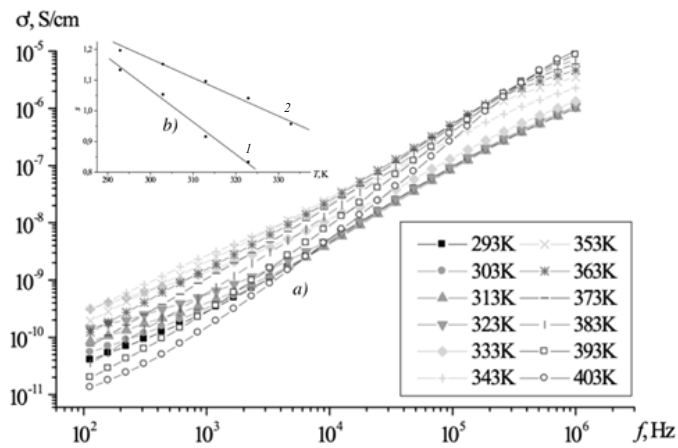


Fig. 2. Plots of the specific conductivity of MF-4SK+Tb samples vs. frequency at different temperatures (a) and of the exponent s vs. temperature for samples MF-4SK (1) and MF-4SK +Tb (2) (b)

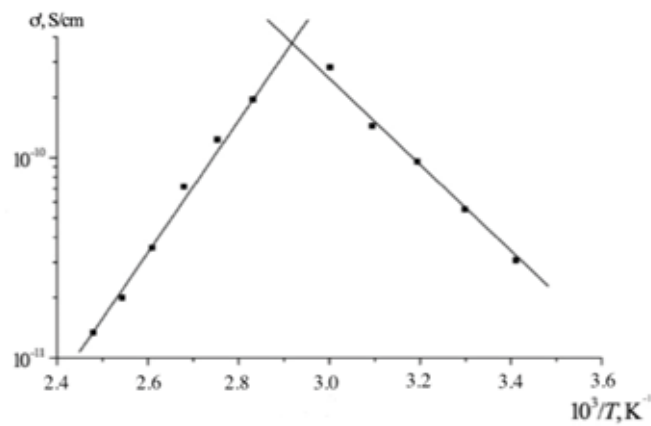


Fig. 3. Temperature dependence of the electrical conductivity of MF-4SK +Tb samples at $f = 1$ Hz

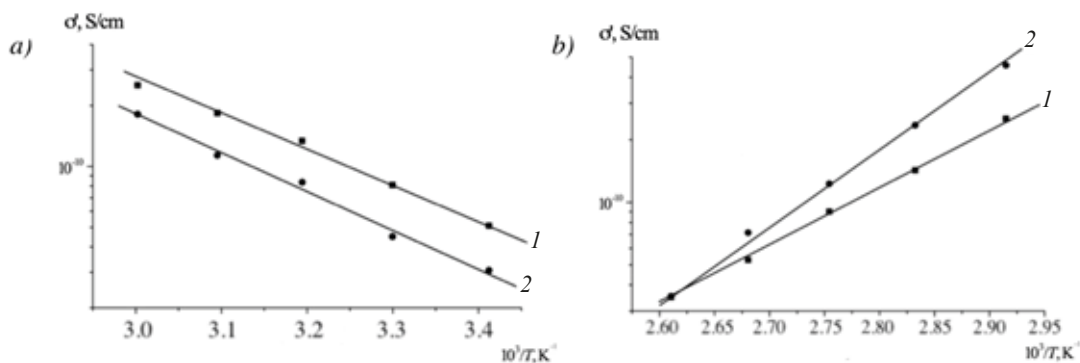


Fig. 4. Temperature dependences of the electricity (a) and specific (b) conductivities of the MF-4SK (1) and MF-4SK +Tb (2) samples on the semiconductor conduction band (a) and on the metal conductivity site (b). The frequency of the measuring field is 1 Hz



The temperature dependence of the electrical conductivity σ' (Fig. 3 reveals the existence of two temperature regions with the presence of a certain critical temperature at which both systems switch from semiconductor to metallic conductivity.

It is notable that the conductivity of MF-4SK samples decreases when they are modified with terbium in the field of semiconductor conductivity (Fig. 4,*a*). At higher temperatures, the opposite effect is observed; that is, the conductivity of modified films becomes more significant than that of the original MF-4SK films (Fig. 4,*b*).

The spectra of frustrated total internal reflection were obtained for the structural identification of the initial membranes and their changes during the modification with terbium. In Fig. 4,*b*, the following absorption bands of characteristic vibrations can be distinguished in the spectrum:

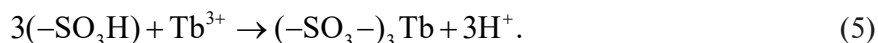
at 1140 cm^{-1} , valence vibrations $-\text{CF}_2$ -groups of the main perfluorinated polymer chain, as well as those at 2850 and 2920 cm^{-1} take place. They correspond to asymmetric and symmetric vibrations of the $-\text{CH}$ and $-\text{CH}_2$ groups;

at 1100 cm^{-1} , the band corresponds to symmetric vibrations of the $S = 0$ bonds of the dissociated sulfogroup $-\text{SO}_3^-$;

in addition, there is a peak of 1740 cm^{-1} related to deformation vibrations of water molecules (corresponds to the literature data).

As a result of the modification, the water content in the membranes decreased, which was confirmed by the absorption bands' weakening at the peak of 1740 cm^{-1} .

Based on the obtained data, it can be assumed that the decrease in the conductivity of the Nafion samples during their modification with terbium in the field of semiconductor conductivity can be explained by adsorption of water in the volume of the polymer matrix and a decrease in the number of protons due to their substitution with terbium ions according to the following scheme:



Until modification, the pores of membranes containing hydrophilic functional polar sulfogroups are easily filled with water. At the same time, the hydrophilicity of the membranes is so strong that even after drying at a temperature of $100 - 105\text{ }^\circ\text{C}$, limiting temperature of preservation of the porous structure, each proton of the membrane binds two water molecules forming a hydrogen ion of the composition H_5O_2^+ [$\text{H}_2\text{O}-\text{OH}^{2+}$], which, as it is known, exists in hydrates of strong acids [12].

An estimate of the value of the conditional area per one sulfogroup was made, amounting to 25 \AA^2 . Quantitative determination of the number of sulfonate groups in the membrane was obtained based on the results of acid-base titration with alkali using methyl orange as an indicator. The result was $0.84 \pm 0.05\text{ mol/g}$ of a membrane.

The topography of the distribution and the high activity of the membrane sorption centers determine the maximum filling of the membrane surface. At higher temperatures, the conductivity of the modified films becomes more significant than that of the original MF-4SK films. It can be explained by an increase in dissociation of protonated sulfogroups. In addition, as the membranes are heated above $110\text{ }^\circ\text{C}$, the number of water molecules per sulfogroup decreases (from 21 to 11) [12]. All this leads to an increase in the concentration of hydrogen ions and an elevation in mobility as it heats up, and consequently, an increase in the conductivity of the membranes.

Summary

During the experiment, the temperature dependencies of the specific conductivity σ' was revealed. These dependencies correspond to the power law.

It varies in two temperature regions with the presence of a certain critical temperature at which both systems switch from semiconductor conductivity to metallic one.

A decrease in the conductivity of the samples was found when they were modified with terbium (III) chloride in the field of semiconductor conductivity. This is due to the adsorption of water in the volume of the polymer matrix and a decrease in the number of protons due to their replacement by terbium ions. At higher temperatures, the opposite effect was observed, namely, the conductivity of the modified films became more significant than that of the original

MF-4SK films, which indicated an increase in the dissociation of protonated sulfogroups.

For a quantitative assessment of sorption, the spectrophotometric control allowed to propose a scheme of the ion-exchange mechanism of sorption fixation of terbium ions in the membrane in a quantitative ratio of 1: 3 (see Eq. 5).

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