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Hybrid materials based on MF-4SC perfluorinated sulfo cation-exchange membranes and silica with proton-acceptor properties

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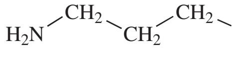
Hybrid materials based on perfluorinated sulfo cation-exchange MF-4SC membranes with silica nanoparticles in the pores, whose surface is modified by hydrocarbon fragments containing amino groups [3-aminopropyl and 3-(2-imidazolin-1-yl)propyl] that impart it with proton-acceptor properties, were obtained. In has been shown that this modification results in a decrease in ion exchange capacity, water uptake and diffusion permeability of the membranes, whereas the ionic conductivity of the membranes with low content of modifying groups increases in comparison with the membrane that contains only SiO_2. The observed phenomenon, non-typical of ion-exchange materials, was explained using the model of the semielacticity of membrane pore walls.

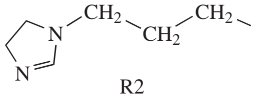
The perfluorinated sulfo cation-exchange membranes such as Nafion (Du Pont, USA), Dow (Dow, USA) and MF-4SC (LTD Plastpolymer, Russia), which are widely used in the development of alternative energy sources and water treatment systems, are of keen interest.[1,2] A way of improving the properties of such membranes involves the development of hybrid materials containing nano-sized additives, for example, hydrated silica.[3] A promising way of this modification method is changing the donor-acceptor properties of silica particle surface by chemical bonding of fragments containing amino groups. On the other hand, the majority of researchers give preference to modify surface with proton-donor groups that enhance the water uptake and concentration of carriers in membranes,[4] while the properties can also be improved by the modification of nanoparticle surfaces with proton-acceptor groups.

The purpose of this work was to study the properties of hybrid materials based on an MF-4SC membrane and hydrated silica[†] whose surface is modified by hydrocarbon fragments containing amino groups [3-aminopropyl (R1) and 3-(2-imidazolin-1-yl) propyl (R2)], which impart it with proton-acceptor properties.



$H_2N-CH_2-CH_2-CH_2-$

R1



R2

In the case of MF-4SC membrane modification by SiO_2 nanoparticles, the maximum conductivity is reached at a dopant content of 3 wt%.[5] Therefore, we used samples with 3 wt% SiO_2 with a surface modified by 5 or 10 mol% of R1 and R2 (with respect to the silica amount).

Transmission electron microscopy (TEM) has shown that isolated particles with sizes of 5–10 nm are formed in the hybrid membrane matrix (Figure 1). Incorporation of SiO_2 particles with modified surface results in a decrease in the ion exchange capacity (IEC) from 0.95 to 0.65–0.88 mg-equiv. g^{-1} in comparison with that of MF-4SC + 3% SiO_2 (Table 1). The IEC decreases with the concentration of modifying groups increase.

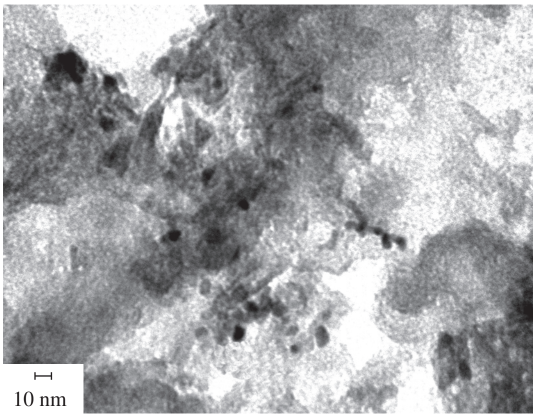


Figure 1 TEM image of a MF-4SC + 3% SiO_2 membrane (5 mol% R1).

Materials containing silica with modified surface are characterized by lower water uptake than MF-4SC and MF-4SC + 3% SiO_2 (Table 1). At the same concentration of modifying groups, a smaller water uptake is observed for membranes containing more bulky R2 groups.

The ionic conductivity of all hybrid membranes is higher than that of the initial MF-4SC (Figure 2). The modification of silica with R1 and R2 groups results in an additional increase in conductivity in comparison with that for MF-4SC + 3% SiO_2. Conductivity changes differently with the increase in the concentration of amino-containing fragments: it grows for R1 but diminishes for R2. The maximum conductivity was reached for the MF-4SC + 3% SiO_2 membrane (10 mol% R1).

Modification of silica surface with proton-acceptor groups leads to a considerable change in diffusion permeability rate and

Table 1 IEC and water uptake in membranes.

Sample	IEC, mg-equiv. g^{-1}	w_{H_2O} (%)
MF-4SC	0.93	18.1
MF-4SC + 3 wt% SiO_2	0.95	18.6
MF-4SC + 3 wt% SiO_2 + 5 mol% R1	0.74	18.5
MF-4SC + 3 wt% SiO_2 + 10 mol% R1	0.65	13.7
MF-4SC + 3 wt% SiO_2 + 5 mol% R2	0.88	12.6
MF-4SC + 3 wt% SiO_2 + 10 mol% R2	0.73	10.5

[†] The materials were obtained by a published casting procedure[5] from a polymer solution containing a calculated amount of precursors for the following synthesis of silica and silica with modified surface.

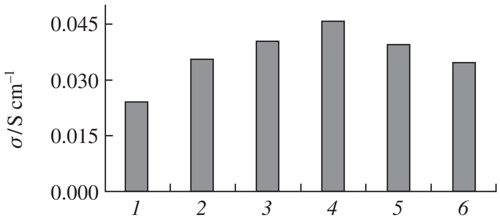


Figure 2 Ionic conductivity of membranes: (*1*) MF-4SC, (*2*) MF-4SC + 3% SiO_2, (*3*) MF-4SC + 3% SiO_2 (5 mol% R1), (*4*) MF-4SC + 3% SiO_2 (10 mol% R1), (*5*) MF-4SC + 3% SiO_2 (5 mol% R2) and (*6*) MF-4SC + 3% SiO_2 (10 mol% R2) at 40 °C and 100% relative humidity.

H^+/Na^+ interdiffusion through the membrane. At a low content of the modifying groups R1 and R2 (5 mol%), the diffusion permeability coefficients of HCl and NaCl solutions through the membrane decrease in comparison with those for MF-4SC + 3% SiO_2 (Table 2), which indicates that the anion diffusion rate is reduced. Since a rise in conductivity is observed for these membranes, it can be concluded that the modification improves the cation transfer selectivity. An increase in the concentration of proton-acceptor groups on the SiO_2 surface results in an increase in diffusion permeability coefficients by more than half an order of magnitude (Table 2). A growth of the modifying group size on transition from R1 to R2 is accompanied by a lowering of diffusion permeability by a factor of 2 or more. The H^+/Na^+ interdiffusion coefficients depend on the type and concentration of the modifying group in a manner similar to diffusion permeability (Table 2).

Thus, the incorporation of silica particles with proton-acceptor groups on the surface into the membrane matrix considerably affect the water uptake and ionic mobility. This occurs for a number of reasons. Amino groups interact with some of the protons of SO_3H groups in the MF-4SC membrane and form strong hydrogen bonds (NH_x^+–SO_3^-). Therefore, a part of protons is not involved in ion exchange or ion transport processes. This is confirmed by a decrease in the IEC of membranes containing SiO_2 with modified surface (Table 1). In this case, the number of bound protons is determined by the concentration of modifying groups on the surface and the size of the group. The IEC of the membranes containing silica with more bulky R2 groups is higher than that of the membranes with R1 groups, though the R2 group contains a twofold number of nitrogen atoms. This is explained by the fact that a part of nitrogen atoms in the R2 groups become hardly accessible and do not interact with membrane protons. In MF-4SC type membranes, the highest affinity with water molecules is manifested by acid protons whose concentration determines the water uptake of membranes.[6] Therefore, the samples doped by silica with proton-acceptor groups on the surface should contain less water than a membrane doped by SiO_2, which is in good agreement with the experimental data (Table 1). The water uptake in membranes doped by SiO_2 with R2 groups is much lower than that in membranes doped by SiO_2 with R1 groups, whereas, conversely, the IEC is higher. Therefore, it can be concluded that the membrane properties are determined not only by the concentration of charge carriers (free protons). In accordance with a model of the semielasticity of membrane pore walls,[7] the water uptake and conductivity of modified MF-4SC membranes are determined by changes in the pore size and hence the size of channels connecting the pores. The silica particles with modified surface are larger than those of unmodified SiO_2; hence, the solution volume inside a pore decreases. Since amino groups form strong bonds with the membrane sulfo groups, the elasticity of the pore walls decreases. This hinders the sorption of additional water. Therefore, the water uptake in membranes doped by SiO_2 with more bulky R2 groups on the surface is much lower than that with R1 despite the higher concentration of free protons.

Table 2 Diffusion permeability (*P*) of NaCl and HCl solutions and H^+/Na^+ interdiffusion coefficients (cm^2 s^{-1}) for the membranes.

Membrane	Diffusing solution		
	0.1 M NaCl/ H_2O	0.1 M HCl/ H_2O	0.1 M HCl/ 0.1 M NaCl
MF-4SC	1.1×10^{-7}	5.5×10^{-7}	6.3×10^{-6}
MF-4SC + 3 wt% SiO_2	1.8×10^{-7}	5.0×10^{-7}	1.0×10^{-5}
MF-4SC + 3 wt% SiO_2 + 5 mol% R1	8.8×10^{-8}	4.7×10^{-7}	8.9×10^{-6}
MF-4SC + 3 wt% SiO_2 + 10 mol% R1	4.5×10^{-7}	2.8×10^{-6}	5.2×10^{-5}
MF-4SC + 3 wt% SiO_2 + 5 mol% R2	4.6×10^{-8}	2.1×10^{-7}	6.65×10^{-6}
MF-4SC + 3 wt% SiO_2 + 10 mol% R2	2.9×10^{-7}	1.3×10^{-6}	5.2×10^{-5}

Changes in the conductivity of hybrid membranes with different types and concentrations of modifying groups on the silica surface are determined by the same factors as the water uptake. A decrease in the concentration of R1 on the SiO_2 surface results in an increase in conductivity. If the surface is modified by the more bulky R2 group, the conductivity is lower and reduced with the content of the modifying group due to a decrease in the water uptake.

The diffusion permeability of membranes is determined by the diffusion rate of the anion whose mobility is lower. The reduction of the diffusion permeability in hybrid membranes containing silica with surface modified by small amounts of proton-acceptor groups in comparison with MF-4SC and MF-4SC + 3 wt% SiO_2 membranes (Table 2) is due to a decrease in the solution volume inside pores.[4] The majority of cations are localized near the pore walls that are negatively charged due to fixed SO_3^- groups, and form a thin (1 nm) Debye layer. Modification of membranes has already no effect on this layer. Anions are excluded from this space and localized in the electrically neutral ('free') solution in the centre of a pore (in the case of unmodified membranes) or near the surface of a SiO_2 particle.[4] In modified membranes, the 'free' solution volume where anions can diffuse is smaller than that in the initial membrane, which hinders the process. A growth of the modifying group size on transition from R1 to R2 provides an additional decrease in diffusion permeability.

At higher degree of modifying groups on SiO_2 surface (10 mol%), the coefficients of both diffusion permeability and H^+/Na^+ interdiffusion increase sharply (Table 2). Since this nearly does not result in conductivity changes (Figure 2), it can be assumed that through pores or caverns are formed in the membrane. Ions can easily diffuse through them. These pores can appear due to formation of large precursor associates for the following formation of dopant particles if its concentration is high. Their hydrolysis in the matrix of an already formed membrane causes a considerable volume decrease with the formation of volumetric porous structures or the removal of a part of products from the membrane. On the other hand, according to the semielasticity model of membrane pores,[7] an increase in the size of dopant particles produces regions with high internal stress and micro-cracks in the membrane. They do almost not affect the conductivity measured in contact with distilled water. Water fills the cracks thus ensuring their low conductivity that does not contribute to the overall membrane conductivity. At the same time, diffusion measurements are performed in contact with concentrated solutions that considerably enhance the ion transfer rate as they fill the pores.

Thus, it has been shown that incorporation of silica particles with surface proton-acceptor groups [3-aminopropyl and 3-(2-imidazolin-1-yl)propyl] into the MF-4SC membrane matrix results in a decrease in the water uptake and ion exchange capacity and an increase in ionic conductivity in comparison with a membrane containing unmodified SiO_2. At a low concentration of modifying groups on the SiO_2 surface (5 mol%), the diffusion permeability is reduced and the selectivity of the ionic transfer process rises. This results from a decrease in the free volume inside the pore in modified membranes.

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References

1 K. D. Kreuer, S. J. Paddison, Ec. Spohr and M. Schuster, *Chem. Rev.*, 2004, **104**, 4637.

2 A. B. Yaroslavtsev, Yu. A. Dobrovolsky, N. S. Shaglaeva, L. A. Frolova, E. V. Gerasimova and E. A. Sanginov, *Usp. Khim.*, 2012, **81**, 191 (*Russ. Chem. Rev.*, 2012, **81**, 191).

3 D. J. Jones and J. Roziere, *Inorganic/organic Composite Materials. Handbook of Fuel Cells – Fundamentals, Technology and Applications*, John Wiley & Sons, Ltd., Chichester, UK, 2003, p. 2826.

4 A. B. Yaroslavtsev, *Nanotechnol. in Russia*, 2012, **7**, 437.

5 E. Yu. Safronova and A. B. Yaroslavtsev, *Zh. Neorg. Khim.*, 2010, **55**, 1499 (*Russ. J. Inorg. Chem.*, 2010, **55**, 1587).

6 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535.

7 S. A. Novikova, E. Yu. Safronova, A. A. Lysova and A. B. Yaroslavtsev, *Mendeleev Commun.*, 2010, **20**, 156.

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