Hybrid Materials Based on the Nafion Membrane and Acid Salts of Heteropoly Acids $M_xH_{3-x}PW_{12}O_{40}$ and $M_xH_{4-x}SiW_{12}O_{40}$ (M = Rb and Cs)

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Abstract—The effect of the modification of Nafion membranes with nanoparticles of acid salts of heteropoly acids has been described. Ion conductivity at high and low relative humidity (RH), diffusion permeability, and mechanical properties of hybrid materials have been studied. It has been shown that the membrane modification with the acid salts of heteropoly acids makes it possible to increase the ionic conductivity both at high and low humidity, with the conductivity being determined by the amount of charge carriers at the surface of the dopant particles. The most significant effect of dopant incorporation is observed at low humidity. The conductivity of the sample Nafion + 5 wt % of $Cs_xH_{4-x}SiW_{12}O_{40}$ at room temperature is $\sigma = 4.1$ mS/cm and it is more than two times as high as the conductivity of the initial Nafion membrane at RH = 30%. By modifying with the acid salts of heteropoly acids, the diffusion permeability of the hybrid membranes is reduced as compared to the initial membrane, thereby suggesting an increase in cation transport selectivity along with an increase in proton conductivity. Introduction of small amounts of the dopant do not cause deterioration of the mechanical properties of the membrane.

Keywords: Nafion, heteropoly acids, ion conductivity, diffusion permeability, mechanical properties

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INTRODUCTION

In recent decades, the problem of finding nonpolluting energy sources is crucial. One solution is to use low-temperature fuel cells (FC) working on different types of fuel. At the same time, there is a steady tendency of annual increase in the number of studies to obtain solid polymer electrolytes for low-temperature fuel cells, since these devices are already used in stationary power plants of direct and backup power supply and as a power source of mobile devices [1–4]. To date, the most promising solid polymer electrolytes are sulfonated perfluoropolymer cation exchange membranes of the Nafion type, which have not only high conductivity, but also chemical resistance and mechanical strength [5–7]. Their main disadvantage is the pronounced dependence of their conductivity on the relative humidity.

To increase the conductivity of ion exchange membranes, in particular at low humidity, various organic or inorganic compounds are incorporated into their pores [8–15]. Modification of Nafion membranes with heteropoly acid hydrates ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiMo_{12}O_{40}$) which possess an unprecedentedly high proton conductivity among solid electrolytes [16] can result in a significant increase in conductivity even at high temperatures [9,

16–19]. However, heteropoly acids are soluble in water and can therefore be easily washed out from the membrane matrix. To avoid this, they are converted into insoluble acid salts [20–22]. This modification is less effective as compared with materials doped with heteropoly acids, but can significantly increase their stability.

The advantage of acid salts of heteropoly acids is the ease of preparation of particles with a small size [23, 24] so as they can be introduced into the membrane matrix using the most convenient method from the technological point of view— casting from a polymer solution.

To date, acid cesium salt of phosphotungstic heteropoly acid is predominantly used as the dopant; the salt of silicotungstic heteropoly acid is used as well, although less frequently [25, 26]. An important task is to compare the influence of types of cations and anions of acid salts of heteropoly acids used to modify the Nafion membrane.

The aim of this work was to prepare Nafion hybrid membranes with different contents of acid salts of heteropoly acids $M_xH_{3-x}PW_{12}O_{40}$ and $M_xH_{4-x}SiW_{12}O_{40}$ (M = Rb and Cs) by casting a polymer solution containing dopant nanoparticles and to study ionic con-

ductivity, diffusion permeability, and mechanical properties of these membranes.

EXPERIMENTAL

Reagents and Materials

A Nafion polymer solution (Aldrich, 5% solution in lower aliphatic alcohols) was used as the material for membrane casting. Silicotungstic ($H_4SiW_{12}O_{40} \cdot xH_2O$, from Aldrich) and phosphotungstic ($H_3PW_{12}O_{40} \cdot xH_2O$, from Acros) heteropolyacids, rubidium nitrate ($RbNO_3$, from Aldrich, 99%), cesium carbonate (Cs_2CO_3, from Aldrich, 99.9%), solutions of nitric and hydrochloric acids (from Khimmed, high pure), and deionized water (resistance of 18.2 MΩ) were used.

Synthesis of Acid Salts of Heteropoly Acids

Medium salts of phosphotungstic and silicotungstic heteropoly acids were obtained by precipitation from aqueous solutions of the corresponding heteropoly acids using an excess of cesium carbonate and rubidium nitrate solutions added in accordance with the procedure described in [24]. The resulting precipitates were washed with distilled water, centrifuged, and decanted. To obtain acid salts the corresponding normal salts were treated with dilute nitric acid, washed with distilled water, and dried in air at 110°C.

Preparation of Hybrid Membranes

Hybrid membranes were prepared by casting a solution of the Nafion polymer, in which the calculated amounts of acid salts of heteropoly acids were preliminarily added. The concentration of dopants in the matrix of the membrane varied from 0 to 7 wt %. To homogenize the mixture, it was stirred for 1 h using a magnetic stirrer (1400 rpm). The resulting solution was poured onto glass Petri dishes and dried in air at room temperature for 24 h followed by 1 h at 60°, 70°, 80°, and 85°C and 4 h at 60°C to remove the solvent. The membranes were carefully removed from the surface of the Petri dishes and subjected to hot pressing at a temperature of 200°C and 1 atm for 5 min to provide better mechanical stability. The membranes were conditioned to ensure the standard conditions. This required their sequential double treatment at room temperature with a 5% HCl solution for 1.5 h and washing with deionized water until disappearance of the reaction for Cl- ions.

Investigation Methods

Microstructure of samples was studied by transmission electron microscopy (TEM) on a JEOL JEM-2100 microscope (accelerating voltage of 200 kV). Membranes were preliminarily dispersed ultrasonically in ethanol to reduce the thickness of the sample areas to be examined by TEM.

X-ray powder diffraction (XRD) studies were performed on a Rigaku D/MAX-2000 diffractometer (CuK_α radiation). XRD data were processed using the Rigaku Application Data Processing software and compared with the PDF2 database. The membrane samples were preliminarily dried at 150°C. The coherent scattering domain (CSD) size was calculated from the X-ray powder diffraction patterns according to the Debye−Scherrer formula.

The water uptake of the membranes was determined by thermogravimetry using a NetzschTG 209-F1 thermobalance. The experiment was carried out in platinum crucibles at a heating rate of 10 K/min up to 200°C. To standardize all samples, they were brought to a constant weight at a relative humidity of 95 and 32%. To ensure the necessary conditions we used saturated solutions of $CaCl_2$ and Na_2HPO_4 (95 and 32%, respectively). The water uptake (in %) was calculated from the difference between the membrane weight before and after heating with respect to the weight prior to heating.

The proton conductivity of membranes was measured in contact with water and in air at varied relative humidity in the temperature range of 25−80°C. To set the required humidity and temperature we used a Binder MKF115 constant climate chamber (humidity accuracy was ±2.5%). The resistance was measured by impedance spectroscopy in accordance with the double-contact method using carbon electrodes with active surface area of about 0.25 cm^2 and a 2B-1 AC bridge in the frequency range of 10 Hz−2 MHz. The value of the conductivity was calculated from the resistance determined as the intercept of the impedance plot with the ohmic resistance axis.

To determine the diffusion permeability, the sample was placed in a cell consisting of two compartments, each being 32 cm^3 in volume. One of them contained a 0.1 M HCl solution, the other contained deionized water stirred at a constant rate. Changing the pH in the chamber, which originally contained water, was controlled using an Expert-001 pH-meter (Ekoniks Ekspert) every 3 s. The pH-meter was calibrated using standard buffer solutions. The experiment was finished when pH of the solution reached the constant value. The diffusion permeability was determined using the equation:

$$P = \frac{dc}{dt}\frac{Vh}{S\Delta c}, \qquad (1)$$

where V is the volume of the solution, cm^3; h is the membrane thickness, cm; Δc is the concentration gradient, mol/cm^3; t is the time, s (P value was determined with the error of less than 1%). The rate of concentration change $\frac{dc}{dt}$ was determined as the change in concentration of H$^+$ ions over a predetermined time interval in the cell that initially contained water.

The mechanical properties were studied using a Tinius Olsen H5KT tensile testing machine with a 100 N force sensor at room temperature $T = 27 \pm 2°C$ and a relative humidity of RH $= 20 \pm 2\%$. Rectangular samples of 100 mm in length and 10 mm in width were used, which had been held to acquire a constant weight at a relative humidity of 95 and 32% prior to the experiment. Five experiments were conducted for each composition. The thickness and width of each sample were determined immediately before the experiment as the average value at five points along the entire length (with a Mitutoyo micrometer, accuracy of 0.001 mm). The basic length was 60 mm. Engineering stress related to the initial cross-sectional area of the sample was used when interpreting the results. Young's modulus (MPa) was determined from the slope of stress–strain curves in the elastic deformation range. The yield point was determined as the intersection of the tangents to the curve segments corresponding to elastic and plastic strains. The values of Young's modulus, yield point, tensile stress, and elongation at break were obtained for each curve, and mean values were calculated for each series of samples (error was calculated using Student's t-test at a confidence level of 95%).

Fig. 1. TEM images of the hybrid membrane Nafion + 3 wt % $Cs_xH_{3-x}PW_{12}O_{40}$.

RESULTS AND DISCUSSION

According to our TEM data, the shape of particles of heteropoly acid salts in the membrane matrix is close to spherical and their size mainly fall in the range of 4−10 nm; however, larger particles are also formed (Fig. 1). The CSD size calculated from the X-ray diffraction data is 12−14 nm for all membrane samples and therefore does not depends on the dopant concentration. Since the dopant particles are hydrophilic, it should be expected that during the casting of the membrane, pores composed of hydrophilic functional groups would be formed around them. In this case, with increasing dopant concentration the number of pores in which the particles are located is increased. According to the scanning electron microscopy data, the size of particles of acid salts of heteropoly acids in the powder and even values of their CSD are considerably greater [24] than the particle size in the membrane matrix. This results from the fact that larger particles give the greatest contribution to the CSD, in spite of the fact that smaller ones are also present in the sample. From a comparison of the particle size before and after the membrane formation we can conclude that there has been the degradation of agglomerates and, seemingly, of individual crystals as well. This is most likely to occur at the stage of homogenization of the solution. Since the exchange of alkali metal cations proceeds on the surface of particles of heteropoly acid salts, the degree of substitution must increase with decreasing their size [23]. After the preparation of the membrane, it was conditioned in an acid solution in which all alkali metal cations were replaced by protons on the surface. Therefo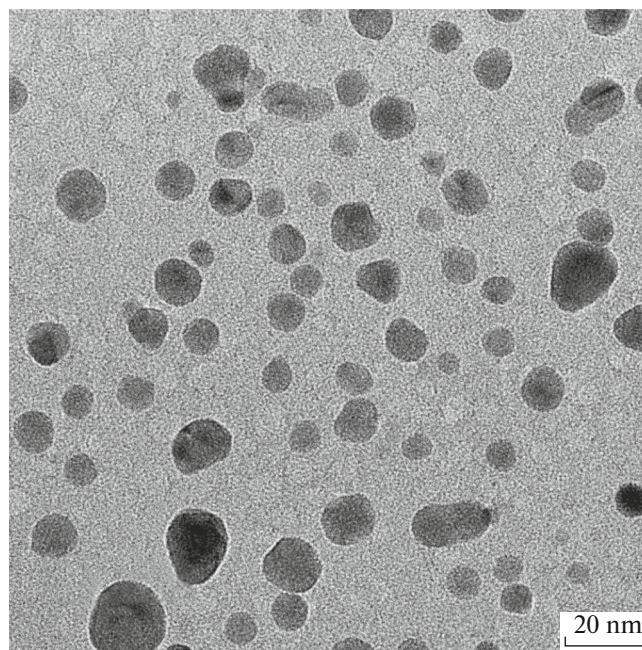re, the composition of salts in the powder form is expected to be different from that in the membrane matrix; in the second case, we can expect a higher degree of substitution. Moreover, in the modification with salts of silicotungstic heteropoly acid, whose CSR values are decreased in a greater extent, the substitution degree will vary to a greater extent as compared to the modification with the phosphotungstic salts.

The type of salt has no effect on the water uptake of membranes. According to the TGA data, the water uptake of the hybrid samples at RH = 95% is close to the initial Nafion membrane and is about 20%. When 7% of the dopant is introduced, the water uptake is reduced to 17%. When the relative humidity is 32%, the water uptake of all samples is almost the same to be 3.5%.

Ionic Conductivity at High Humidity

Figure 2 shows the ionic conductivity measured in contact with water as a function of the amount of acid salts of heteropoly acids introduced. The conductivity of hybrid membranes is increased as the amount of the dopant increases and reaches its maximum value at a concentration of 3–5 wt %. With increasing the concentration to 7 wt %, the conductivity of the sample doped with $Cs_xH_{3-x}PW_{12}O_{40}$ is also decreased as compared to that of the unmodified Nafion membrane.

Table 1 collates the ionic conductivities measured in contact with water for the membranes that contain 3 wt % different acid salts of heteropoly acids. The conductivity of the hybrid membranes is higher than that of the initial Nafion membrane. The samples
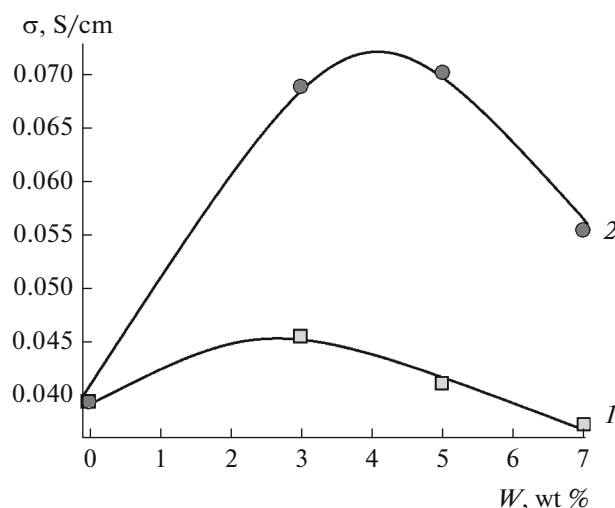
Fig. 2. Ionic conductivity of hybrid Nafion membranes as a function of the concentration of acid salts of heteropolyacids therein: (*1*) $Cs_xH_{3-x}PW_{12}O_{40}$, (*2*) $Cs_xH_{4-x}SiW_{12}O_{40}$. Measurements were made at a relative humidity of 100% in contact with water at a temperature of 40°C.

based on the silicotungstic salts possess higher conductivity relative to the case of phosphotungstic acid salts. The maximum value is achieved for the membrane containing $Cs_xH_{4-x}SiW_{12}O_{40}$; it is 1.7 times greater than the conductivity of the initial Nafion membrane.

Increasing the ionic conductivity by introducing acid salts of heteropoly acids is due to an increase in the concentration of protons in the material, which act as charge carriers and are involved in ion transport. During the membrane formation by casting the polymer solution in the presence of the dopant particles, hydrophilic pores are formed around hydrophilic nanoparticles of acid salts. The homogeneity of distribution of the particles introduced and their size largely determine the transport properties of the resulting materials. The decline in conductivity after reaching the dopant concentration of 3–5 wt % is due to blocking the conduction channels.

Since the particle size of the salts is practically identical according to the CSD data, it can be assumed

Table 1. Ionic conductivity (mS/cm) of test membranes containing 3 wt % dopant as measured at the 100% relative humidity in contact with water and a temperature of 40°C

Dopant	σ, mS/cm
–	39.5
$Rb_xH_{3-x}PW_{12}O_{40}$	48.5
$Cs_xH_{3-x}PW_{12}O_{40}$	45.5
$Rb_xH_{4-x}SiW_{12}O_{40}$	61.6
$Cs_xH_{4-x}SiW_{12}O_{40}$	68.9

that the conductivity of the membrane is determined by the number of protons occurring on the surface of the particles. As noted above, the degree of replacement of alkali metal cations by protons is determined primarily by the particle size. Therefore, the number of protons and, hence, conductivity in the materials containing the salts of tetrabasic silicotungstic heteropoly acid are greater than in the materials containing the salts of tribasic phosphotungstic heteropoly acid.

The size of the dopant particles (12–14 nm) is substantially larger than the pore size of the initial Nafion membrane, which is no more than 5 nm [27]. Therefore, a greater number of functional sulfo groups, which is limited by their concentration in the chains, are needed to form so voluminous pores around the particle. This reduces the volume of solution in the pore, thus increasing steric hindrances during ion transport. It is most likely for this reason that the activation energy of conductivity of the membranes is slightly increased from 17 to 19–24 kJ/mol by introducing the dopant.

Ionic Conductivity at Low Humidity

The conductivity of both initial and hybrid membranes decreases with decreasing humidity. The dependence of the conductivity of the dopant content at a relative humidity of 30% passes through a maximum at a 3–5 wt % concentration of a heteropoly acid salt (Fig. 3). The conductivity of the sample Nafion + 5 wt % $Cs_xH_{4-x}SiW_{12}O_{40}$ is 4.1 mS/cm and more than twice higher as the conductivity of the Nafion membrane. When the dopant concentration exceeds 5%, the conductivity of the hybrid membranes become comparable or even lower than that of the initial Nafion membrane. The activation energy of conductivity of the hybrid membranes differs by 15% or less from that of the initial membrane and is 35–40 kJ/mol.

The observed effect is due the fact that the inclusion of dopant particles in the membrane pores impedes blocking the channels during dehydration and opens the possibility of alternative proton transfer along the surface of particles of acid salts of heteropoly acids.

Diffusion Permeability

When modifying Nafion membranes with particles of acid salts of heteropoly acids, their diffusion permeability for a 0.1 M HCl solution decreases (Table 2). During the measurement of diffusion permeability, the simultaneous transfer of cations and anions through the cation exchange membranes occurs. However, the rate-determining step is the transfer of anions, the concentration of which in the membrane is much lower. Therefore, a decrease in the diffusion permeability and a simultaneous increase in the ionic conductivity of the membranes is an indication of enhancement of cation transport selectivity by introducing a low concentration of the dopant.

This enhancement is due to redistribution of the ion concentration as a result of membrane modification. The dissociation of the sulfo groups localized on the pore walls imparts a negative charge to them. The main part of cations are located along the walls, forming an electrical double layer, and anions on the contrary are displaced to the center of pores [28]. However, particles of heteropoly acid salts occur in the center of pores in the hybrid membranes, and the dissociation of OH groups on the surface of the particles imparts a negative charge to the surface. The anions are displaced from these pores not only because of the steric factor, but also as a result of formation on the surface of the particles of the second Debye layer opposite to the one forming near the pore walls [28]. This complicates anion transport and leads to a reduction in diffusion permeability. At the same time, since the particle size in this case is much higher than in the synthesis inside the membranes, nanoparticles at a concentration of about 3 wt % not necessarily occur in each pore, and anion transport paths can be through the vacant pores. Therefore, in most cases, the decrement in diffusion permeability is rather small.

As the dopant concentration increases, the formation of the system of pores and channels becomes unpredictable and large hollow regions (cavities) can occur in places of close localization of bulky particles, through which the anions are transferred faster as compared with pores [28]. Therefore, at a high dopant concentration, the diffusion permeability changes in a less predictable manner and can significantly increase (Table 2).

Mechanical Properties

To study the mechanical properties, samples based on the Nafion membrane containing 3 wt % dopant were taken. The properties were evaluated by analyzing stress−strain curves. It was found that the elongation and at break and the breaking stress for the same composition may be very different in different experiments, despite the fact that the other parameters and the curves were close to each other. Significant differences in the strength and elasticity of the samples are associated with the heterogeneity of the structure of the system of pores and channels, which are similar to microcracks in solids and reduce the strength of materials. This feature is observed not only in membranes obtained by casting, but also in samples prepared by extrusion, which are characterized by a more homogeneous system [29]. Thus, the tensile stress and elongation at break were measured with a large error. With decreasing the relative humidity, the elasticity of the membranes is greatly reduced (from 80−120% at a relative humidity of RH = 95% to 20−70% at RH = 30% for Nafion), while the strength is less reduced (from 12.3 ± 0.5 MPa at RH = 95% to 10.1 ± 1.6 MPa at RH = 30% for Nafion).

By modifying the membranes with salts of heteropoly acids, the strength and elasticity are varied within the error as compared with the unmodified
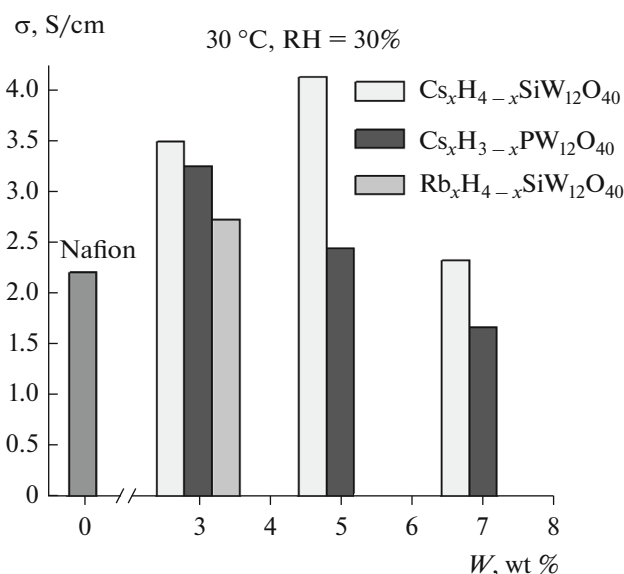

Fig. 3. Ionic conductivity of hybrid membranes with varied amount of acid salts of heteropoly acids as measured at a relative humidity of 30% and $t = 30°C$.

Nafion membrane. As the relative humidity decreases, Young's modulus of elasticity and proportional limit stress decrease (Table 3). At the same time, the modification has almost no effect on their values. Differences from the initial Nafion membrane exceeding the error are noticeable only in the case of introduction of $Rb_xH_{4-x}SiW_{12}O_{40}$ (Young's modulus increases) or $Cs_xH_{3-x}PW_{12}O_{40}$ (proportional limit stress decreases at low relative humidity). The increase in Young's modulus with the decreasing relative humidity is due to the decrease in the amount of water, which acts as a plasticizer, in the membrane. It is a positive result that the presence of nanoparticles of acid salts of heteropoly acids has no detrimental effect on the mechanical properties. Note that the effect is observed only for a small volume fraction of the inor-

Table 2. Diffusion permeability ($P \times 10^7$ cm^2/s) of a 0.1 M HCl solution through membranes into water

Dopant	$P \times 10^7$, cm^2/s	
	3 wt %	7 wt %
−	4.9	
$Rb_xH_{3-x}PW_{12}O_{40}$	4.1	4.1
$Cs_xH_{3-x}PW_{12}O_{40}$	1.9	1.8
$Rb_xH_{4-x}SiW_{12}O_{40}$	3.6	4.0
$Cs_xH_{4-x}SiW_{12}O_{40}$	4.3	7.7

Table 3. Young's modulus and yield point of the test Nafion membranes containing 3 wt % dopant as measured after holding at different relative humidities

Dopant	Young's modulus, MPa	Proportional limit stress, MPa
Relative humidity RH = 95%		
–	192 ± 11	8.0 ± 0.9
$Cs_xH_{3-x}PW_{12}O_{40}$	210 ± 12	8.7 ± 0.2
$Cs_xH_{4-x}SiW_{12}O_{40}$	198 ± 6	8.3 ± 0.5
$Rb_xH_{4-x}SiW_{12}O_{40}$	247 ± 17	8.5 ± 0.7
Relative humidity RH = 30%		
–	267 ± 16	7.4 ± 0.2
$Cs_xH_{3-x}PW_{12}O_{40}$	265 ± 23	6.8 ± 0.4
$Cs_xH_{4-x}SiW_{12}O_{40}$	267 ± 19	7.8 ± 0.95
$Rb_xH_{4-x}SiW_{12}O_{40}$	277 ± 14	7.5 ± 0.8

ganic component, which does not alter significantly the polymer matrix in this case.

CONCLUSIONS

The influence of modification of Nafion membranes with nanoparticles of rubidium and cesium acid phosphotungstates and silicotungstates on their properties depending on the concentration of the additives has been studied. The presence of the nanoparticles increases the ionic conductivity at both high and low relative humidities. The conductivity value and the position of the maximum of the conductivity as a function of the amount of the additive vary depending on the type of acid salt. At low humidity, membranes containing 5 wt % $Cs_xH_{4-x}SiW_{12}O_{40}$ possess the highest conductivity, being more than twice the conductivity of the initial Nafion membrane. The membranes modified with acid salts of heteropoly acids, have lower values of diffusion permeability as compared to the initial Nafion membrane, indicating an increase in cation transport selectivity together with an increase in proton conductivity. The introduction of small amounts of the dopant does not cause deterioration of the mechanical properties of the membrane. Thus, it can be concluded that hybrid membranes of this type hold promise as solid electrolytes in low-temperature fuel cells.

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