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Ion conductivity of hybrid ion exchange membranes incorporating nanoparticles

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ABSTRACT

The data on the ionic conductivity of hybrid membrane materials including nanoparticles of inorganic compounds and polyaniline have been presented. To explain the phenomenon of the ionic conductivity increase in these systems, a model of semielasticity of the membrane pores walls has been proposed. The additional contribution to the increase in conductivity at low humidity was explained by the surface of the incorporated nanoparticles participation in the transfer processes.

Keywords: Ion-exchange membranes; Hybrid membranes; Nanocomposite materials; Ionic conductivity; Transport properties; Model of the semielasticity

1. Introduction

One of the main problems of modern chemistry is to ensure production cleanness, waste neutralization, as well as finding of new environmental-loving energy sources [1–3]. The solution of these problems is often associated with the use of membrane materials [4]. However existing materials do not meet the growing requirements of modern industry and science. Therefore membrane modification and hybrid membranes containing inorganic and macromolecular components syntheses are developed intensively [5,6]. Modification of relatively small number of commercially available membranes allows to obtain materials with various properties. Different approaches, including chemical or mechanical surface treatment or volume modification have been used for that purposes [4–9]. One of the most promising membranes with high ion conductivity is perfluorinated sulfonated Nafion membranes. The most promising approach to the modification of Nafion membranes is to obtain bulk modified materials such as hybrid organic/inorganic membranes, which are widely used in alternative energy production. The inorganic particles can be introduced as: (i) a precursor for nanoparticles formation or (ii) performed nanoparticles. The first method results in the obtaining of nanoparticles with small size (about 3–5 nm) because membrane matrix prevent the particles growth. The second method allows to obtain materials with different dopant content (1–20 wt.%). A variety of fillers, including hydrated oxides such as silica, zirconia, zirconium acid phosphate, phosphotungstic acid (PWA), molybdophosphoric acid, organically modified silicates, carbon nanotubes have been used for the preparation of Nafion based hybrid membranes [4,5,10–13]. High ionic conductivity (especially at low humidity), thermal and mechanical stability can be mentioned among the advantages of hybrid membranes [5,14,15]. These membranes present very promising characteristics such as low fuel cross-over and provide the increase of the capacity of fuel cells. At the same time there is no common explanation for the phenomenon of conductivity increase in hybrid membranes.

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This paper describes the ion transport process in hybrid materials based on MF-4SC membrane as an example. Membrane MF-4SC is the perfluorosulfonic cation-exchange membrane (Russian analogue of Nafion) described properly before. See for example [16,17].

In this paper the explanation of the proton conductivity increase in hybrid Nafion type membranes was suggested.

2. Experimental

Hybrid membranes have been obtained by two different methods. Under the first one, additives were synthesized in the pores of commercial samples of MF-4SC membrane (in situ method), as described in [18–21]. This method allows to synthesize hybrid membranes with a 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. The second method is membrane casting from polymer solution containing precursor for further particle synthesis [22,23]. This method allows us to incorporate up to 13.5 vol.% (15 wt.%) of silica and 26 vol.% (14 wt.%) of polyaniline (PANI) into membrane matrix. According the methods mentioned above the following membranes were obtained: MF-4SC/SiO_2, MF-4SC/SiO_2/PWA, MF-4SC/ZrO_2, MF-4SC/PANI, MF-4SC/Ag.

Membranes have been kept in desiccators at various relative humidity (RH) value, given by the saturated solutions of inorganic salts in order to prepare samples with different moisture content. Thermogravimetric analysis (TGA) of samples was performed with the use of Netzsch-TG 209 F1 thermal analysis system in the platinum crucibles, heating rate 10°/min. The water uptake (the number of water molecules, corresponding to one sulfonic group $n = [H_2O]/[SO_3]$ in the investigated membranes was calculated from the mass difference of air-dried membrane and the membrane, heated at 110°C according to the relation:

$$n = W \; / \left(18 * \mathrm{SEC}\right) * 10^3 \qquad (1)$$

W - part of lost water, 18 - water molecular weight (g/mol), SEC- sorbtion exchange capasity.

The impedance analyzers 2B-1 with a frequency range from 10 Hz to 6 MHz and carbon/membrane/carbon symmetrical cells with an active surface area about 0.25 cm^2 were used for proton conductivity measurement in the temperature range 20–100°C in contact with water and at 25°C at different RH values. The conductivity values were obtained by the semicircle extrapolation to the resistance axis.

NMR spectra were recorded at room temperature by using a high-resolution NMR spectrometer AVANCE III 500 (Bruker).

3. Conductivity

The proton conductivity data for some MF-4SC membranes modified with hydrated silica and zirconia, as a function of temperature are shown in Figs. 1,2.

In most cases, hybrid membranes have the higher proton conductivity than the polymer-only system measured under the same conditions. The activation energy

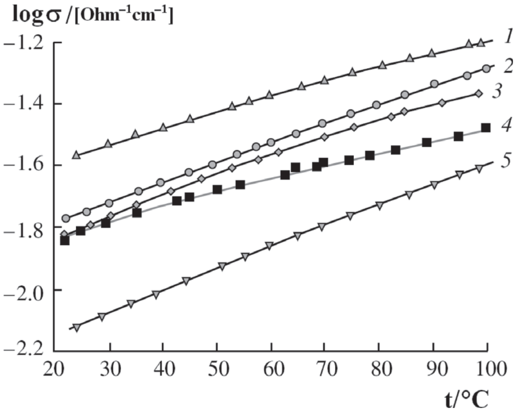

Fig. 1. Proton conductivity as a function of temperature for MF-4SC membranes modified with hydrated zirconia by in situ method, (1,2) using $ZrCl_4$ and (3,4) zirconium propoxide as a precursors. Precipitation was carried out using ammonia (1,3) and NaOH (2,4) solutions. Line (5) corresponds to the unmodified MF-4SC sample. Measurements were carried out at 100% RH.

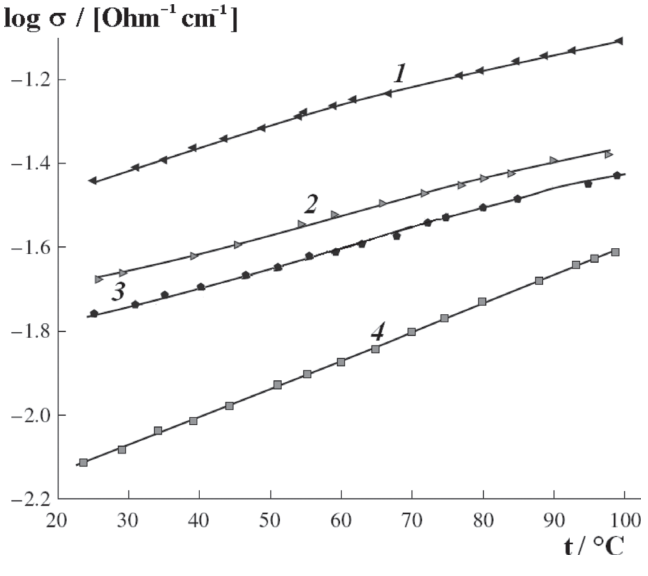

Fig. 2. Proton conductivity as a function of temperature for MF-4SC modified with hydrated silica by in situ method. Silica content is about 4.4 vol.% (1), 2.6 vol.% (2), 1.7 vol.% (3). Line (4) corresponds to the unmodified MF-4SC sample. Measurements were carried out at 100% RH.

of conductivity of the membranes decreases from 13.7 ± 0.6 kJ/mol for the initial membrane to 10–12 kJ/mol for modified samples.

Modification of the membranes by film casting from polymer solution containing a precursor for further nanoparticles preparation leads to the formation of isolated particles with the sizes higher than in the case of the hybrid materials in which nanoparticles were synthesized via in situ reaction in a pre-formed polymer matrix. This difference can be explained by the absence of limitations for particles growth in the membranes obtained by in situ method. The dependence of ion conductivity as a function of silica and zirconia content in the membrane obtained via casting method passes through a maximum at about 2.6 vol.% of SiO_2 and 1.9 vol.% of ZrO_2 (Fig. 3). In all cases mentioned above the growth of membranes proton conductivity can be explained by additional water sorption by hydrophilic nanoparticles surface.

Acid protons concentration increase in the membrane matrix can result in the additional conductivity increase. Thus incorporation of PWA into MF-4SC membrane leads to the increase in the number of carriers concentration and to the increase of proton conductivity. Effect of conductivity growth is most significant at low RH. Decrease in the RH value results in the all membranes conductivity decrease (Fig. 4). However, the conductivity for hybrid samples is slightly higher than that of unmodified membrane at high RH value, but this difference increases with the decrease of RH. The proton conductivity of membrane with silica is higher than that for the initial MF-4SC membrane by a 1.5 orders of magnitude at RH = 9%. The hybrid effect reaches by a 2.5 orders of magnitude in the case of simultaneous incorporation of silica and PWA.

At the same time the proton conductivity increase of the hybrid membranes can be achieved by the incorporation of hydrophobic or proton acceptor groups. In this case, the growth of membranes proton conductivity cannot be explained by the additional water sorption by hydrophilic nanoparticles surface and acid protons concentration increase. Thus incorporation into MF-4SC matrix 2–3 vol.% of silver nanoparticles allows to increase twice the ionic conductivity of the membranes at room temperature and leads to its activation energy decrease up to 7.8 ± 0.5 kJ/mol while electronic conductivity remained low and amounts to 0.1–0.2% of ionic conductivity.

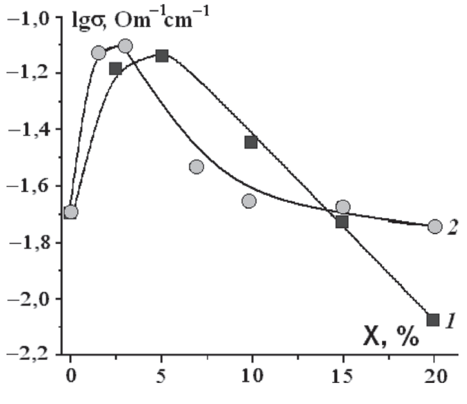

Fig. 3. Proton conductivity as a function of oxide content (wt.%) for membranes obtained via casting method (1) MF-4SC + ZrO_2, (2) MF-4SC + SiO_2 at room temperature and RH = 100%.

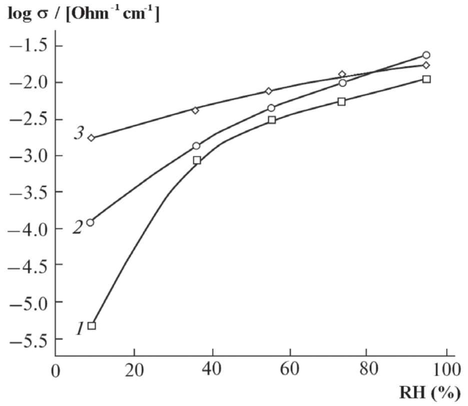

Fig. 4. Proton conductivity as a function of RH for the membranes obtained by in situ method: (1) unmodified MF-4SC, (2) MF-4SC + SiO_2, (3) MF-4SC + SiO_2 + $H_3PW_{12}O_{40}$ at room temperature.

Proton conductivity of xPANI-(1-x)MF-4SC hybrid membranes as a function of polyaniline content at room temperature (where x – volume ratio of PANI fraction) is shown in Fig. 5. The significant proton conductivity

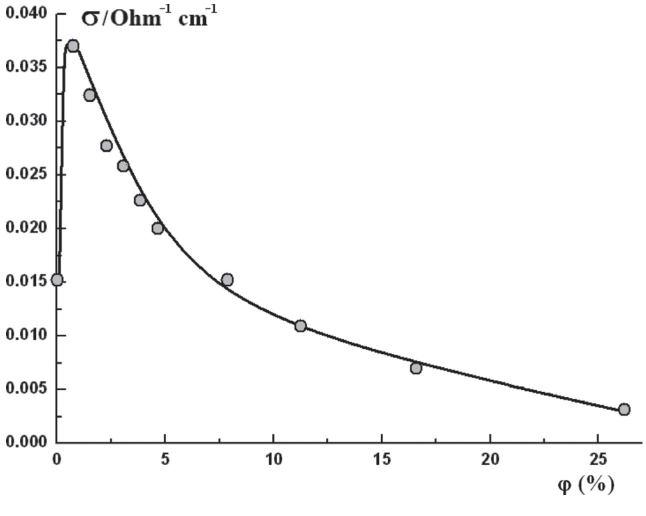

Fig. 5. Proton conductivity of hybrid membranes as a function of volume PANI fraction at room temperature and RH = 100%.

increase for MF-4SC membrane doped by small amounts of PANI (1.5 vol.%) is observed. However, further increase in the PANI content leads to the conductivity decrease with a simultaneous increase in its activation energy up to 15–17 kJ/mol. These changes are determined by the concentration of current carriers (protons of SO_3H-groups) decrease and formation of rather strong H-bonds between protons of SO_3H-groups and nitrogen atoms of polyaniline which results in exception of considerable part of protons from transport. Note that the obtained membranes are also characterized by the low contribution of the electronic conductivity.

4. Discussion

4.1. Conductivity at 100% relative humidity

The Nafion type ion-exchange membranes consist of hydrophobic perfluorinated chains and the hydrophilic functional groups [24,25]. According to the Gierke model self-organization takes place in membrane matrix [26,27]. It is presumed that there are clusters of sulfonate-ended perfluoroalkyl ether groups that are organized as the inverted micelles, arranged in a lattice and filled by water molecules. These micelles form pores (3–5 nanometers in size), which are connected by channels filled by SO_3H groups and water molecules (1–2 nm in size) (Fig. 6 a). At the same time Nafion type membranes are the strong acid and protons can easily dissociate and move in the aqueous solution containing within the pores. The ion transport in this membranes is realized through the pores and channels system. According to the Gierke model, the walls of the membrane pores are flexible. So pores and channels sizes can increase or decrease as the function of membranes water content, which depends on the environmental humidity [26,27]. According to that membrane conductivity strongly depends on the humidity [25]. The structure and interactions of water species in hydrated Nafion membranes as a function of water content were described in [28].

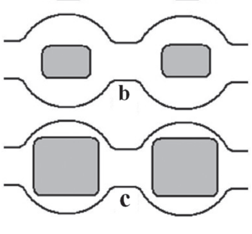

Fig. 6. Scheme of pore structure for the (a) initial and (b,c) modified with nanoparticles membranes in the case of the model of the semielasticity of membranes pores and channels.

The sharp increase of the ionic conductivity of hybrid materials first was discovered by Liang. This phenomenon can be attributed to the formation of additional defects, caused by the sorbtion processes at the phase boundary [29,30]. These defects became the main carriers in the case of ion transport. In order to achieve the maximal defects concentration the surface of the grains should be maximal and the dopant particle size should be minimal. Another important factor is the particles surface affinity to the electric carriers sorbtion.

From this perspective, the optimal outcome should be achieved with the weak base (such as PANI) introduction in sulfonate cation-exchange membrane MF-4SC. Indeed, the introduction of small PANI amounts leads to the partial MF-4SC protons sorption and to the membrane conductivity increase (Fig. 5). Further conductivity decrease with increase in PANI content is caused by the exception of too mach carriers (protons) from the transfer process.

The increase in ion conductivity in hybrid materials is commonly attributed also to the additional water sorption by hydrophilic nanoparticles surface that facilitate ion transfer [18,19,31]. This effect can be observed in the case of membranes modification by silica or zircona. Water uptake of these systems increased slightly. Nevertheless, the growth of proton conductivity for MF-4SC membrane doped by hydrophobic silver nanoparticles or polyaniline can be achieved also. But according to the TGA data silver and PANI incorporation leads to the decrease of membrane water uptake.

The above facts indicate that the membranes conductivity increase can be enhanced by the various nature additives introduction and there is no common explanation for the phenomenon of conductivity increase in hybrid membranes.

Fig. 7 shows the diffusion coefficients of hybrid membranes MF-4SC calculated from the NMR data and conductivity data. Proton diffusivities calculated from ^1H NMR relaxation are determined mostly by proton and water molecules migration in the wide pores where most part of protons are located. These values are much higher than those calculated from conductivity data that are determined by proton migration through the narrow channels. At the same time, the modification leads to the increase in ionic conductivity compared with the initial MF-4SC. At the same time ^1H NMR relaxation rate in modified membranes can be both higher and lower in comparison with that of the initial MF-4SC (Fig. 7). This shows that the proton conductivity increase can be attributed to the incorporated nanoparticles influence on the channels sizes.

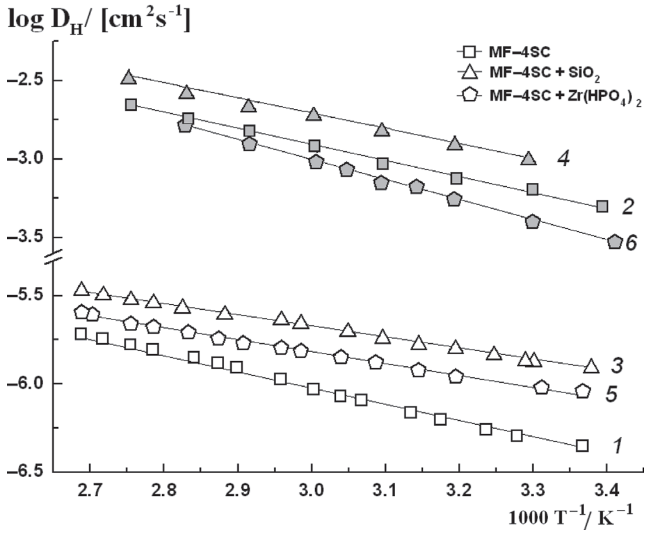

Fig. 7. Arrenius dependences of proton diffusion coefficients calculated from conductivity data (1), (3), (5) and NMR spectroscopy data (2), (4) (6) for MF-4SC membrane (1), (2) and MF-4SC modified by silica (3), (4) and acid zirconium phosphate (5), (6) [32].

The dopant nanoparticles formation is occurred in the membrane pores. The formed nanoparticles occupy a part of the pore volume. At the same time, the number of acid protons remains the same after modification, in the most cases. In this connection, the water molecules number within the membrane matrix remains the same or even increases slightly after hydrophilic particles introduction. It was confirmed by the TGA data. So, the total membrane pore volume increased almost 1.5 times after 3 vol.% of SiO_2 incorporation. The hydrophobic particles incorporation results in the membranes water uptake decrease slightly, but in this case noticeable pore volume increase can be observed also.

The pore size growth should lead to the increase in the sizes of channels also (Fig. 6 a, b). The channels expansion should lead to the increase in the conductivity, since it is determined by proton transfer in the narrow membrane channels where proton mobility is minimal. The activation energy of conductivity should decrease and approaches to the activation energy for aqueous acidic solutions (5 kJ/mol). That was observed in practice.

Further increase in nanoparticles volume (>3–4 vol%) leads to decrease in conductivity and growth of activation energy. In the case of composites based on solid electrolytes this fact can be explained by blocking of the conductive particles surface by dopant [33,34]. This explanation can not be applied for the hybrid membranes. At the same time, it is easy to notice that the increase in nanoparticle volume up to 3–4 vol% will be followed by the decrease in water uptake. The specific pore volume practically stoped to grow. This allows to conclude that the membranes pore walls elasticity is limited. Either the pores cannot expand more than a certain volume or the further expansion demands the significant increase in expanded forces (according to Hook low). The driving force of the pore expansion is the decrease in water chemical potential inside the pores due to its interaction with the protons of-SO_3H groups. This force should remain the same after modification, but the elastic forces increase during pores expansion should lead to a decrease in water uptake.

Based on above-mentioned assumptions, we can conclude that the high dopant concentration leads to the blocking of proton transfer routes. This reduce the mobility of the solution, located inside the in the narrow space between the membrane pore walls and the dopant particles (Fig. 6 c). It results in the membrane conductivity decrease and the activation energy increase.

4.2. Conductivity at low relative humidity

High ionic conductivity at low humidity can be mentioned among the main advantages of hybrid membranes (Fig. 4). There are two different explanations for this phenomenon. In this case two effects are important. The first of them is similar to that described above. The humidity decrease results in partial membranes dehydration and in dramatic decrease of pore volume. However, the pores size in the hybrid membranes retains higher. So, in the case of 10% RH the pores volume consists 12% of the whole volume of membrane containing 4 vol.% silica. This value is twice higher than the pores volume of the initial MF-4SC under the same conditions (5%). Obviously, the channels sizes in this case differ rather more significantly than those for membranes at high humidity.

Fig. 8 explains the nature of another effect influencing on hybrid membranes conductivity increase at low RH. The schemes of membrane pores walls under different conditions are presented. There are a large number of water molecules in the pores at high humidity (Fig. 8 a). Therefore, SO_3H groups are dissociated, and the proton transfer is realized by Grotguss mechanism between closely located water molecules [35]. The humidity decrease results in membranes dehydration. As shown by the NMR data, the remaining water molecule associated with protons and form the $H_5O_2^+$ ions. The oxygen atoms involved in the transfer process are located in a sufficiently large distance one from another at low hydration degree. Under these conditions, the proton conductivity is limited by the proton jumps (Fig. 8b) [36]. The increase in the length of proton jumps leads to an activation energy increase and decrease of jump frequency.

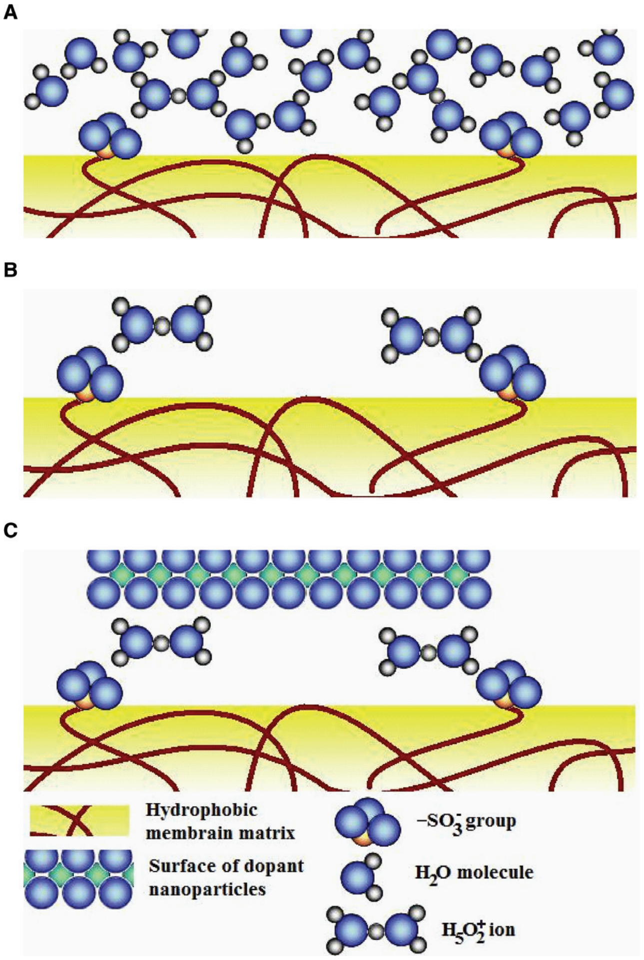

Fig. 8. Scheme of pore walls and interface solution boundary under various condition (a) initial membrane at high humidity, (b) initial membrane at low humidity, (c) hybrid membrane at low humidity.

The membranes modification leads to the large number of additional oxygen-containing groups introduction into their pores. These oxygen atoms are able to participate in the proton transfer process too (Fig. 8c). Due to above-mentioned reason the proton jump length is significantly reduced. It also makes a great contribution to hybrid membranes conductivity increase at low humidity.

Note that the doping agent surface nature has a great influence on the membrane conductivity at low humidity [17]. Thus, the additional phosphotungstic acid (PWA) introduction into membrane containing SiO_2 leads to conductivity increase more than an order of magnitude at 10% RH in comparison with the MF-4SC + SiO_2 membrane (Fig. 4). This effect is determined by the additional charge carriers (acidic protons) incorporation and decrease of the dopant particles proton acceptor ability. This results in less proton transport inhibition near the surface.

Hybrid membranes of such type can possess high conductivity at higher temperatures. For example conductivity of Nafion/TiO_2+WO_3 nanocomposite membrane consists 5.0×10^{-2} $Ohm^{-1} cm^{-1}$ at 135°C [37].

In conclusion, the ion-exchange membranes modification by nanoparticles can results in the conductivity growth. It is caused mainly by the dopant influence on pores and channels structure. It has been observed that an additional factor for the conductivity increase of hybrid membranes at low RH is the participation of dopant particles surface in the transport processes.

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