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Relationships between water uptake, conductivity and mechanical properties of hybrid MF-4SC membranes doped by silica nanoparticles

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The effects of modifying MF-4SC perfluorosulfonic membrane with hydrated silica nanoparticles on the mechanical properties, water uptake and ionic conductivity have been compared. It has been found that the maximum values of the Young's modulus, strength, water uptake and conductivity of the membrane, along with the minimum storage modulus of elasticity, are observed at low dopant concentrations (3–5 wt%). The results are well described within the model of limited elasticity of membrane pore walls.

The properties of hybrid organic/inorganic membrane materials have been widely studied in the past few decades. The main effort is directed at determining the effect of the physicochemical nature of the additive and its concentration on the properties of materials.[1–6] Previously, we suggested a model of limited elasticity of membrane pore walls,[7] according to which the reasons of membrane conductivity variation upon modification lie in changes of the system of pores and channels due to the presence of dopant particles. Incorporation of a small amount of an additive increases the pore size to some extent, which results in simultaneous growth of the size of the connecting channels and an increase in conductivity. As the dopant concentration increases, so does the size of incorporated particles. Once a certain concentration has been reached, a further growth in the pore size becomes more complicated. As a result, the free space volume inside the pores is reduced, with a resulting decrease in the water uptake and conductivity of the material. The effects of membrane modification on mechanical properties (strength, hardness, elasticity) are important but have been studied insufficiently. It was assumed[8] that modification of a membrane considerably affects its mechanical properties.

The purpose of this work was to clarify the relationship between water uptake, conductivity and mechanical properties of ion exchange membranes and the concentration of hydrated silica in the membrane, with consideration for the effect of the dopant on the system of pores and channels. The perfluorosulfonic membrane MF-4SC in acid form was chosen as the model for this study.

The membranes were obtained by casting procedure described previously.[9,†] Prior to studies of conductivity, mechanical properties and dynamic mechanical analysis (DMA), membrane samples were pre-exposed to a relative humidity (RH) of 95%.[‡]

According to the transmission electron microscopy (TEM) membrane modification results in the formation of isolated nanoparticles with the size of 5–10 nm.[§] Based on the plots of stress *vs*. strain for the studied membranes, the following values were obtained: the Young's modulus, which characterizes the membrane resistance to strain (its hardness); the yield point corresponding to the start of irreversible deformations caused by unfolding of macromolecule coils and their movement relative to each other; stress and relative elongation at break (Table 1). The dependences of the Young's modulus and yield point on the silica content pass through a maximum at 3 wt% SiO_2, similarly to the dependences of conductivity and water uptake (Figure 1). If 5 wt% SiO_2 or more is incorporated, the Young's modulus and

Table 1 The Young's modulus, yield points, stress and strain at break for MF-4SC membranes containing various amounts of silica.

SiO_2 content (wt%)	Young's modulus/MPa	Yield point/MPa	Break stress/ MPa	Break strain (%)
0	47.6	4.7	14.7	284
1.5	47.8	5.4	13.7	231
3	**50.6**	**5.6**	**16.9**	**297**
5	40.8	4.2	12.5	260
7	40.3	4.5	11.6	232
10	32.6	3.1	6.3	69

† The polymer solution (a 10 wt% solution of MF-4SC perfluorinated ion-exchange resin in isopropanol produced by LTD Plastpolymer, Russia) was mixed with a predefined amount of the precursor (tetraethoxysilane, Fluka, >98%) for subsequent SiO_2 preparation, the solution was casted onto Petri dishes, and the solvent was removed. The resulting films were cautiously removed from Petri dishes and treated with an ammonia solution to convert the precursor into hydrated silica. The SiO_2 concentration was varied from 0 to 10 wt%.

‡ The ion conductivity was measured with the use of impedance spectroscopy in a frequency range from 10 Hz to 2 MHz using 2B-1 impedance analysers. The experiment was performed in cells with constant pressure on the membrane at RH = 95% and T = 27±1 °C. Carbon sheets were used to improve the contact between the membrane and electrodes.

Stress-strain experiments were performed using an INSTRON 5965 universal testing machine under ambient conditions (RH = 20±2% and T = 27±1 °C). The gauge length of the samples was adjusted to 12 mm, the width was 3 mm. The strain rate was 1 mm min^{-1}.

DMA were carried out with a TA Instruments DMA Q800, using the film/fiber tension clamp. Temperature spectra were measured by subjecting a rectangular film sample of *ca*. 20×2×0.1 mm to an oscillatory sinusoidal tensile deformation at 1 Hz (0.05 N preload force). Measurements were carried out in the temperature range 30–200 °C at a rate of 3° min^{-1}. The mechanical response data were analyzed in terms of the elastic (storage) modulus (E') and viscous (loss) modulus (E''); tan E''/E' was analyzed as a function of temperature to measure the material damping characteristics such as vibration and sound damping phenomena.

§ TEM micrographs were obtained with the use of Jeol JEM-1011 at an accelerating voltage of 100 kV. Before the TEM measurements the membranes were dispersed ultrasonically in methanol and supported onto carbon-coated Cu grids.

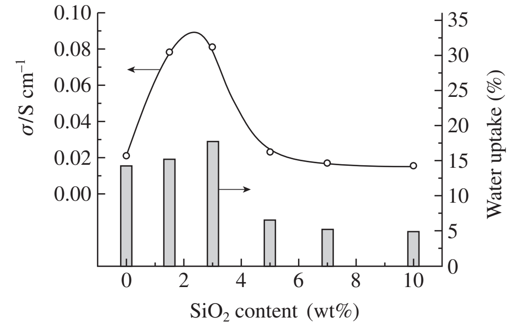

Figure 1 Plots of ionic conductivity (30 °C) and water uptake *vs.* silica concentration in the MF-4SC membrane.

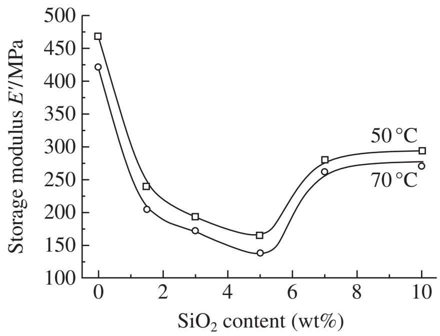

Figure 2 Plots of storage modulus *vs.* silica concentration in the MF-4SC membrane at various temperatures.

the yield point become smaller than those of the unmodified MF-4SC membrane.

Some general trends may be noted: the highest strength and elasticity and the maximum yield point are observed in membranes that contain a small dopant concentration (up to 3 wt%), while its increase from 3 to 10 wt% is accompanied by a pronounced worsening of mechanical properties (Table 1). In fact, at 10 wt% SiO_2 the break stress decreases more than twofold, while the break strain decreases fourfold in comparison with the unmodified MF-4SC membrane. Note that, unlike the other parameters, the maximum break stress and strain can differ noticeably between experiments with the same membrane composition. Therefore, the difference in break tensile of the unmodified membrane and samples with small dopant concentrations lie within experimental error, and in fact we can only state that it, at least, does not decrease.

The change in the mechanical properties of membranes is related to the effect of the dopant on the system of pores and channels. Membrane pores are analogues of defects or micro-cracks that considerably reduce the mechanical strength of solids. The larger the number and size of defects, the lower the strength of materials.[10] Since pores and channels are randomly arranged in a membrane, some of the samples break under relatively small strain, whereas others are much stronger. For this reason, the stress and strain at break show the largest discrepancy.

As the silica concentration in the membrane increases, the osmotic pressure that attempts to deform pores from the inside grows, and so does the pore size.[8] However, if a small amount of the dopant is added, osmotic pressure just compensates the elastic deformation forces, and, despite the increase in the pore size, the strength and hardness of membranes even rise in comparison with the unmodified MF-4SC. An increase in osmotic pressure is, in effect, equivalent to some inherent force that deforms the pores and the membrane itself, therefore subsequent deformation requires a higher force to be applied. It results in an increase in the Young's modulus and mechanical strength in the case of membranes with 1.5 or 3 wt% SiO_2. However, as the dopant concentration and particle size increase, the membrane deformation becomes too strong, so the material strength and the Young's modulus decrease abruptly (Table 1). Furthermore, water present in the MF-4SC membrane serves as a plasticizer that reduces the material elasticity.

According to literature data, analysis of DMA results allows one to identify the interactions that occur in the membrane matrix. The storage modulus (E') in Nafion-type membranes in the temperature range up to 100–110 °C mainly characterizes the strength of electrostatic interactions inside ion clusters.[11,12] The E' value for hybrid membranes is lower than that for the unmodified MF-4SC membrane and strongly depends on the dopant content (Figure 2). It decreases considerably as the SiO_2 amount is raised from 0 to 5 wt% but then increases somewhat. Presumably a decrease in E' upon membrane modification is due to changes in the network of hydrogen bonds in the matrix of the unmodified MF-4SC. Initially, pore widening due to the modification is accompanied by a decrease in the concentration of sulfonic groups on the pore walls and, conversely, an increase in the fraction of hydrophobic areas on them. This results in weakening of hydrogen bonds in the interstitial solution. On the other hand, at high dopant concentrations, the size of its particles grows, whereas the pore size changes less strongly. As a result, formation of new bonds between sulfonic groups and a dopant particle, *i.e.*, a kind of polymer linking, becomes possible. For this reason, the dependence of storage modulus E' on SiO_2 content is non-monotonous (Figure 2).

Thus, the results of studies of the mechanical properties of MF-4SC hybrid membranes containing various amounts of silica correlate with data on water uptake and ionic conductivity and agree with the model of limited elasticity of membrane pore walls. Incorporation of small dopant amounts enhances the membrane hardness and strength, along with weakening of the continuous chain of hydrogen bonds inside the ion clusters.

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