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DIELECTRIC SPECTROSCOPY OF PERFLUOROSULFONIC MEMBRANES IN PROTON- AND TERBIUM-SUBSTITUTED FORMS

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Abstract. The present study was aimed to reveal the mechanisms of electrical conductivity of the perfluorosulfonic membrane (MF-4SK) in the proton-substituted form and an effect of Tb ions modified this matrix on these mechanisms. The frequency dependences of the complex permittivity at a temperature of 293 K and the temperature dependences of it at a frequency of 1 kHz for samples of the both forms have been measured. An increase in the permittivity ϵ' value with decreasing frequency and increasing temperature was brought out. The maxima of the dielectric loss factor were obtained for the layers of the studied systems at different temperatures. The obtained experimental data allowed us to assume that there were distributions over relaxation times for relaxation oscillators. A transition from classical to quantum mechanical charge transfer was discovered and interpreted for the original and modified membranes.

Keywords: perfluorosulfonic membrane, dielectric spectroscopy, proton, terbium, temperature dependence and frequency one

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ДИЭЛЕКТРИЧЕСКАЯ СПЕКТРОСКОПИЯ ПЕРФТОРСУЛЬФОНОВЫХ МЕМБРАН В ПРОТОНО- И ТЕРБИЕВОЗАМЕЩЕННЫХ ФОРМАХ

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Аннотация. Представленное исследование ставило целью выявить механизмы электрической проводимости перфторсульфоновой мембраны (МФ4-СК) в протонозамещенной форме (Н-форма) и влияние ионов тербия, модифицирующих данную матрицу (Ть-форма), на эти механизмы. Проведены измерения частотных зависимостей комплексной диэлектрической проницаемости при температуре 293 К и ее температурных зависимостей на частоте 1 кГц для образцов обеих форм. Выявлен рост величины ϵ' при уменьшении частоты и повышении температуры. Обнаружены максимумы фактора диэлектрических потерь ϵ'' в слоях исследуемых систем при различных температурах. Полученные экспериментальные данные позволили предположить существование распределения по временам релаксации релаксаторов. Для модифицированной и немодифицированной мембран был обнаружен и интерпретирован переход от классического переноса заряда к квантовомеханическому.

Ключевые слова: перфторсульфоновая мембрана, диэлектрическая спектроскопия, протон, тербий, температурная и частотная зависимости

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Introduction

The polytetrafluoroethylene-sulfonated Nafion polymer membrane and its Russian counterpart MF-4SK are widely used in fuel cells as solid electrolyte with high ionic conductivity. Fuel cells can serve to replace batteries in cars and mobile devices, as they do not have to be recharged, offering an extended service life. Advantages of using membranes in fuel cells include their high thermal and chemical resistance. Polytetrafluoroethylene-sulfonated membranes are actively studied by various physical and chemical methods.

Swollen perfluorosulfone membranes containing potassium ions in their matrix have been studied better than others. The modern understanding is that such membranes have a reverse micellar structure (the water present in the membrane is surrounded by a polymer matrix with functional ionic groups).

Unlike salt forms of Nafion-type membranes, other substituted forms of perfluorosulfonic membranes have been studied in less detail; this mainly concerns the conductivity mechanisms in the high temperature range and at low humidity.



The goal of this study consisted in identifying the mechanisms of electrical conductivity of a perfluorosulfonic membrane in proton-substituted form and the effect that terbium ions modifying this matrix have on these mechanisms.

We considered both of these membrane forms (abbreviated as H- and Tb-forms).

Experimental procedure

The experimental samples were the Russian counterpart of the Nafion membrane, the MF-4SK membrane (manufactured by JSC Plastpolymer, St. Petersburg), with the thickness of $220.0 \pm 0.5 \mu\text{m}$ thick and the area of $1\text{--}2 \text{ cm}^2$.

The membrane was pre-cleaned of impurities sorbed from the air by boiling in a nitric acid solution (65 wt%) for several hours. Next, the samples were washed in distilled water from the excess of singly charged NO_3^- anions, and then dried to a constant mass at a temperature of 90°C .

The dielectric spectra of the given layers (temperature and frequency dependences of the complex permittivity components) were recorded with a Concept-81 broadband dielectric spectrometer (at the Center for Collective Use of Dielectric Spectroscopy at the Herzen State Pedagogical University of Russia) in the frequency range $f = 1\text{--}10^5 \text{ Hz}$ and temperature range $T = 273\text{--}403 \text{ K}$.

The real and imaginary parts of the impedance $Z^*(\omega)$ (ω is the angular frequency of alternating current) were measured. We also obtained frequency and temperature dependences of complex permittivity and conductivity. The relative error of the experiment did not exceed 5%.

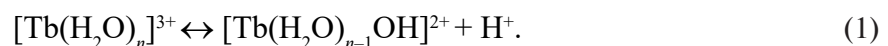
The values of the system's relaxation parameters were found by processing the obtained dielectric spectra, that is, fitting the curves to the two-parameter empirical Havriliak–Negami function [1] using the Novocontrol Winfit software. The positions of the dielectric loss maxima were thus detected, and the Havriliak–Negami (HN) parameters for the considered relaxation processes were determined.

Experimental results and discussion

Fig. 1,*a* shows the frequency dependences of permittivity ϵ' for samples of the two systems at room temperature. We observed an increase in the permittivity ϵ' with a decrease in frequency, pointing to likely interphase polarization. The polarization of the spatial charge in the studied membranes under normal conditions is explained by the presence of moisture. Perfluorosulfone membranes are hygroscopic, so the water they absorb accumulates in hydrophilic ionic regions [2–4]. The increase in ϵ' in the low frequency range may also be explained by the manifestation of dipole relaxation polarization caused by the presence of polar groups in the polymer structure.

The growth in ϵ' with increasing temperature (Fig. 1,*b*) is caused by an increase in the number of protons and their mobility, leading to a change in their number at the interphase boundaries. Furthermore, when the temperature rises in the considered narrow range (320–420 K), the contribution of dipole-orientation polarization increases, since the orientation of the dipoles is facilitated if they are initially rigidly clamped within the polytetrafluoroethylene carbon framework of the membrane.

Doping of MF-4SK membranes with terbium increases the permittivity of the system by about 25%, which is due to the strong polarizing effect of terbium ions Tb^{3+} on water molecules in the polymer matrix, consequently increasing the number of protons in the system by the proposed scheme:



Analyzing the experimental temperature dependences of the imaginary part of complex permittivity (the dielectric loss factor) that we obtained, we detected the presence of dispersion for this quantity. The maxima of dielectric losses were detected (Fig. 2); their presence can be explained by the relaxation processes that generate these losses [6].

We estimated the distributions of relaxors over relaxation times using the experimental data obtained for the frequency dependences of the dielectric loss tangent and the loss factor, i.e.,

$$\text{tg}\delta = f_1(\omega), \quad (2)$$

$$\epsilon'' = f_2(\omega). \quad (3)$$

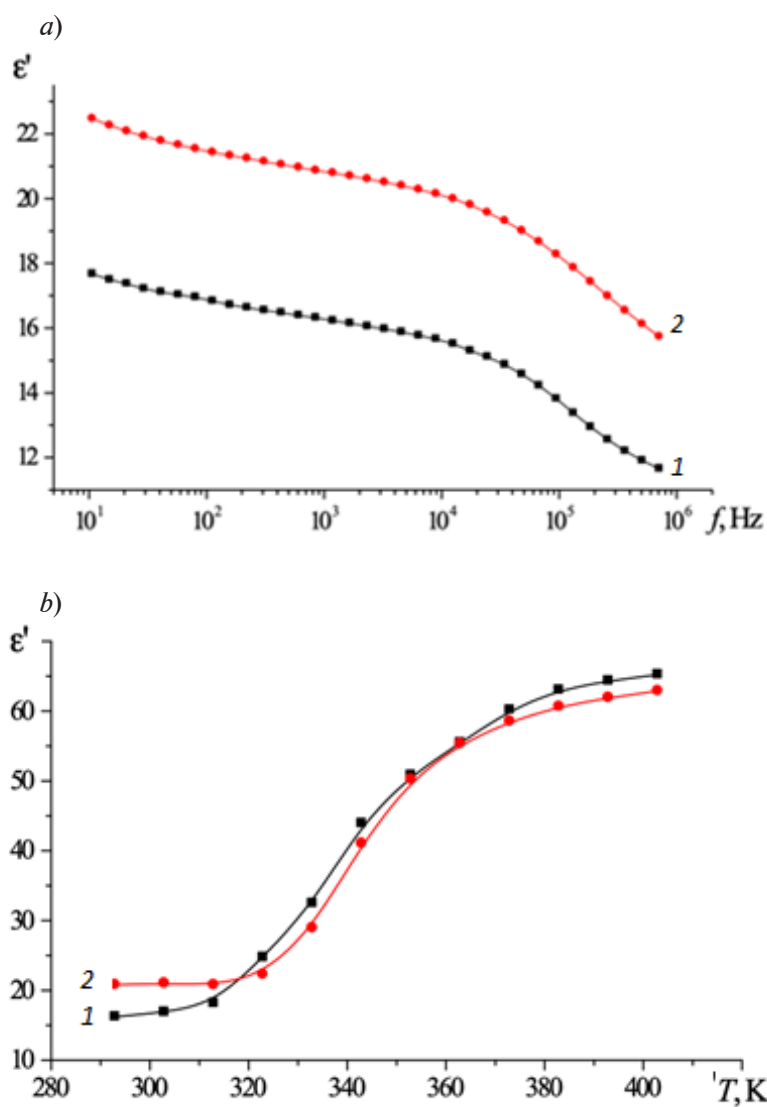


Fig. 1. Frequency dependences at temperature $T = 293$ K (a) and temperature dependences at frequency $f = 1$ kHz (b) of the real part of complex permittivity in MF-4SK (1) and MF-4SK + Tb (2) membrane samples

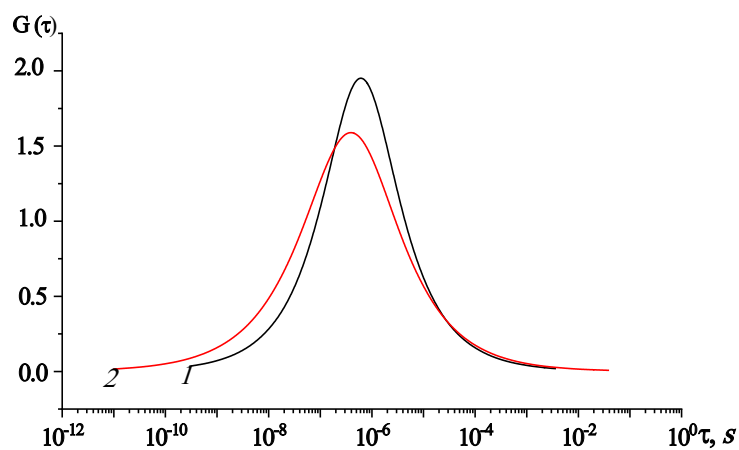


Fig. 2. Forms of relaxor distribution functions over relaxation times $G(\tau)$ for MF-4SK (1) and MF-4SK + Tb (2) samples at temperature $T = 323$ K



The relaxation parameters $\Delta\varepsilon$, τ_{\max} , α , β were determined within the Havriliak–Negami approximation by fitting the experimental curves to a function of the form

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha}]^{\beta}}, \quad (4)$$

where ε_{∞} is the permittivity at the high-frequency limit; $\Delta\varepsilon$ is the difference between the low-frequency permittivity and the permittivity at the high-frequency limit; τ , s, is the relaxation time; α , β are the exponents describing the asymmetry and width of the corresponding spectra.

Analyzing the experimental data obtained, we made an assumption that the distribution of relaxors over relaxation times corresponds to the Cole–Davidson and Cole–Cole models for the cases of asymmetric and symmetric distributions of relaxors. According to our assumptions, functional groups $-\text{CF}_2$, $-\text{CH}$ and $-\text{CH}_2$, as well as hydrophilic polar sulfogroups $-\text{SO}_3$, detected by infrared scanning of the studied membranes [7], can act as such relaxors.

The table gives the activation energies E_{ar} of the detected processes, calculated from the temperature dependence of the most probable relaxation time τ_{\max} (Fig. 3).

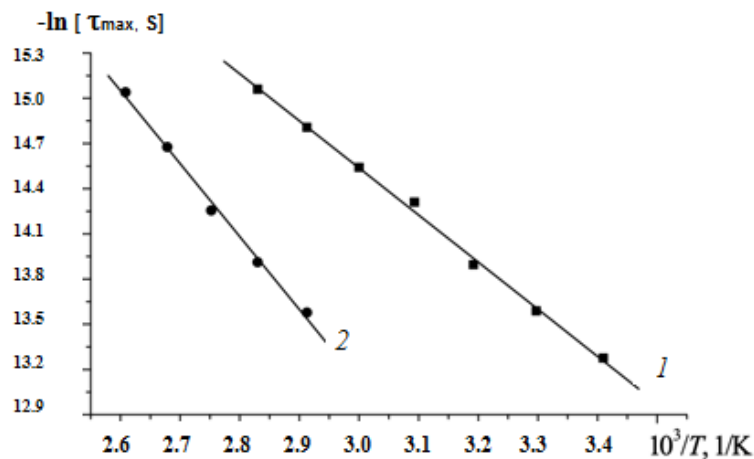


Fig. 3. Temperature dependences of the most probable relaxation time τ_{\max} for MF-4SK (1) and MF-4SK + Tb (2) samples

The permittivity dispersion detected during measurements in combination with the dielectric loss maxima in the mid-frequency range likely points to a mechanism of dipole relaxation polarization in the samples considered.

The regularities obtained can be explained within the framework of the model proposed in [8], where the structure of disordered systems is interpreted as a set of dipoles, each with its own relaxation time depending on the activation energy required for charge carriers to overcome the potential barrier.

Table

Activation energies of relaxation processes in the studied samples

| Sample | Temperature range, K | Activation energy E_{ar} | |
|-------------|----------------------|----------------------------|-----------------|
| | | eV | 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 |

Analyzing the frequency dependences of specific conductivity σ' of MF-4SK polymer matrices, both original and terbium-doped, we reached a conclusion that these dependences follow a power law inherent to many amorphous and crystalline semiconductors:

$$\sigma'(\omega) \sim \omega^s, \quad (5)$$

where σ' , S , is the conductivity; s is the exponent.

Considering the temperature dependence of the factor s for samples of both systems, we discovered two temperature regions: as the temperature increases, the parameter s first decreases (region I at $T = 313$ K), and then increases (region II at $T = 323$ K). The obtained power-law dependence (5) of conductivity on frequency and the variation in the value of the parameter s with increasing temperature point to a hopping conductivity mechanism when charge carriers (ions and electrons) make thermally activated jumps within the disordered structure of the systems considered [9].

According to the Correlated Barrier Hopping model (CBH) [10], an increase in temperature in the range of 280–330 K is accompanied by a decrease in the value of the parameter s for modified and non-modified membranes (see Fig. 10 in [10]), which is in good agreement with the CBH model suggesting that charge carriers hop between energy states, overcoming potential barriers.

According to this model, the value of the exponent s is determined by the following dependence:

$$s = 1 - 6kT/W_M, \quad (6)$$

where W_M is the height of the potential barrier, T is the temperature, k is the Boltzmann constant.

The increase in the value of s can be explained by using the Austin–Mott model [12], which we observed for both systems under study.

In view of the structure of the given membranes, the transition from the classical conduction mechanism to the quantum mechanical one in the temperature range considered can be explained as follows.

At low temperatures, the displacement distance of the charge carrier is incomparable with the time for which the electric field is applied (this was confirmed in [2]); as a result, the protons can only travel to limited distances within the sample, and not all protons approaching the interfacial boundary can overcome it.

The situation is different in the high-temperature region. Proton motion is no longer limited to conductive inclusions; the protons can move freely in the sample volume, since the distance traveled by the particle is proportional to the force application time.

Conclusion

We considered the mechanisms of electrical conductivity in a proton-exchange perfluorosulfonic membrane and the effect of terbium ions introduced into the membrane matrix (Te-modified membrane) on these mechanisms. We measured the temperature and frequency dependences of complex permittivity in both samples.

Analyzing the obtained results, we detected an increase in the real part of permittivity with a decrease in frequency and an increase in temperature.

Measuring the dielectric loss factor ε'' in the layers of the given systems at different temperatures, we found a maximum of this value for both non-modified (MF-4SK) and terbium-doped (MF-4SK + Tb) membranes (MF-4SK is the Russian equivalent of the Nafion membrane). Analysis of the obtained experimental data lead us to assume that there is a distribution over relaxation times for relaxors, which can be functional groups $-\text{CF}_2$, $-\text{CH}$ and $-\text{CH}_2$, as well as hydrophilic functional polar sulfogroups $-\text{SO}_3$, in accordance with the Cole–Davidson and Cole–Cole models.

The power dependence (5) of conductivity on the frequency and the variation in the parameter s with an increase in temperature (6) are typical for the hopping conductivity mechanism.

A transition from the classical charge transfer mechanism to the quantum mechanical one was established for the samples of the two systems considered.



Charge transfer in the studied objects has an activation character with activation energies

$$E_1 = (0.33 \pm 0.01) \text{ eV and } E_2 = (0.37 \pm 0.01) \text{ eV}$$

for MF-4SK and MF-4SK + Tb, respectively.

Introducing a terbium impurity into the polymer matrix causes a decrease in the conductivity of the initial membranes, which 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.

The study offers further insights into perfluorosulfone membranes, which can be useful for designing and constructing fuel cells with improved characteristics.

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