



Improving the conductivity and permselectivity of ion-exchange membranes by introduction of inorganic oxide nanoparticles: impact of acid–base properties

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Abstract

In the present paper, the influence of acid–base properties of inorganic particles in ion-exchange membrane-based nanocomposites on their physicochemical and transport properties was investigated. For this purpose, particles of Zr, Ti, and Si oxides have been synthesized in situ in the system of pores and channels of the membranes. Depending on the acid–base properties of oxides, introduction of nanoparticles can increase or decrease the water uptake, conductivity, and selectivity. A new approach to cross-linking of ion-exchange membranes by incorporating ZrO₂ particles into their matrix is proposed. Such cross-linking provides an improvement of swelling, conductivity, and salt permselectivity of the membrane in Na⁺-form. These parameters are important for successful application of such materials in direct and reverse electrodialysis, electrodeionization, and diffusion dialysis. For example, incorporation of 10 wt% of zirconia leads to a “cross-linking” of the membrane, i.e., binding of 45–50% of sulfonic groups, accompanied by a decrease of the water uptake by more than twofold and an increase of apparent transport numbers.

Keywords Charge transport · Composites · Graft-copolymers · Membranes · Nanoparticles · Cross-linking

Introduction

In recent years, the use of ion-exchange membranes in water treatment, waste water purification, desalination of food products, electrochemical synthesis, and energy production is widely expanding [1–4]. In particular, such processes as electrodialysis and electrodeionization [5, 6], dialysis, reverse electrodialysis [7, 8] etc. are carried out extensively. Ion-exchange membranes play key roles in these processes. As a result of self-organization phenomena, pores and channel structure are formed within such membranes [9–12]. Such pores (ionic nanoclusters) has inverted micellar structure and

contain mobile ions formed due to the dissociation of ionogenic groups (counter-ions) with sorbed water molecules. This provides a high rate of ion transfer in the membranes [10].

The higher is the water uptake of the membranes, the greater is their ionic conductivity. However, the undesirable transfer of co-ions (having the charge of the same sign as the groups fixed on pore walls) and non-polar molecules or molecules with non-polar fragments (such as hydrogen, oxygen, methanol etc.) is enhanced at the same time. As a result, a trend towards lowering of membrane permselectivity or selectivity with increasing conductivity is observed [13–15]. Therefore, for various membrane processes, it is necessary to control ion-exchange capacity, flexibility of polymer chains, and their cross-linking degree, which determine water uptake of the membranes, their conductivity, and permselectivity [16].

Membrane water uptake is usually controlled by varying either the fraction of a conductive polymer or its cross-linking degree [17]. In a number of membrane preparation methods, such as the paste method [18], both ways to control the water uptake can be used simultaneously. But when, for example, the membrane casting is used, cross-linking becomes complicated and requires either additional treatment steps or introduction of specific groups that are cross-linked during film formation [17, 19, 20]. The latter significantly increase the cost

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of the membranes. This is the case of the membranes based on polyetheretherketones, polysulfones, or block co-polymers based on polystyrene and polyolefins. At relatively low sulfonation degrees, the mentioned polymers possess good transport and mechanical properties. However, the membranes with high functionalization degree lose their mechanical properties in contact with water or even dissolve in it [21, 22].

Currently, the modification of ion-exchange membranes by inorganic and organic nanoparticles is a subject of extensive investigation [23–30]. The majority of studies in this field are dedicated to synthesis of hybrid materials for fuel cells (FC) in order to increase their proton conductivity and decrease gas permeability [24]. For this purpose, particles with an acidic surface are often incorporated into the membranes. Such particles promote an increase in the membrane water uptake and in the concentration of carriers [26, 31]. However, in a number of studies, hybrid materials are synthesized with inorganic particles coupled to the surface of membrane pores [27, 32, 33]. Thereby, an excessive expansion of pores leading to loss of mechanical properties and permselectivity is prevented. Operating conditions and, as a result, required membrane characteristics are significantly different for applications in fuel cells and in processes such as direct and reverse electrodialysis, electrodeionization, dialysis etc. More affordable materials based on sulfonated polystyrene are preferred in these processes [5]. It is of both practical and fundamental interest to extend the mentioned approach to improving the properties of sulfonated polystyrene-based membranes [25].

The aim of the present study is to explore a possibility of controlled change of water uptake and properties of membranes based on sulfonated polystyrene via modification with inorganic nanoparticles (Zr, Ti, and Si oxides). Impact of doping on transport properties of the membranes is compared to the traditional approaches to conductivity/selectivity control: change in cross-linking degree and proportion of the hydrophobic polymer. The use of grafted membranes is highly advantageous in this case, since grafting degree and cross-linking degree can be varied during membrane preparation [34].

Materials and methods

Synthesis of grafted cation-exchange membranes Backbone polymethylpentene film (TPX®_MX002, GoodFellow, Great Britain) was subjected to UV-radiation (Hg-lamp 950 W) for 30 min. The obtained material was stored for 24 h prior to styrene grafting. Styrene was distilled before the synthesis to remove the inhibitors. For this purpose, styrene (Sigma-Aldrich >99%) was mixed with NaOH (“Khimmed sintez” LLC, dry, “chemically pure” grade) and stirred for 1 h, followed by distillation under argon atmosphere at 70 °C (pressure 60 mmHg). Synthesis of polystyrene on the film surface was carried out in a reactor, where the activated films were placed. Grafting was carried out in 70 vol% solution of distilled styrene

in methanol (“Khimmed sintez” LLC, “special purity for gradient HPLC” grade) with an addition of 1.5 mg FeSO₄·7H₂O (“Khimmed sintez” LLC) per 1 mL of the mixture. Synthesis was performed at the solution boiling point (≈68–70 °C) under vigorous stirring for 2 to 4 h, depending on the required grafting degree. After the synthesis membranes were washed with toluene (“Khimmed sintez” LLC) and acetone (“Khimmed sintez” LLC) to remove the forming homopolymer, and then dried. To perform sulfonation, the obtained films were placed in 1.5 vol% solution of chlorosulfonic acid (“Khimmed sintez” LLC) in 1,2-dichloroethane (“Khimmed sintez” LLC) and stirred in a shaker for 20 min. The methanol (“Khimmed sintez” LLC, “special purity for gradient HPLC” grade) was added to the system to quench the sulfonation. After washing with acetone, the film was placed in a 2 M NaCl solution, kept for 2 h at 70–90 °C, and, after multiple washings, was used for investigation.

The amount of grafted polystyrene was evaluated as grafting degree (GD, wt%), which was calculated according to the equation

$$GD = \frac{m_g - m_0}{m_g} \cdot 100 \quad (1)$$

where m_0 and m_g are the film masses before and after the grafting copolymerization stage, respectively.

Synthesis of modified membranes Synthesis of hydrated amorphous oxides was carried out in situ within the grafted membranes in the Na⁺-form. To obtain ZrO₂ membrane, samples were kept in 1 M, 0.5 M, and 0.1 M solutions of ZrOCl₂·8H₂O (“Khimmed sintez” LLC, “chemically pure” grade) for 24 h. Afterwards, the surface of the films was briefly washed to remove excess of ZrOCl₂ and soaked in 1 M NaOH (“Khimmed sintez” LLC, dry, “chemically pure” grade) solution for 1 day.

To synthesize SiO₂ membrane, samples were kept in a mixture of TEOS (“Khimmed sintez” LLC, “pure for analysis” grade) and i-PrOH (“Khimmed sintez” LLC, chemically pure grade) for 24 h. Volumetric proportion of TEOS/i-PrOH was varied from 1:1 to 4:1. Afterwards, the membranes were removed from the solution, their surface was washed to remove excess of the precursor, and they were soaked in 1 M HCl solution for 1 day.

To synthesize TiO₂ membrane, samples were kept in 1 M, 0.5 M, and 0.1 M solution of TiOCl₂ (“Khimmed sintez” LLC, “chemically pure” grade) for 24 h. Afterwards, they were removed from the solution, their surface was washed to remove excess of the precursor, and they were soaked in 1 M NaOH solution for 1 day.

Methods of investigation

X-ray diffraction analysis of the samples was carried out using Rigaku D/MAX 2200 diffractometer, CuK_α radiation. Rigaku

Application Data Processing software was used to process the spectra. The size of crystalline domains was calculated according to the Scherrer equation [35]. The instrument width, i.e., resolution function of the diffractometer, was determined in a special diffraction experiment using the standard powder of lanthanum hexaboride LaB₆ (Standard Reference Material® 660a). Analysis of the microstructure was carried out using transmission electron microscope Jeol JEM 2100 (Shared Equipment Center MISIS), accelerating voltage was 200 kV. IR-spectra were recorded using a Fourier transform IR-spectrometer Nicolet iS5 with an ATR accessory (diamond crystal).

Ionic conductivity of membranes was measured in a 4-electrode cell by impedance spectroscopy in 0.5 M sodium chloride solution at 25 °C. A detailed procedure for determining the ionic conductivity is given in a previous paper [14].

Determination of apparent transport numbers was carried out according to a procedure described previously in detail [36]. The cell was filled with 0.5 M NaCl solution on one side and with 0.1 M NaCl solution on the other side. Calculation of transport numbers (t_{+app}) was done according to the following equation

$$t_{+app} = \frac{E_m}{\frac{RT}{F} \ln\left(\frac{a_1}{a_2}\right)} \quad (2)$$

where E_m is the measured membrane potential, mV; R is the universal gas constant; T is the absolute temperature, K; F is the Faraday constant; a_1 and a_2 are the electrolyte activities (the values were found by extrapolation of tabulated values by a continuous function, a_1 (0.5 M NaCl) = 0.339, a_2 (0.1 M NaCl) = 0.0783). The accuracy of t_{+app} determination was $\pm 0.5\%$.

Determination of water uptake was carried out gravimetrically. Water was removed from the surface of the membrane in the Na⁺ form using filter paper. Afterwards, the membrane was weighted (m_1), dried for 2 h under vacuum at 70 °C, and weighted again (m_2). Water uptake ($\omega(\text{H}_2\text{O})$, wt%) was calculated according to the following equation

$$\omega(\text{H}_2\text{O}) = 100 \cdot (m_1 - m_2) / m_1 \quad (3)$$

To determine the dopant content, the membrane was converted to the H⁺-form and annealed for 12 h at 700 °C to ensure complete burnout of the polymeric part of the membrane. Residue was weighted (m_3); calculation of the dopant content ($\omega(\text{dopant})$, wt%) was carried out using the following equation

$$\omega(\text{dopant}) = 100 \cdot m_3 / m_2 \quad (4)$$

The ion-exchange capacity was determined by keeping the membranes in the hydrogen form in a 1.0 M solution of NaCl; then, an aliquot portion of the solution was titrated with

0.01 M NaOH. After that, the membrane was washed in distilled water, dehydrated for 1 h in vacuum at 70 °C, and weighed (m_4). The ion-exchange capacity (IEC, mmol g⁻¹ of the dry membrane) was calculated from the equation

$$\text{IEC} = \frac{c_1 \cdot V_1 \cdot V_2}{V_3 \cdot m_4} \quad (5)$$

where c_1 and V_1 are the concentration and the volume of the titrating solution (mmol/mL and mL), V_2 is the volume of the 1.0 M solution of NaCl, V_3 is the aliquot volume taken for titration.

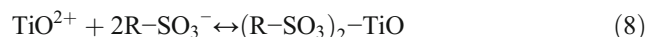
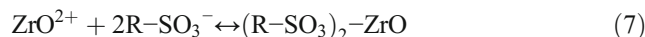
Molality of the inner solution (C_{inn} , mol kg⁻¹) was calculated from the water uptake ($\omega(\text{H}_2\text{O})$, wt%) and ion-exchange capacity (IEC, mmol g⁻¹) according to the equation

$$C_{inn} = \text{IEC} \cdot \left(\frac{100}{\omega(\text{H}_2\text{O})} - 1 \right) \quad (6)$$

Results and discussion

Characterization of hybrid membranes

When ion-exchange membranes are kept in ZrOCl₂ and TiOCl₂ salts, the oxocations are sorbed following an ion-exchange mechanism:



During further treatment with alkali nanoparticles of hydrated oxides, ZrO₂·nH₂O and TiO₂·mH₂O are formed within the membrane pores. The presence of zirconia was confirmed by high-resolution transmission electron microscopy (TEM). Sizes of the majority of particles lie within the range of 2–5 nm (Fig. 1). The size is most likely limited by the sizes of pores according to the Gierke model [10]. At the same time, a few larger particles can be seen in the figure, which probably corresponds to the particles formed at the membrane surface.

According to X-ray diffraction data, the residue after annealing of the samples doped with hydrated zirconium oxide is monoclinic ZrO₂. X-ray diffraction patterns of the residue after annealing of the membranes doped with titanium oxide feature reflexes of the anatase form of TiO₂. Particle sizes estimated from the Scherrer equation are 13 and 20 nm for ZrO₂ and TiO₂, respectively. The residue after annealing of the membranes doped with silica remains amorphous. SiO₂ formation is confirmed using IR-spectroscopy by the presence of a characteristic band of Si–O stretching vibration at 1000–1100 cm⁻¹.

It is generally recognized that incorporation of hydrophilic oxides in the pores of Nafion® type membranes can

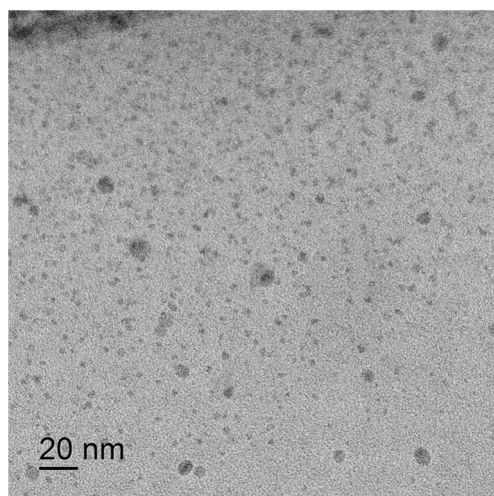


Fig. 1 TEM image of the membrane doped with zirconium oxide

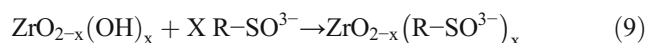
lead to an increase in water uptake [26, 37–39], which is in good agreement with our results for the membranes doped with silica (Table 1). On the other hand, according to the literature, the introduction of titanium or zirconium

Table 1 Main physicochemical parameters of the initial and doped membranes with varying dopant content

Membrane, dopant	$\omega(\text{dopant})$, wt%	IEC mmol g^{-1}	$\omega(\text{H}_2\text{O})$, wt%	C_{inn} , mmol g^{-1}
GD = 30%		1.6	30	3.7 ± 0.1
ZrO ₂	1	1.0	19	4.3 ± 0.2
	2	0.91	14	5.6 ± 0.3
	3	0.83	14	5.1 ± 0.3
GD = 60%		1.9	44	2.3 ± 0.1
ZrO ₂	7	1.1	29	2.7 ± 0.1
	9	0.90	27	2.4 ± 0.1
	12	0.88	26	2.5 ± 0.1
GD = 42%		1.8	39	3.1 ± 0.1
TiO ₂	5	1.7	33	3.5 ± 0.1
	6	1.6	29	3.9 ± 0.1
	10	1.5	29	3.7 ± 0.1
GD = 63%		2.1	51	2.0 ± 0.1
TiO ₂	4	2	49	2.1 ± 0.1
	7	1.9	45	2.3 ± 0.1
	10	1.7	37	2.9 ± 0.1
GD = 35%		1.8	41	2.6 ± 0.1
SiO ₂	2	1.8	42	2.5 ± 0.1
	2	1.9	41	2.7 ± 0.1
	4	2	45	2.4 ± 0.1
GD = 71%		2.2	50	2.3 ± 0.1
SiO ₂	5	2.3	49	2.4 ± 0.1
	5	2.3	51	2.2 ± 0.1
	8	2.3	55	1.9 ± 0.1

oxide nanoparticles can lead to the preservation or reduction of conductivity and water uptake [40–43]. In our case, incorporation of titanium or zirconium oxides leads to a decrease in the water uptake. Moreover, when the membranes are doped with zirconia, the ion-exchange capacity (IEC) decreases dramatically, whereas for the samples doped with TiO₂, such changes are less pronounced (Table 1).

The change in IEC is associated with binding of sulfonic groups by the oxide surface. Binding efficiency should decrease as the acidity of the respective oxides increases in the following sequence ZrO₂-TiO₂-SiO₂ [44, 45]. This process can be described by the formation of “salt” bridges according to the eq. (9).



Similar processes occur during sulfonation or phosphorylation of zirconium and titanium oxides [46–48], as well as during their use as anion-exchange materials [49]. Formation of such salt bridges limits membrane swelling, similar to introduction of a cross-linking agent or decreasing the fraction of the conductive polymer in traditional approaches to control the swelling of ion-exchange membranes.

In order to prove that cross-linking takes place, an additional experiment was carried out. Pure polystyrene sulfonate, which is responsible for conductive properties of the obtained membranes, demonstrated high water solubility. However, after consecutive treatment with ZrOCl₂ and NaOH solutions, the material lost this property. It confirms that such treatment leads not only to water displacement, but also to polymer cross-linking due to formation of salt bridges.

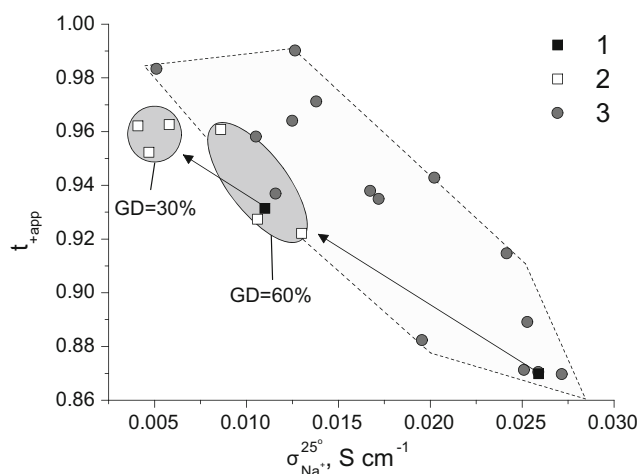


Fig. 2 Apparent transport numbers as a function of ionic conductivity for initial (1, 2) and zirconia-doped membranes (3); 1 = initial membranes used in the present study, 2 = hybrid materials obtained from these membranes, 3 = previously described grafted membranes [14] with varying grafting degree (proportion of ion conducting polymer) and cross-linking degree

Table 2 Ionic conductivities and transport numbers of the initial membrane with 65% polystyrene grafting degree and some of the corresponding hybrid membranes with the dopant content of 8–10 wt%

Property	Initial membrane	Dopant		
		ZrO ₂	TiO ₂	SiO ₂
IEC mmole g ⁻¹	2.1	1.1	1.9	2.1
σ_{Na^+} , mS cm ⁻¹	25.3	10.1	22.3	31.6
$t_{\text{+app}}$	88	95	88	81

Influence of doping on transport properties

Incorporation of zirconia in the matrix of the investigated membranes leads to an increase in ionic conductivity and to a decrease in permselectivity (Fig. 2). Furthermore, molality of the inner solution increases dramatically (Table 1). Water uptake decreasing after zirconia incorporation into the membrane matrix is coupled with contraction of pores and as a result channels, which limit the membrane conductivity. The volume of the electroneutral solution in pore centers, through which non-selective transport of co-ions occurs, decreases even to a greater degree. In contrast, the advantage of using traditional cross-linking is that a decrease in charge carrier concentration is not pronounced. It is observed only due to a slight “dilution” after the cross-linking agent is introduced. As a result, the conductivity decrease is smaller in this case (Fig. 2).

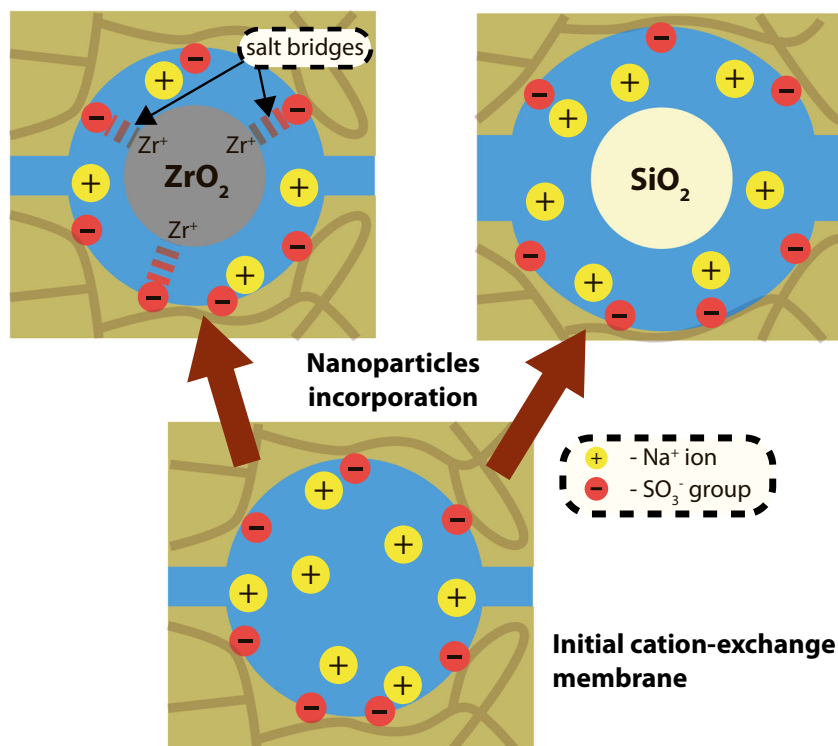
However, in hybrid membranes based on zirconia and a film with a high initial grafting degree (GD = 60%), the molality of inner solution increases only slightly. Still, these membranes have high transport numbers. It is due to the fact that water is partly coordinated by the dopant surface or localized in the hydration shells of the formed salt bridges. Since the hydration shells do not contribute to the IEC of the membrane, the real concentration of solvated mobile ions should be markedly higher.

The strategy of controlling membrane swelling by incorporation of zirconia is similar to ionic cross-linking by mixing a polyacid and a polybase [50, 51], which is widely used for the synthesis of proton-conducting membranes which cannot be cross-linked by any other method. However, this approach is only efficient for the membranes in the protonated form, whereas quite often, non-acidic solutions should be subjected to desalination.

In the case of titanium oxide, which has lower basicity, binding of functional groups is weaker (Table 1), and a change of conductivity and transport numbers is smaller (Table 2). For silica, on the contrary, we observed an increase in conductivity and a decrease in permselectivity, compared to the initial membranes.

According to the membrane pore semi-elasticity model [52], incorporation of nanoparticles results in widening of pores due to the increased osmotic pressure, since a nanoparticle takes up a part of volume. The mentioned effect predominates only in the case of membranes doped by

Fig. 3 Illustration of the nanoparticle incorporation impact on the structure of pores (or ion clusters)-channel systems for zirconia and silica



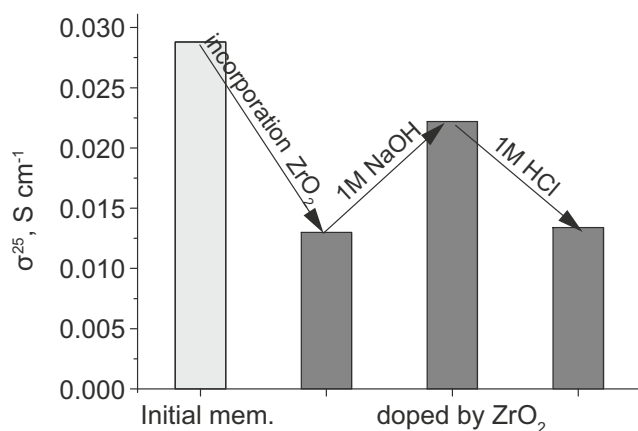


Fig. 4 Change in Na⁺-ionic conductivity of the hybrid membranes in 0.5 M NaCl solution after modification and treatment with alkali and acid solution

silica (Fig. 3). When functional groups of the membrane are bound to the dopant surface, corresponding forces prevent the pores from broadening. Furthermore, the concentration of counter-ions formed due to the dissociation of $-\text{SO}_3\text{Na}$ groups decreases. The sum of the mentioned phenomena leads to the effects observed for membrane doping with different oxides (Table 2). The effects are illustrated on Fig. 3.

The obtained results can be compared with a previous study [26], where fabrication of a series of hybrid materials based on perfluorinated homogeneous Nafion® membranes and the same oxides has been reported. Silicon and titanium oxides demonstrate behavior similar to these data. Silica incorporation leads to an increase in water uptake and conductivity, while titanium oxide has little effect on these parameters. The situation is directly opposite in the case of zirconia. According to the reported data [22], conductivity as well as water uptake of the obtained membranes were markedly higher, compared to the initial one. Most likely, the discrepancy arises from further treatment of the hybrid membranes. We assume that after boiling in sulfuric acid, the sulfonated form of zirconia was obtained. As a result, no salt bridges were formed between the functional groups of the polymer and the zirconia surface. Introduction of such particles led to an increase in conductivity and water uptake. We observed a similar effect previously, when ion-exchange membranes were doped with zirconium oxide, zirconium phosphate [28], and zirconium oxide with surface phosphate groups [43].

The reversibility of salt bridge formation can be demonstrated. When the membrane is treated with 1 M solution of sodium hydroxide, the sulfonic groups bound to the oxide surface are substituted with OH-ions. After alkali is removed by repeated washing with 0.1 M NaCl solution, conductivity of these membranes increases twofold, compared to the ones not treated with alkali (Fig. 4). Enhanced conductivity of such membranes is preserved for several days. After treatment with

acid solution and washing with 0.1 M NaCl, ionic resistance is restored via regeneration of salt bridges between the oxide surface and the functional groups. Conductivity of the membranes with “bound” groups also remains stable. In other words, the salt bridges between the membrane polymer and dopant nanoparticles can be broken down and restored on demand by treatment with solutions of different acidity. This makes it possible to control conductive properties by pH varying.

Conclusion

In the present study, we demonstrate that incorporation of inorganic oxides of different nature is an efficient way to control water uptake, conductivity, and permselectivity of ion-exchange membranes. Doping with silica increases water uptake and conductivity. Introduction of titanium or zirconium oxide changes the properties of the membranes in the opposite direction. The fact that the reason for this phenomenon is peculiar cross-linking of the membrane via salt bridge formation was shown. Since a part of functional groups are involved in such cross-linking, its efficiency is lower, compared to traditional cross-linking of polymeric chains where no decrease of ion-exchange capacity can be observed usually. The proposed procedures are simple to realize and can be efficiently used with a wide range of ion-exchange membranes for applications in fuel cells and other processes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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