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Electrophysical properties of polymer membranes with the introduction of rare-earth metal compounds into membrane matrix

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Abstract. The original and modified with terbium(III) chloride perfluorosulfonic membranes were studied by dielectric spectroscopy in a wide range of frequencies (f = 10^0 Hz…10^5 Hz) and temperatures (T = 273 K…403 K). The membrane was modified by ion exchange sorption from an aqueous salt solution for several hours until an equilibrium value was reached. The sorption control was spectrophotometric. During the study, we obtained conductivity data of the samples and discovered their hopping conduction mechanism.

Measurement of the dielectric loss factor ε" in the layers of the sample made it possible to reveal the existence of a process leading to relaxation losses in the samples.

Keywords: perfluorosulfonic membrane, modification, rare earth elements, dielectric spectroscopy, conductivity

Introduction

Perfluorosulfonic membranes belong to a special type of polymer porous structures, the framework of which is formed by a fluorocarbon skeleton and ether chains. Cavities and channels are formed inside the membrane structure. The inner surface of these channels has polar functional groups: $–SO_3^-$–COO^-, etc. Membranes can be in protonated and ionic forms, such as K or Na. Currently, membrane of this type is used in fuel cells as a solid electrolyte. At the same time, perfluorosulfonic membranes have such useful properties as high proton conductivity, chemical and mechanical inertness to aggressive environments. The temperature range of membrane exploitation is relatively small. It is 290–363 K. A higher or lower temperature leads to a violation of the porous structure and of the integrity. The conductivity of the membrane also decreases. Modifications of such membranes with substances of organic and inorganic nature make it possible to increase the mechanical and thermal stability and to maintain or even increase proton conductivity at high temperatures and low relative humidity.

It is known that the introduction of mineral acids into membranes leads to an increase in the proton conductivity, but does not lead to an increase in the thermal stability. And it is an important factor in a membranes' exploitation (Napoli et al. 2013). In another study, substances of inorganic origin (SiO_2, TiO_2) were introduced into membranes. This allows to maintain the membrane conductivity at high temperatures (393 K) (Safronova, Yaroslavtsev 2015).

In the available body of literature, there is not much information devoted to studying the properties of membranes modified with composites of rare earth metals, which makes it possible to observe unique spectral and luminescent properties. It is also of interest to study the electrophysical properties of polymer systems based on conclusion of rare-earth metal composites in the membrane matrix. For example, the lanthanides have a polarizing effect on water inside membranes. This leads to changes in the conductivity of the resulting systems.

Samples and research methods

In our study, we investigated perfluorosulfonic membranes (MF-4SK type, PlastPolimer LLC, Saint Petersburg, Russia). Thicknesses of the samples were 170–200 micrometers.

Dielectric spectroscopy was chosen as a research method. The spectra were taken using the Concept-81 setup in the frequency range f = 100 Hz…105 Hz and in the temperature range T = 273 K…403 K. The experiment was carried out on the Concept 41 setup (Novocontrol Technologies GmbH & Co). The setup consists of a frequency impedance analyzer (frequency range: 3×10^{-6} Hz – 20×10^{6} Hz), a measuring cell, a temperature control system (temperature range: –100 °C – +250 °C), an automatic data acquisition system, and a Dewar vessel with an evaporation and nitrogen gas supply system. We also studied the temperature dependence of the conductivity for the original and modified samples. The temperature dependence of the logarithm of the current was obtained on a TSC-II setup (Setaram) in the mode in which the sample is placed in a constant field during linear heating.

Chemical modification of the membrane was carried out by keeping the sample in an aqueous solution of $TbCl_3$ for 90 minutes. The concentration of the solution is 10^{-3} mol/l. Sorption control was carried out by using the spectrophotometric method on a Shimadzu UV-2550 spectrophotometer. And it was determined by the intensity of the absorption peak of terbium (λ_{max} = 219 nm).

Experimental results and discussion

As a result of the experiment, the frequency dependences of the specific conductivity σ of the original and modified MF4-SK membranes were obtained at different temperatures (Figs. 1, 2).

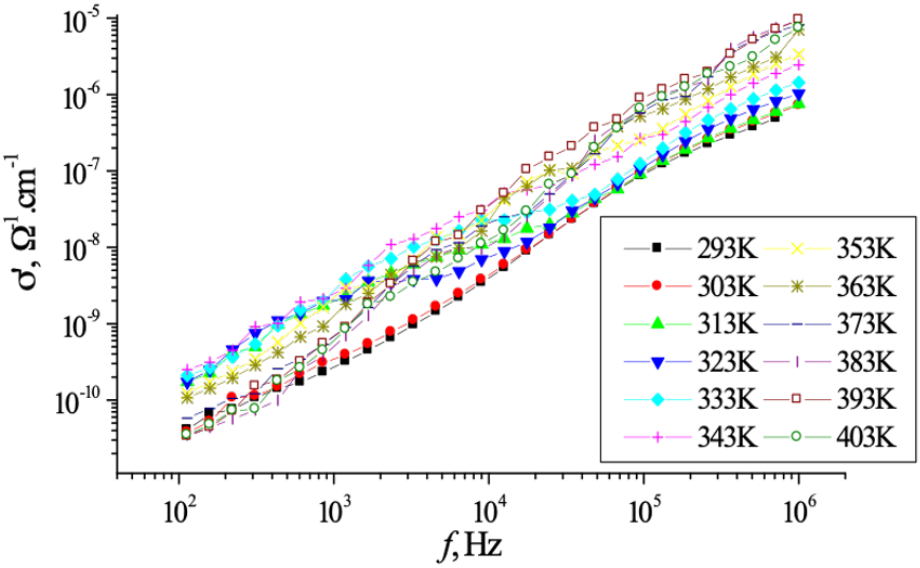

Fig. 1. Frequency dependencies of the specific conductivity σ' for samples of the MF-4SK system at different temperatures

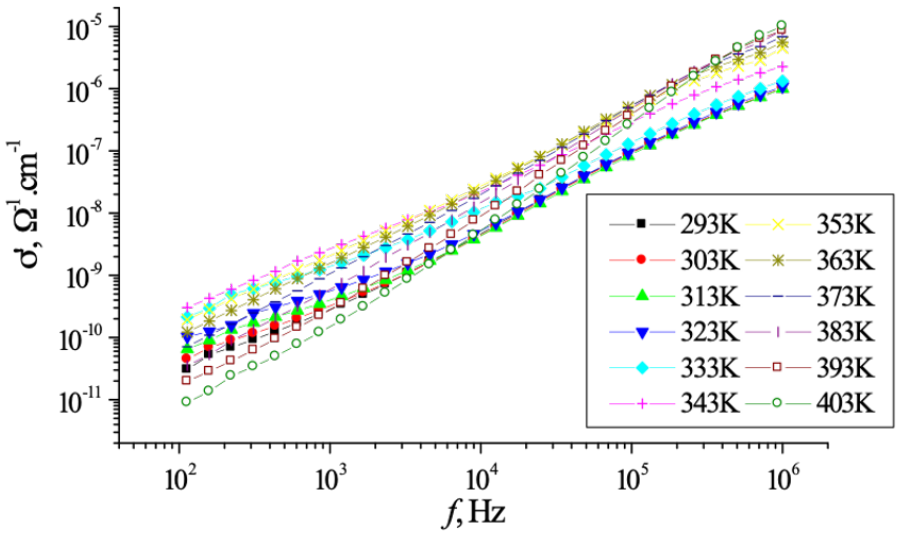

Fig. 2. Frequency dependencies of the specific conductivity σ' for samples of the MF-4SK+Tb system at different temperatures

The obtained frequency dependence of the conductivity obeys a power law. An analysis of the literature data has shown that this dependence is characteristic of most amorphous and crystalline semiconductors. And it is observed in many disordered systems characterized by hopping conductivity (Ivanchev et al. 2012). It can be assumed that when the membrane is modified with a terbium salt, the conductivity of the membrane increases at high temperatures because of an enhancement of water dissociation in the composition of aquated terbium ions $[Tb(H_2O)n]^{3+}$. As a consequence, the number of protons and their mobility in the system increase. The power-law characteristics of the frequency dependence σ and characteristics of the temperature dependence of the exponent s (Fig. 3) indicate the existence of a hopping mechanism of conduction in the frequency and temperature range under study.

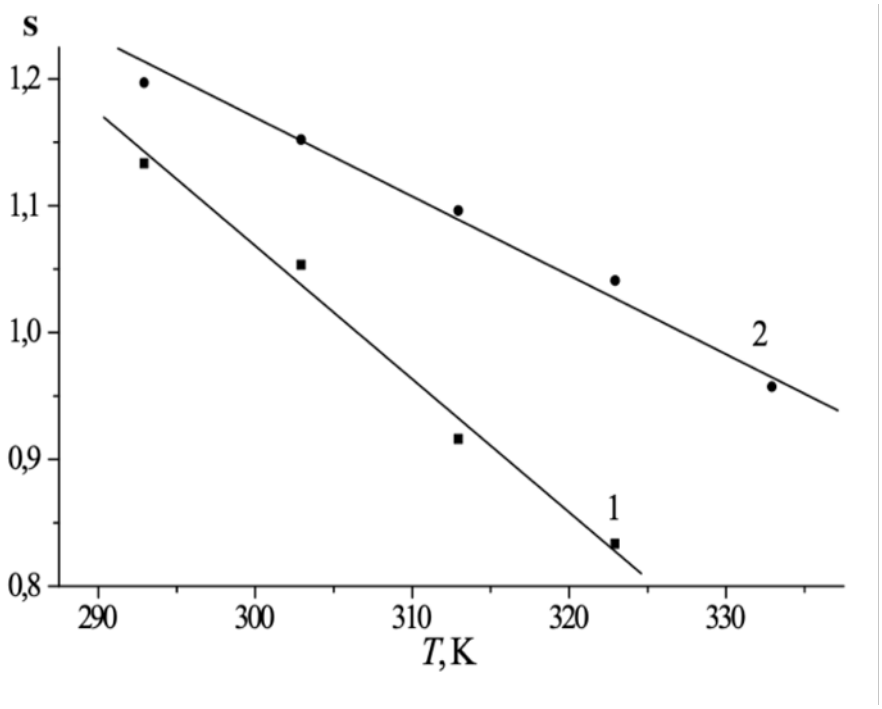

Fig. 3. Temperature dependencies of the exponent s. 1—original sample, 2—modified sample

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The proton nature of the sample conductivity was confirmed by studying the temperature dependence of the transfer parameters using the experimental setup TSC-II (Setaram) (Fig. 4).

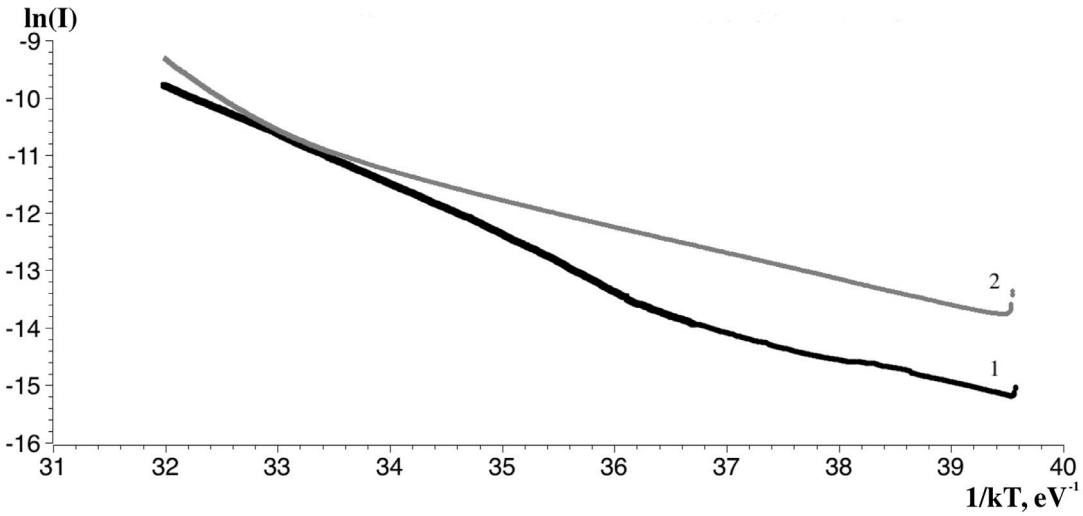

Fig. 4. Dependencies of the logarithm of the current on the reciprocal temperature. 1—original sample, 2—modified sample

For the original sample, a change in conductivity was observed in the region of 36.7 eV^{-1} (corresponding to a temperature of 316.2 K). For the modified sample, a shift in conductivity to higher temperatures is observed and corresponds to a value of 33.5 eV^{-1} (346.1 K). There is a shift in the region of critical temperatures during the modification of films, as in the case of the dispersion of the specific conductivity in an alternating field.

The data collected during the pilot study of the dielectric loss factor ε" in the original and modified samples revealed the existence of a maximum of this value in the medium frequency region. Data were obtained at various temperatures. Collected data indicate the existence of a process leading to relaxation losses in the samples (Figs. 5, 6). (Mustafaeva 2008).

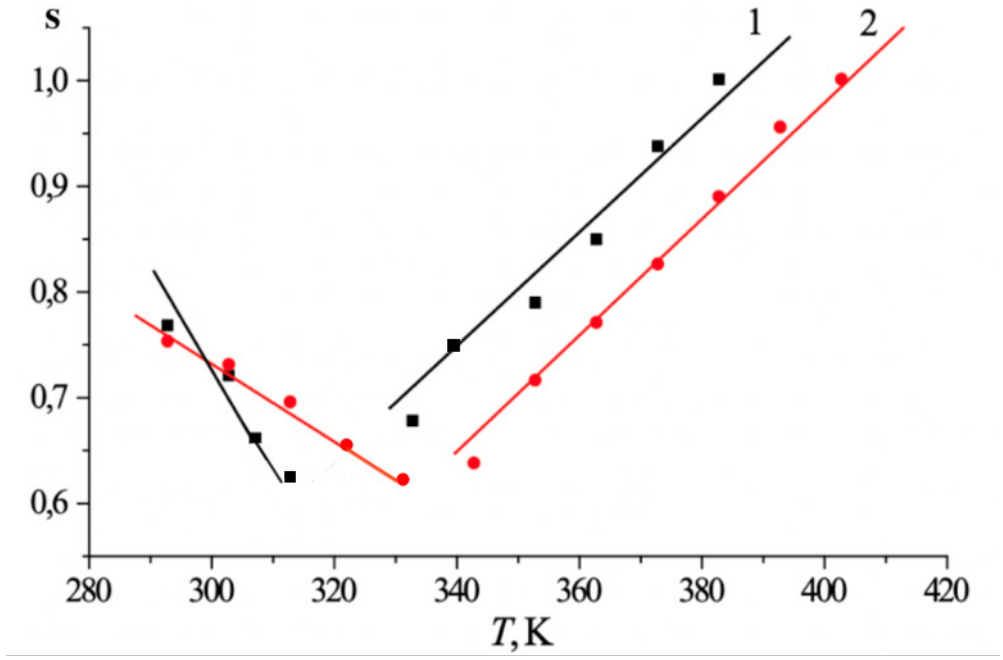

Fig. 5. Temperature dependencies of the exponent *s* for samples of two systems in normalized units of measurement. (1)—MF-4SK, (2)—MF-SK + Tb

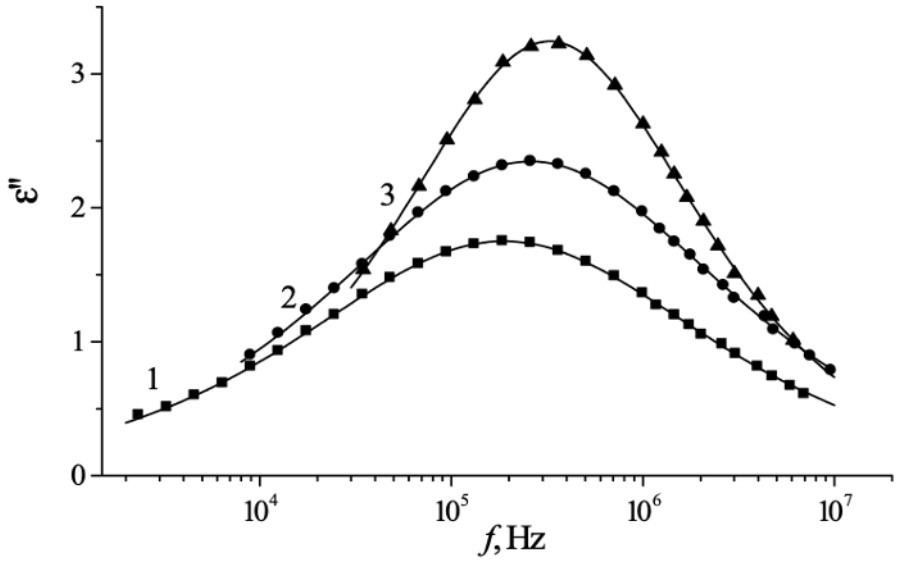

Fig. 6. Frequency dependencies of the complex permittivity's imaginary part (loss factor ε") for MF-4SK at different temperatures 1—303 K, 2—323 K, 3—333 K

The approximation of experimental curves (Figs. 6, 7) makes it possible to obtain values of the relaxation parameters within the Havriliak—Negami model: Δε, τmax, α, β.

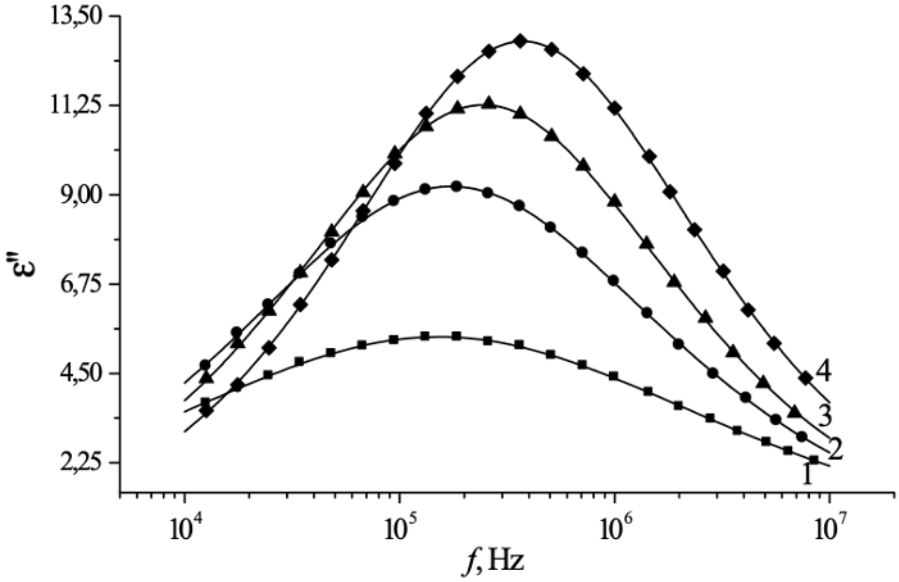

Fig. 7. Frequency dependencies of the imaginary part of complex permittivity (loss factor ε") for MF-4SK+Tb (process II) at different temperatures: 1—343 K, 2—353 K, 3—363 K, 4—373 K

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The obtained values indicate the existence of a distribution of relaxers over relaxation times in accordance with the Cole-Davidson and Cole-Cole models (Table 1).

Table 1. The values of the relaxation parameters of both systems, obtained by approximating the experimental dependences of the loss factor ε" on frequency at different temperatures

System	Temp.[K]	D_Eps	Tau-Max [s]	Alpha	Beta
MF-4SK	293	6.6150e + 00	1.047e – 06	5.7810e – 01	1.0000e + 00
	303	7.3550e + 00	8.464e – 07	5.6600e – 01	1.0000e + 00
	313	8.0440e + 00	9.291e – 07	5.4930e – 01	9.8960e – 01
	323	9.5670e + 00	6.134e – 07	5.8080e – 01	1.0000e + 00
	333	1.0250e + 01	4.872e – 07	7.1850e – 01	1.0000e + 00
	343	1.6570e + 01	3.731e – 07	6.8990e – 01	1.0000e + 00
	353	2.1960e + 01	2.901e – 07	6.8210e – 01	1.0000e + 00
MF-SK + Tb	343	2.8150e + 01	1.045e – 06	4.6800e – 01	1.0000e + 00
	353	3.6900e + 01	9.136e – 07	6.0250e – 01	9.3130e – 01
	363	4.0700e + 01	6.481e – 07	6.4380e – 01	1.0000e + 00
	373	4.4010e + 01	4.256e – 07	6.7600e – 01	9.8940e – 01
	383	4.4830e + 01	3.268e – 07	7.2910e – 01	1.0000e + 00

In the systems under study, fluorine-carbon, carbon-hydrogen fragments of the membrane core and polar sulfo groups found in the IR spectrum of the membranes can act as relaxers (Jonscher 1977). The activation energy of the relaxation process was determined from the temperature dependence of the most probable relaxation time. The results for the membranes of the two systems are presented in Table 2.

Table 2. The values of the activation energy of the relaxation process for films of two systems, obtained using the exponential Arrhenius law

System	Temperature range, K	E_a, eV	E_a, kcal/mol
MF–4SK	293…353	0.27 ± 0.02	6,21 ± 0,45
MF–4SK+Tb	343…383	0.42 ± 0.01	9,63 ± 0,20

Conclusions

All in all, the study of the electrophysical properties of polymer membranes with the addition of compounds of the rare earth metal (terbium) to their matrix made it possible to fix the hopping mechanism of charge transfer for both pure and modified membranes. The dispersion of the dielectric loss factor is characterized by the presence of the maximum of this parameter in the medium frequency range. The observed differences in the values of the polarization parameters for the films of the two systems are explained by the structural changes. The original polymer is going through these changes when it is modified with a terbium.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

N. A. Lapatin modified the membrane and analyzed the dielectric spectra; R. Castro investigated the membrane using the method of dielectric spectroscopy and analyzed the spectra; E. A. Karulina analyzed the dielectric spectra; T. V. Reztsov conducted the experiment on the TSC-II facility.

All the authors discussed the final work and took part in writing the article.

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