

On the mechanism of increasing ion conductivity in hybrid membranes

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Ion conductivity of hybrid membrane materials with incorporated nanoparticles of inorganic compounds and polyaniline was considered. A new theory of semielasticity of membrane pore walls was suggested in order to explain the phenomenon of increasing ion conductivity in such systems. It was assumed that in the low humidity region an additional contribution to the conductivity increase is made by the transfer over the incorporated nanoparticles surface.

Key words: ion-exchange membranes, hybrid membranes, nanocomposites, ion conductivity.

Purity control in industry, waste decontamination, first of all, treatment of waste waters, and search for new ecologically safe energy sources became especially important in recent decades.^{1–3} These problems can be solved mainly by using diverse membrane materials,⁴ which yet do not always meet growing demands of science and industry. Therefore, works in the area of modification of membrane materials, especially, production of hybrid membranes containing inorganic and high-molecular-weight components are now being pursued intensively.^{5,6}

Various approaches including either chemical or mechanical treatment of the surface or modification of the volume are applied for the synthesis of materials with diverse properties using comparatively few number of production-run membranes.^{4,6,7} The methods of preparation of volume-modified hybrid materials of the organic/inorganic type are most promising and they are widely used in alternative power engineering.^{5,6,8,9}

Most frequently, inorganic nanodispersed particles or a precursor for their further preparation are incorporated into a solution from which the membrane is casted. The efficiency of this modification decreases because of aggregate formation. However, the walls of nanopores, which are present in the matrix of the prepared membrane, can efficiently isolate formed particles and decrease surface tension, thus providing the thermodynamic stability of the nanoparticles. That is why, the most promising method for the preparation of hybrid materials is the synthesis of nanoparticles directly in the membrane pores, which act as unique nanoreactors.¹⁰ Among the advantages of hybrid membranes is higher ion conductivity, which is substantially manifested at low humidity.^{5,10,11} At the same time, we found no single explanation of this phenomenon in the literature.

An attempt is made to summarize our recent results to explain an increase in the ion conductivity in the hybrid membranes.

Experimental

Composite membranes were prepared by two different methods. According to the first method,^{12–15} additives were synthesized in pores of the prepared perfluorinated sulfocationite membrane MF-4SC (*in situ*). The composite membranes with the dopant content up to 4.4 vol.% (5 wt.%) and 1.9 vol.% (5 wt.%) for silica and zirconia nanoparticles, respectively, and 2.8 vol.% (12 wt.%) for silver nanoparticles were thus synthesized. The second method involves casting of composite membranes from a solution of polymer with a precursor for the further synthesis of particles.^{16,17} This method made it possible to incorporate up to 13.5 vol.% (15 wt.%) silica and 26 vol.% (14 wt.%) polyaniline (PAni) into the membrane matrix. Tetraethoxysilane (TEOS, ≥98%, Fluka) and a solution of zirconium tetrachloride (Merck) or zirconium propoxide (Aldrich, 70% solution in propan-1-ol) were used to prepare the precursor. Nanoparticles of PAni were synthesized by the polymerization of aniline hydrochloride (Merck) in a solution of MF-4SC in a water–isopropyl alcohol binary solvent in the presence of ammonium persulfate (98%, Riedel-Haen). In the synthesis of nanocomposites with incorporated silver particles, ion-exchange saturation of the MF-4SC membrane with silver cations (0.1 M AgNO₃) was alternated with reduction.

Results and Discussion

Results of investigation of the hybrid membranes. Uniform, visually homogeneous membrane materials were obtained in all experiments on modification. According to the transmission electron microscopy (TEM) data, particles 3–7 nm in size are formed by the *in situ* synthesis of composite membranes with incorporated silica and zirconia particles, while the casting method produces particles 5–10 nm in size. The metal particles formed are characterized by the bimodal distribution. The particles 20–60 nm in size are localized on the membrane surface, where the particle size is spatially unrestricted. After the

short-term treatment of the membrane with nitric acid, these particles are removed from the surface. The repeated TEM analysis showed that the main part of the reduced metal is presented by particles 2–5 nm in size, which are formed in the membrane pores restricting their size.

Particles varying in size from 3 to 7 nm are also formed by the *in situ* incorporation into the membrane heteropolyacid. For the composite membranes containing silica with heteropolyacid, the particles are in the range of 8 to 11 nm, and that in PANi was 20 nm.

Modification by zirconia nanoparticles. The temperature plots of the proton conductivity for some MF-4SC membranes modified by hydrated zirconia obtained from zirconium tetrachloride and propoxide are given in Fig. 1.

It is seen from the data presented that for the most part of obtained membranes the conductivity value is noticeably higher than that for the reference sample in all temperature range.¹³ The activation energy of conductivity of

the initial membrane is $13.7 \pm 0.6 \text{ kJ mol}^{-1}$, whereas for the modified sample it decreases to 10–12 kJ mol^{-1} . Under other equivalent conditions, the membranes in which zirconium hydroxide was synthesized using an ammonia solution have somewhat higher conductivity. In addition, the conductivity of the membranes somewhat increases when two treatment cycles are carried out. Similar results were obtained for the membranes in which hydrated zirconium oxide was obtained from zirconium propoxide (see Fig. 1, b).¹³

Modification by silica nanoparticles. The temperature plots of the proton conductivity of the MF-4SC membranes modified by hydrated silica are shown in Fig. 2. The dopant content and the conductivity of the membranes can be somewhat different depending on the modification method.¹² At the same time, the data presented show that in terms of conductivity the synthesized samples are superior to the initial sample MF-4SC. As in the case of modification with hydrated zirconia, the activation energy of conductivity of the obtained membranes decreases to 10–11 kJ mol^{-1} .

An alternative way of membrane modification is casting from a polymer solution containing a precursor for the further preparation of silica nanoparticles. The particle size obtained by this method is somewhat larger than that in the case of synthesis of nanoparticles directly inside the prepared membrane. This is due to the fact that the matrix of the non-formed membrane cannot restrict the growth of particle and at the moment of their formation the amount of the precursor and its local concentration turn out to be substantially higher than those for the synthesis inside the membrane.¹⁸ This modification method has an advantage of obtaining homogeneous membranes with a higher content of silica (up to 13.5 vol.%).

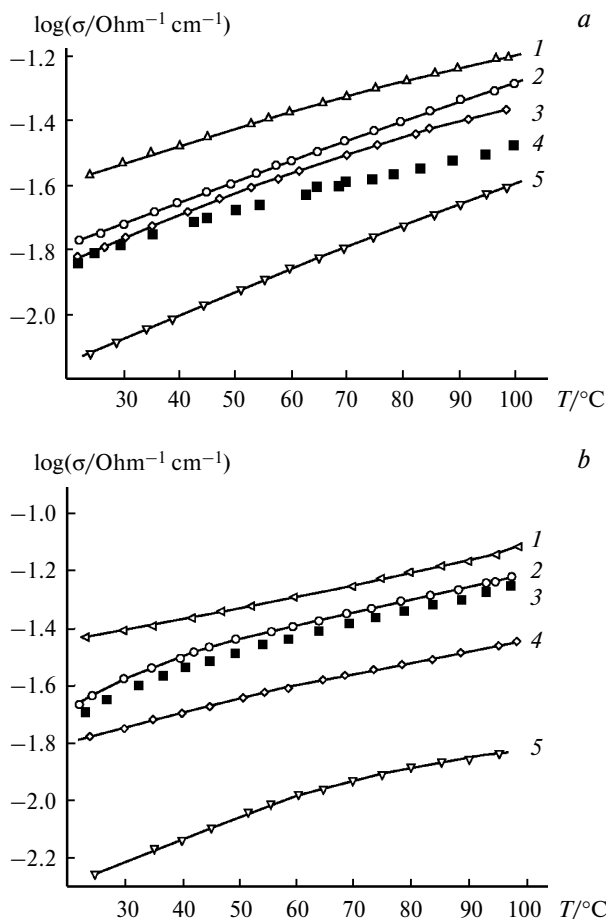


Fig. 1. Temperature plots of the conductivity of some MF-4SC membranes modified by hydrated *in situ* zirconia using ZrCl_4 (a) and zirconium propoxide (b) as precursors: precipitation with solutions of ammonia (1, 2) and NaOH (3, 4) by two (1, 3) and one treatment cycles (2, 4); and the conductivity of the reference sample (5).

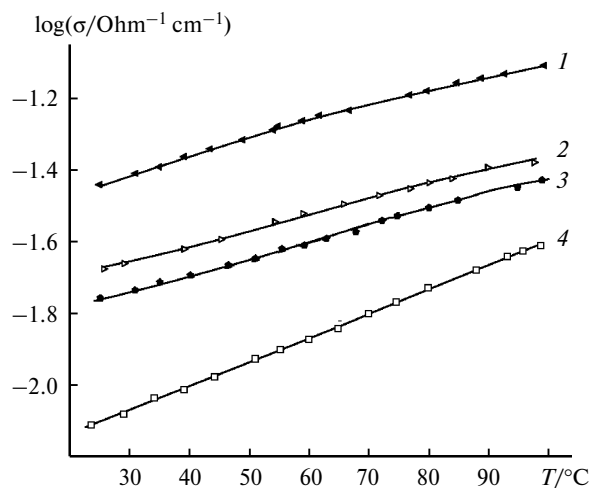


Fig. 2. Temperature plots of the conductivity of some MF-4SC membranes modified by hydrated silica synthesized in the membrane matrix (1–3) with the silica content in the samples 4.4 (1), 2.6 (2), and 1.7 vol.% (3); and the conductivity of the reference sample (4).

The temperature plots of the conductivity of the MF-4SC membranes prepared by casting and containing various amounts of SiO_2 are shown in Fig. 3.¹² The dependence of the conductivity on the silica content in the membrane is described by the curve with a maximum at 2.6 vol.% SiO_2 . Already at a content of 4.4 vol.%, the membrane conductivity is lower than that for the initial membrane MF-4SC. The plot of the activation energy of conductivity vs composition is also non-monotonic and its minimum corresponds to a dopant content of 2.6 vol.%. For the initial membrane the activation energy of conductivity is $19.0 \pm 0.6 \text{ kJ mol}^{-1}$, whereas the introduction of 2.6% SiO_2 decreases it to $13.9 \pm 0.8 \text{ kJ mol}^{-1}$. When the dopant is added in the amount $\geq 4.4 \text{ vol.}\%$, the activation energy of the membranes becomes higher than that for the initial MF-4SC.

Modification by silica nanoparticles with the modified surface. The membranes with silica synthesized by the hydrolysis of tetraethoxysilane in acidic (H^+) and alkaline (OH^-) media were prepared to study the influence of acidity of the surface of incorporated silica particles.¹¹ As expected, the properties of membranes with silica obtained by hydrolysis under various conditions show significant differences (Fig. 4). The conductivity of the membrane MF-4SC + SiO_2 (H^+) is higher than that of MF-4SC + SiO_2 (OH^-) (see Fig. 4, a). At the same time, the activation energy of the conductivity of the membrane MF-4SC + SiO_2 (H^+) is higher than those of the initial membrane and MF-4SC + SiO_2 (OH^-).

The conductivity of all membrane samples decreases with a decrease in relative humidity (RH) (see Fig. 4, b). Especially sharp decrease in conductivity is observed for the initial membrane at the humidity level below 40%. For example, the difference between values of conductivity of MF-4SC at RH 95 and 9% exceeds three orders of magni-

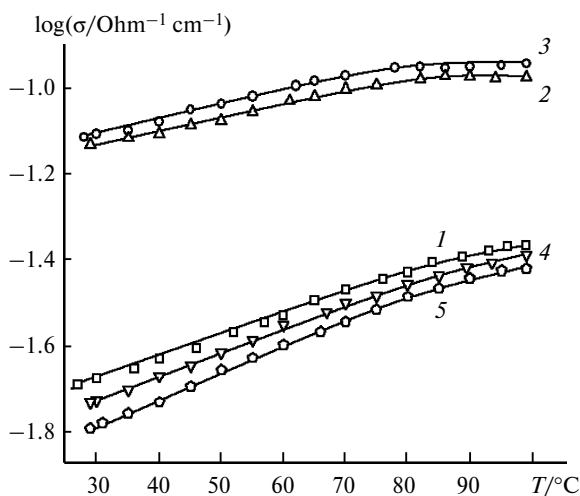


Fig. 3. Temperature plots of the conductivity of the MF-4SC membranes obtained by casting and containing various amounts of silica: 0 (1), 1.3 (2), 2.6 (3), 4.4 (4), and 8.9 vol.% (5).

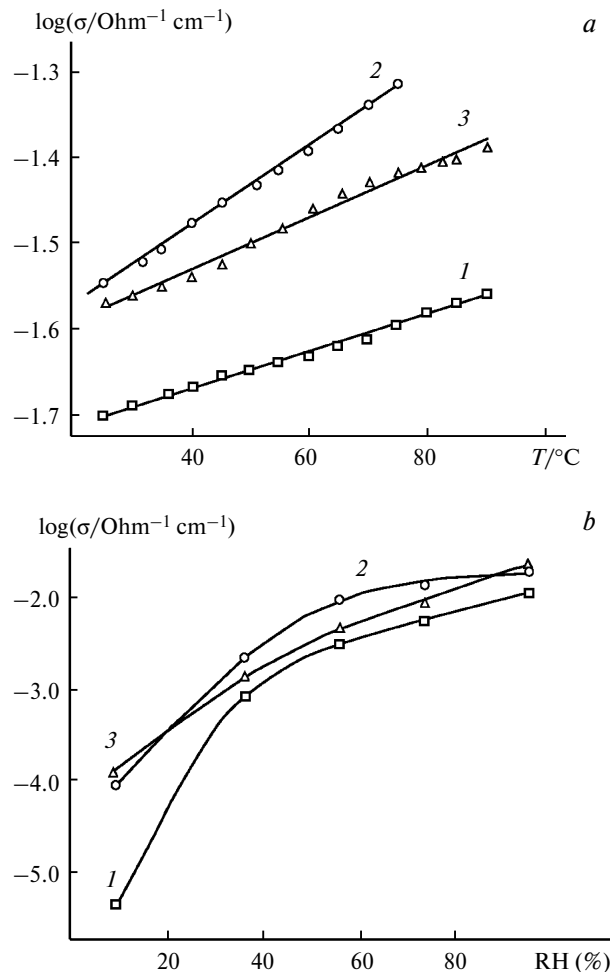


Fig. 4. Conductivity vs temperature (a) and relative humidity at 25 °C (b) for the membranes obtained *in situ*: MF-4SC (1), MF-4SC + SiO_2 (H^+) — precipitation of SiO_2 in an acidic medium (2) and MF-4SC + SiO_2 (OH^-) — precipitation of SiO_2 in an alkaline medium (3).

tude. Doping the membranes with silica makes it possible to considerably enhance the conductivity at low relative humidity. The highest values of conductivity are observed in the case of membranes obtained in an acidic medium (see Fig. 4, b). At the same time, at RH 9% the conductivity of MF-4SC + SiO_2 (OH^-) is somewhat higher than that of MF-4SC + SiO_2 (H^+). At high humidity the conductivity of the initial membrane is insignificantly lower than those for the membranes modified by silica, whereas this difference increases with decreasing humidity and at RH 9% the difference is 1.5 orders of magnitude.

The properties of the membranes can additionally be improved by the introduction of phosphotungstic acid.¹¹ Its incorporation into the membrane matrix increases the number of electricity carriers and, as a consequence, the conductivity increases. The effects becomes most substantial at lowered humidity (Fig. 5). In this case, the plot of the conductivity vs relative humidity becomes more monotonic.

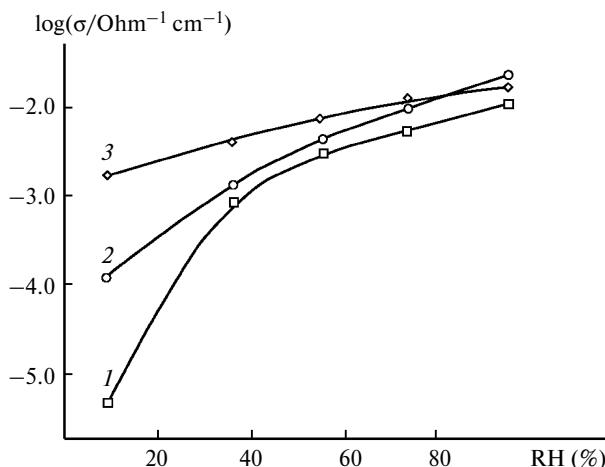


Fig. 5. Plots of the conductivity vs relative humidity at 25 °C for the membranes obtained *in situ*: MF-4SC (1), MF-4SC + SiO₂(OH⁻) (2), and MF-4SC + SiO₂(OH⁻) + H₃PW₁₂O₄₀ (3).

Modification by silver nanoparticles. The temperature plots of the proton conductivity of the initial and composite membranes MF-4SC modified by silver particles are shown in Fig. 6. Some decrease in the proton conductivity is observed upon the incorporation of a small amount of dopant (1.4 vol.% Ag). At the same time, an increase in the concentration of the incorporated dopant with an increase in the number of treatment cycles enhances the conductivity. The contribution of electron conductivity remained insignificant, being 0.1–0.2%, which is not much higher than that for the initial membrane MF-4SC (0.05%). This indicates that the concentration of the incorporated dopant is not high enough to generate direct electrical contacts between metal particles. Also note that the modification of the membranes by silver particles decreases the activation energy of conductivity to 7.8 ± 0.5 kJ mol⁻¹ for the membranes with high silver content.¹⁴

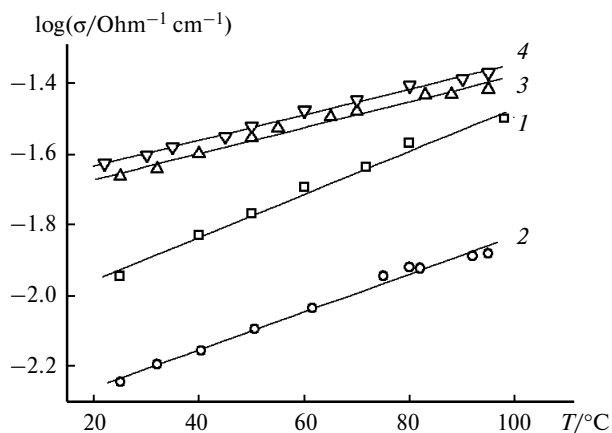


Fig. 6. Temperature plots of the conductivity of the MF-4SC membranes modified by silver: 0 (1), 1.4 (2) 2.4 (3), and 2.8 vol.% Ag (4).

Modification by PANi nanoparticles. The plot of the proton conductivity for the system $x\text{PANi} \cdot (1 - kh)\text{MF-4SC}$ (kh is the mole fraction of PANi units per one functional group of MF-4SC) vs composition is presented in Fig. 7.¹⁷ When these results are compared with the data obtained for the membranes containing PANi and acid,⁸ a low electron component of conductivity can be noted as a characteristic feature of the composite membranes prepared in our group. It is most probable that this is due to the fact that the polyaniline fragments are isolated from each other by the matrix of the membrane. A noticeable contribution of electron conductivity is observed only at high PANi content.

The addition of small (1.5 vol.%) amounts of PANi to MF-4SC substantially increases the conductivity of the membranes. Conductivity values higher than that of the initial sample is observed only at low content of PANi (≤ 8 vol.%). The activation energy for the modified membranes is 1–3 kJ mol⁻¹ higher than that for the non-modified membrane. The further increase in its concentration has a detrimental effect both on the conductivity of the membranes and on their mechanical properties. Similar character of varying conductivity is retained up to 100 °C.

Conductivity of the modified membranes at high humidity.

To analyze the nature of transfer in ion-exchange membranes of the Nafion type, first it is necessary to consider their structure. Perfluorinated chains are hydrophobic, whereas functional groups are, on the contrary, hydrophilic. Since the polymer chains are flexible, self-organization processes occur in these membranes. The perfluorinated chains form a basis of the membrane, and the functional groups are joined to form small clusters, whose size is several nanometers and it depends on the flexibility of the chains and the concentration of nonionogenic groups.¹⁹ According to the model of structure of the perfluorinated sulfoacidic membranes,^{20,21} the functional sulfo groups are arranged at the periphery of the cluster

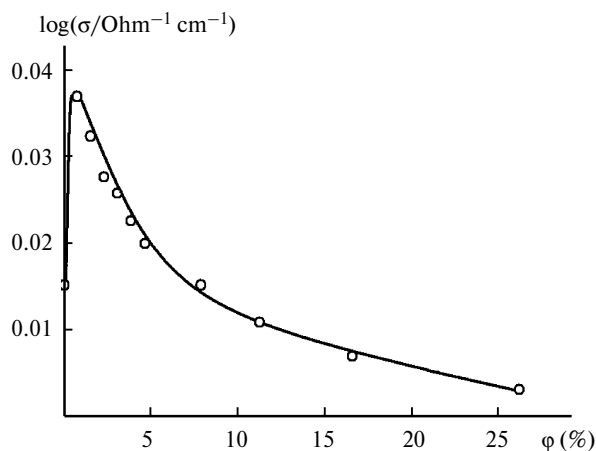


Fig. 7. Conductivity of the composite membranes MF-4SC doped with PANi at various volume fractions of PANi at 25 °C.

and the internal volume is filled with water molecules sorbed in the nanopores due to affinity to the acid incorporated in the pores. Since the perfluorinated sulfocationites are very strong acids, their $-\text{SO}_3\text{H}$ groups dissociate easily and the protons enter an aqueous solution inside the pores. The nanopores are connected to each other by more narrow channels 1–2 nm in size (Fig. 8, *a*). Ion transport in the membranes occurs *via* the system of pores and channels.

According to the model described, the membrane pore walls are elastic and, hence, the pores and channels are constricted or expanded with an increase or decrease in the moisture content of the membranes, and the latter depends directly on the humidity of the environment.^{20,21} Therefore, the conductivity of the membranes also depends strongly on humidity.¹⁹

A sharp increase in the ion conductivity during composite formation is well known.²² This phenomenon is explained by the fact that at the interface the concentration of defects, which are charge carriers in the case of ion transfer, can increase by several orders of magnitude.^{23,24} In addition, the conductivity of a composite is determined, to a great extent, by the degree of dispersity of the ion component and inert phase, the size and shape of pores in the latter, the degree of homogenization of a mixture of components, and even temperature or other conditions of composite treatment. All these factors can exert a substantial effect on the formation of the interface structure. Evidently, to achieve the maximum concentration of defects, the maximum surface area of the interface should

be approached achievable at the maximum surface of the dopant, *i.e.*, at the minimum size of its particles.

Another important factor is the affinity of the surface of dopant particles to protons of the functional groups of sulfo acid. From this point of view, an optimal result should be achieved by the introduction of a weak base, for example, PANi, into the MF-4SC membrane. Indeed, upon the incorporation of small amounts of PANi, some protons of MF-4SC are sorbed and the membrane conductivity increases appreciably (see Fig. 7). The decrease in the conductivity with an increase in the PANi concentration is due to the removal of too many electricity carriers (protons) from the transfer process, because their detachment from PANi is characterized by the high activation energy.

However, the sorption activity of the dopant particle surface does not determine all properties. There are other factors affecting the change in the ion conductivity of hybrid membranes, for instance, the nature of the modifying agent surface. So, the proton conductivity of the systems doped by silica precipitated in an acidic medium is higher than that for analogous systems containing silica precipitated in an alkaline medium (see Fig. 4, *a*), although the latter sorb protons better. In addition, the dissociation constant of the $-\text{SO}_3\text{H}$ groups in perfluorinated membranes of the MF-4SC type is equal²⁵ to 10^6 , which assumes their almost 100% dissociation under high humidity conditions. Therefore, any noticeable influence of additives on an increase in the concentration of defects that exert a determining effect on the conductivity of solid composite electrolytes can be ruled out.

An increase in the moisture content due to the introduction of particles with the hydrophilic surface is considered as another probable reason for enhancing conductivity in the composite membranes.^{12,13} In fact, this effect can make a certain contribution to the conductivity of sulfocationic membranes if they are modified by silicas or zirconias. Some increase in the moisture content is observed in these systems²⁶; however, this increase is not significant enough to explain the substantial conductivity increase. In addition, as shown by the above data, the conductivity of the MF-4SC membrane can be enhanced by the incorporation of silver particles with the hydrophobic surface. Analogous effect can be achieved by the introduction of PANi.^{17,26} The surface of the latter is not hydrophobic because of the presence of nitrogen atoms, but these are the nitrogen atoms that form strong hydrogen bonds with the sulfo groups upon incorporation into MF-4SC.¹⁷ Thus, the hydrophilic sites block each other in the system considered. According to the thermogravimetry data, this noticeably decreases the humidity of the membranes if PANi is incorporated in them.

It can be thus inferred that the conductivity of the membranes can be increased by the incorporation of additives of various nature into the membrane matrix. Let us compare the values of diffusion coefficients calculated from

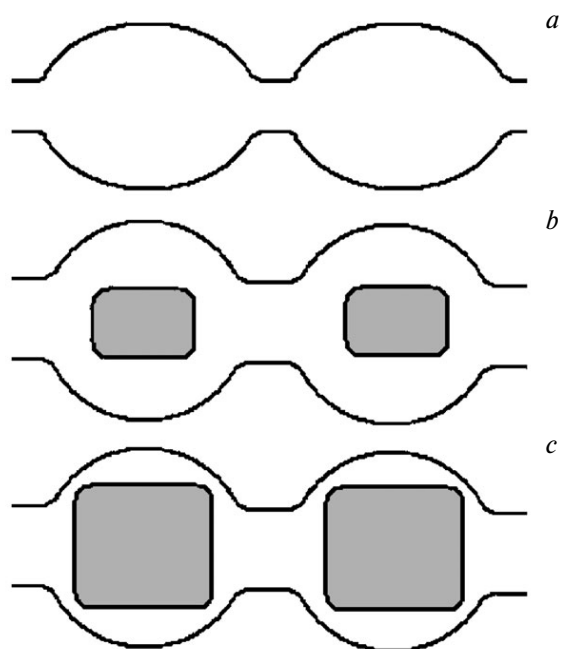


Fig. 8. Scheme of the structure of pores for the initial (*a*) and nanoparticle-modified membranes (*b*, *c*) illustrating the model of semielasticity of pore walls.

the data on NMR spectroscopy and the conductivity of the MF-4SC membranes containing various additives²⁷ (Fig. 9). The diffusion coefficients of proton calculated with allowance for ¹H NMR relaxation are mainly determined by the migration of protons and molecules of water in large pores, inside which the most part of protons is concentrated. Their values are much higher than those for the diffusion coefficients of protons calculated from the values of conductivity determined by proton migration through narrow channels. The ¹H NMR relaxation rate in the composite membranes can be higher or lower than that in the initial membrane (see Fig. 9), while modification increases the ion conductivity of MF-4SC.²⁷ Therefore, an increase in the ion conductivity of the membranes modified by hydrophilic and hydrophobic nanoparticles can mainly be explained by the influence of a dopant on the structure of pores and channels.

It is obvious that the formation of dopant nanoparticles occurs in the membrane pores where the precursor and the reactant interacting with the precursor are localized. The nanoparticles formed occupy a certain pore volume. At the same time, after modification the number of acidic protons remains the same in most cases. According to the data of thermogravimetry, the number of water molecules in the membrane matrix remained unchanged or even somewhat increases after the introduction of hydrophilic particles. For instance, after SiO₂ was incorporated in an amount of 3 vol.%, the total pore volume increases almost by a factor of 1.5: from 22.5 to 33%. Only in the case of introduction of hydrophobic particles, the humidity of the membranes somewhat decreases; however, the calculations show that the nanopore volume increases noticeably in this case as well.

Such a substantial increase in the pore volume should naturally result in an increase in the size of the connecting

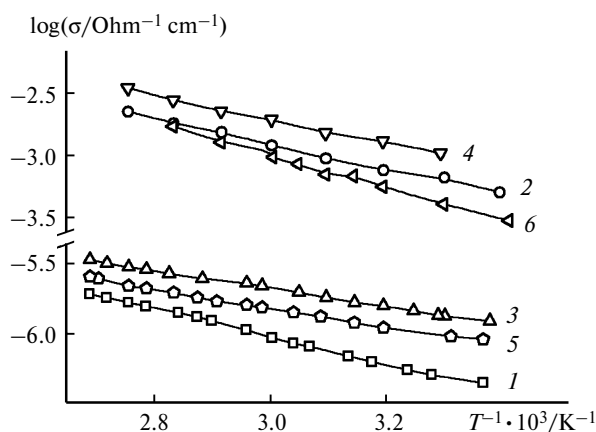


Fig. 9. Arrhenius plots of the diffusion coefficients of a proton for the initial membrane MF-4SC (1, 2) and the MF-4SC membranes modified by silica (3, 4) and acidic zirconium phosphate (5, 6)²⁷: on the basis of conductivity (1, 3, and 5) and NMR spectroscopy (2, 4, and 6) data.

channels (see Fig. 8, *a, b*). Expansion of the latter would lead to the general enhancement of conductivity, since the transfer through narrow channels is the rate-determining step of ion transport in these systems. In addition, the activation energy of conductivity in the considered case should decrease, approaching the activation energy of proton conductivity for aqueous solutions of acids (~5 kJ mol⁻¹), which is confirmed by the experimental data.

The further increase in the volume fraction of nanoparticles (>3–4 vol.%) decreases the conductivity and increases its activation energy. In the case of composites based on solid electrolytes, the explanation offered is that dopant blocks the surface of the conducting particle.^{28,29} This explanation is inappropriate for membranes. At the same time, an increase in the dopant content above this limit is accompanied by a decrease in the humidity of the membranes, and the specific pore volume remains nearly unchanged. It is most likely that elasticity of the membrane pore walls has a certain limit. Pores either cannot expand above some volume or a stronger effort should be applied for their further expansion. The driving force of pore expansion is a decrease in the chemical potential of water inside them due to the interaction with protons of the –SO₃H groups. That is why, an increase in elastic forces upon extension should result in humidity decrease. On the one hand, this does not completely agree with the assumption about the high mobility of the pore walls in the membrane.²¹ On the other hand, the violation of Hooke's law seems improbable.

Although the proposed explanation of conductivity increase in the composite membranes is mainly based on the geometric factors, the influence of the nature of dopant particles on the value of conductivity cannot be excluded. For instance, doping the membranes with silica or zirconia at the equivalent content is more efficient than doping by hydrophobic particles due to the additional sorption of water on the particle surface. In the presence of silica nanoparticles precipitated in an acidic medium, the conductivity is enhanced more strongly than in the case where similar particles are precipitated with an ammonia solution. An additional conductivity increase can be achieved by the simultaneous doping the membranes with silica and heteropolyacids. For the two latter cases it is most probable that the additional effect is provided by an increase in the concentration of charge carriers.

The maximum conductivity of the PANi-modified membranes is achieved at a smaller volume content of the dopant. In addition, with an increase in the volume content of PANi the conductivity decreases much more strongly than the conductivity of the membranes containing silica and metal nanoparticles. This is explained by the fact that protons of the –SO₃H groups are sorbed on the basic hydrogen atoms of PANi and are not involved in transfer processes because of strong hydrogen bonding.

Validity of these conclusions is indirectly confirmed by the fact that the maximum size of the nanoparticles obtained directly in the membrane pores (*in situ* method) is fairly restricted. In the case of homogeneous membranes of the Nafion type, their size does not usually exceed 5 nm even at the multiplication of precipitation process.¹² Larger particles can be formed only on the membrane surface.¹⁴ A dopant amount increases primarily due to the formation of new nanoparticles rather than to their additional growth. Note that analogous results were obtained in the case of nanoparticle formation in pores of the ion-exchange resin MK-40 with the heterogeneous structure containing both small and large pores.¹⁸ Multiple copper precipitation resulted in an increase in the number of new nuclei rather than an increase in the size of the precipitated particles.³⁰

Thus, when the nanoparticle concentration is rather high, these particles can restrict (block) the membrane pores, which decreases the mobility of the solution inside the pores in narrow gaps between the membrane wall and dopant particles (see Fig. 8, *c*). This results, in fact, in the formation of new "channels" determining ion conductivity. As a result, the conductivity decreases and its activation energy increases.

The model of restricted elasticity of membrane pore walls can also explain the change in the mechanical properties of the modified membranes. According to this model, the high content of a dopant should favor mechanical stress and result in the destruction of the membranes under a smaller load. For instance, in the case of the membranes casted with preliminarily produced particles of a dopant or precursor, the samples containing more than 13 vol.% silica, 26 vol.% PANi, or 25 vol.% Ag undergo fracturing during formation.^{14,16,17}

Conductivity of the modified membranes at low humidity. One of the main advantages of a series of hybrid membranes is a substantial increase in the conductivity at low values of humidity of the environment. As already mentioned, the modification of the MF-4SC membranes by silica enhances their conductivity by 1.5 orders of magnitude at 9% humidity, whereas the combined introduction of silica and heteropolyacid increases the conductivity by more than 2.5 orders of magnitude.¹¹ This effect is very significant for using membranes in fuel cells.^{4,5} It is most likely that two effects are principally important in this case. The first of them is analogous to that described above. As humidity decreases, the partial dehydration of the membranes occurs due to which the pore volume decreases sharply. However, the pore size in the hybrid membranes retains higher values. For example, at 9% humidity the pore volume in the membrane containing 4 vol.% silica is 12 % and, under similar conditions, it is more than twice that of the pore volume in the initial MF-4SC (5%). Evidently, in this case, the sizes of the channels connecting the pores differ more substantially than those for the membranes at higher humidity. This pore volume (12%) is

characteristic of the non-modified membrane MF-4SC at ~35–40% humidity, and the conductivity of this membrane is several times higher than that for the membranes doped by silica at 9% humidity.¹⁶ This difference is achieved because a substantial part of the pore volume is occupied by the dopant with low conductivity, and the contact of this dopant with the surface restricts the mobility of neighboring water molecules. This results in the formation of additional regions that restrict the proton transfer. However, the effect from the increasing channel size is substantial in any case.

The nature of another effect favoring an increase in the conductivity of the hybrid membranes at low humidity is illustrated in Fig. 10, that shows the membrane pore wall under different conditions. At high humidity (see Fig. 10, *a*), many water molecules are located near the pore wall. As a result, the sulfo groups are completely dissociated and, hence, the proton transfer following the Grotthuss mechanism³¹ involves neighboring water molecules. The membrane pore walls are nearly excluded from the transfer. A decrease in humidity results in the substantial dehydration of the membrane. However, as shown by the NMR spectroscopic data,³² the proton is coordinated to at least two water molecules due to the substantially lower proton-withdrawing ability of $-\text{SO}_3^-$ groups compared to H_2O molecules. At the same time, at the low degree of hydration, the oxygen atoms involved in the transfer process are separated by a fairly long distance. Under these

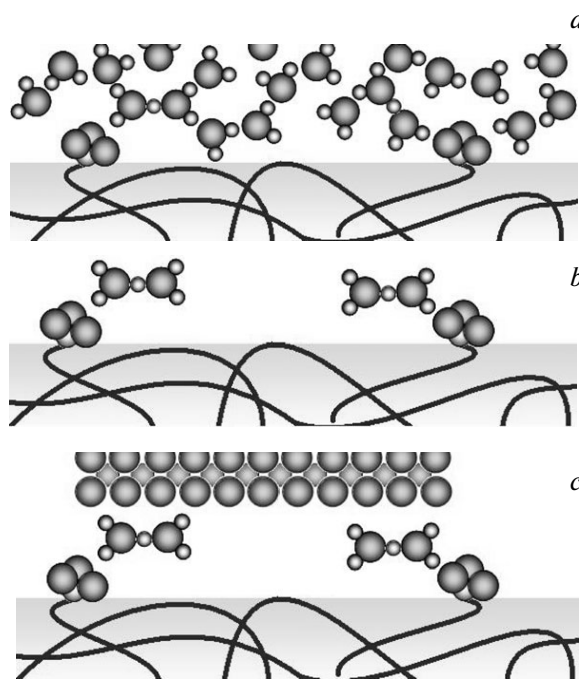


Fig. 10. Scheme of boundaries of pore walls of the membrane and intergrain solution under different conditions: non-modified membrane at the high (*a*) and low (*b*) humidity and the modified membrane at low humidity (*c*).

conditions, the proton conductivity is limited by the proton jump³³ (Fig. 10, *b*). An elongation of the proton jump length results, as it is known, in an increase the activation energy of proton jump and a decrease in the frequency of this process. The factors considered also exert a noticeable effect on a decrease in the value of proton conductivity of the membranes.

When the membranes are doped, their pores incorporate a considerable number of additional oxygen-containing groups capable of participating in the proton transfer (see Fig. 10, *c*). As a result, the length of the jump necessary for proton transfer shortens substantially. This also favors an increase in the conductivity of the hybrid membranes at low humidity.

At low humidity, the nature of the doping agent surface exerts a substantially stronger effect on the value of conductivity than at high humidity.¹¹ For instance, an additional incorporation of heteropolyacid into the membrane containing SiO₂ increases conductivity at 9% humidity by more than an order of magnitude compared to the MF-4SC + SiO₂ membrane. This effects is determined by the incorporation of an additional number of acidic protons (current carriers) and a decrease in the proton-withdrawing ability of the dopant particles, which weakens the inhibition of the proton transfer near their surface.

Thus, an increase in the conductivity of the ion-exchange membranes due to modification by nanoparticles is mainly caused by the effect of the dopant on the structure of pores and channels. The model of restricted elasticity of membrane pore walls was advanced to explain this phenomenon. An addition factor of increasing conductivity of hybrid membranes at low humidity is the participation of the dopant particle surface in transfer processes.

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