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Influence of incorporated nanoparticles on the ionic conductivity of MF-4SC membrane

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Hypothesis of semielasticity of walls of membrane pores was proposed as an explanation of increase in the ionic conductivity in composite ion-exchange membranes containing incorporated nanoparticles of inorganic species and polyaniline.

The perfluorosulfonic cation-exchange membranes such as Nafion (Du Pont, USA), Dow (Dow, USA), and MF-4SC (Plastpolymer, Russia) are widely used in fuel cells production, electrochemical synthesis and water purification.[1,2] However, these membranes are disadvantageous of low conductivity at low relative humidity, narrow operating temperature range (< 100 °C) and relatively low mechanical strength at high temperature. Incorporating of various nanoparticles can improve membrane conductivity, water management, mechanical properties, and bring changes to pore and channel structure.[2–7]

The aim of this work was the investigation of changes in the ionic conductivity of the membrane after modification with oxide, metal and polyaniline (PAni) nanoparticles. Membrane MF-4SC was taken as a model.

Composite membranes were prepared by two different methods. According to the first one, additives were synthesized *in situ* in MF-4SC membrane pores as described.[8,9] In this manner, composite membranes with dopant content up to 4.4 vol% (5 wt%) for silica and 2.8 vol% (12 wt%) for metal nanoparticles were prepared. Second method consisted in casting of composite membranes from solution of polymer and precursor for further particle synthesis.[10,11] This method provided incorporation of SiO_2 up to 13.5 vol% (15 wt%) and PAni up to 26 vol% (14 wt%). The transmission electron microscopy showed that in all cases isolated nanoparticles (2–6 nm) were formed in membrane matrix.

Experiments revealed that modification of MF-4SC membrane by small amounts of silica and PAni results in the increase in proton conductivity (Figure 1). The proton conductivity curve as a function of additive content has the maximum at 2.6 vol% of SiO_2 and 1.5 vol% of PAni. Earlier the growth of proton conductivity of composite membranes was explained by additional water sorption by hydrophilic nanoparticles surface that facilitate ion transfer.[12] However, PAni incorporation leads to the decrease in water content due to the strong hydrogen bond ($-SO_3\cdots HN-$) formation.[11] The increase in the ionic conductivity in composite materials is commonly attributed to the decrease of defect formation energy at the phase boundary[13] owing to a partial sorption of SO_3H protons by oxides or base nitrogen atoms of PAni. At the same time MF-4SC membrane is a strong acid[14] where degree of dissociation of its SO_3H groups should be close to 100% for all hydrated membranes, and the starting membrane already has many defects. Nevertheless, these assumptions cannot explain the growth of proton conductivity for MF-4SC membrane doped by hydrophobic silver or copper nanoparticles (Figure 2). Therefore, another explanation for the ionic conductivity increase in composite MF-4SC membranes with incorporated nanoparticles, based on semielasticity property of walls of pores and channels, was proposed. According to the Gierke's model,[15] self-organization takes place in Nafion-type membrane matrix. This results in formation of channel connected nanopores (2–5 nm) filled with SO_3H groups and water molecules. Thus, it is possible to expect nanoparticle formation in these pores after modification. Taking into account the wall semielasticity we supposed that the pores and channels are expanded in the presence of nanoparticles (Figure 3). Hence, the growth of the ionic conductivity of membrane modified by hydrophilic and hydrophobic nanoparticles can be explained mainly by the dopant influence on pore and channel structure. Thermal analysis confirms the expansion of membrane pores after modification. Incorporated nanoparticles occupied certain volume of pores. The fact that the number of acid protons after modification remains the same

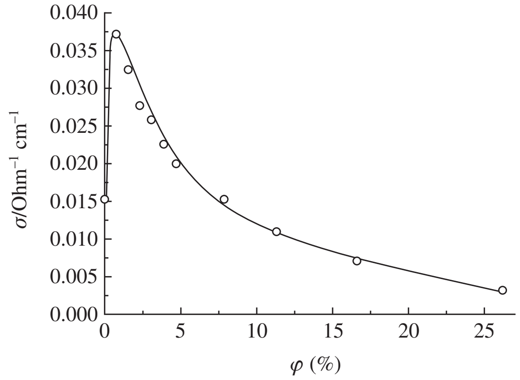

Figure 1 Ionic conductivity of PAni doped composite membranes *vs.* PAni content at room temperature.

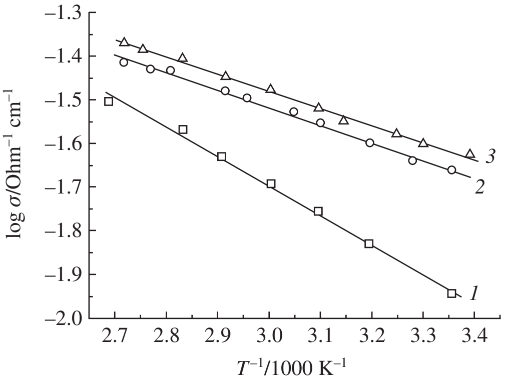

Figure 2 Arrhenius dependences of proton conductivity for MF-4SC membranes with different Ag content: (*1*) pure; (*2*) 2.3 vol% Ag; (*3*) 2.8 vol% Ag.

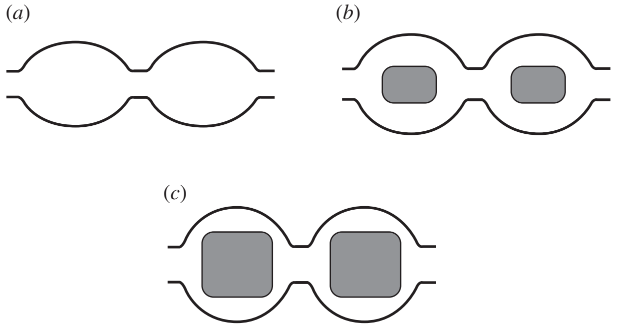

Figure 3 Scheme of pore structure for (*a*) starting and (*b*), (*c*) modified by nanoparticles membranes in the case of semielastic pore walls model.

means that sorption of additional water leads to the increase in total pore volume and channel size (Figure 3). In the case of the semielasticity of membrane pores further increase in nanoparticle volume (> 3–4 vol%) will be followed by the decrease in water uptake. In fact, water uptake for the membrane containing 4.5 vol% of additional phase is less than that for the starting sample.

Above-mentioned assumption is confirmed by proton conductivity and its activation energy data. Membrane modification by small amount of additional phase results in both conductivity increase and conductivity activation energy decrease that are determined by proton transfer in the narrow membrane channels where proton mobility is minimal. So, we can conclude that the growth of proton conductivity can be explained by the increase in the channel size. Further increase in nanoparticle volume (> 3–4 vol%) leads to the blocking of proton transfer routes, which results in decrease in conductivity and growth of activation energy. In the case of PAni-modified membranes less volume content for maximal conductivity and more rapid decrease in conductivity in comparison with silica and metal nanoparticles containing membranes can be caused by partial sorption of SO_3H protons by basic nitrogen atoms of PAni and their exclusion from the transfer processes due to strong hydrogen bond formation.

Our hypothesis is also confirmed by comparison of proton diffusion coefficients calculated from conductivity and NMR spectroscopy data[16] (Figure 4) for the starting membrane and membranes doped by silica and acidic zirconium phosphate. Proton diffusivities calculated from ^{1}H NMR relaxation are determined mostly by proton and water molecules migration in wide pores where most 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. Note that if modification leads to increase in ion conductivity in the membrane in comparison with the starting MF-4SC, ^{1}H NMR relaxation rate of this membrane can be both higher and lower compared to that of the starting one (Figure 4). This confirms influence of incorporated nanoparticles on the channel size.

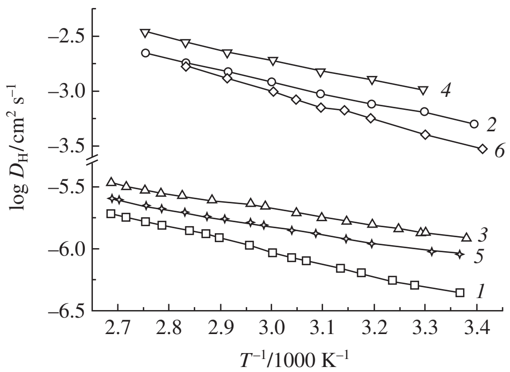

Figure 4 Arrhenius dependences of proton diffusion coefficients calculated from (*1*), (*3*), (*5*) conductivity data and (*2*), (*4*), (*6*) NMR spectroscopy data for (*1*), (*2*) MF-4SC membrane and MF-4SC modified by (*3*), (*4*) silica and (*5*), (*6*) acid zirconium phosphate.[15]

Semielasticity of walls of the pore model can also explain the change in mechanical properties of modified membranes. According to this model high dopant content should promote mechanical stress and breaks in membrane structure. Therefore, membranes containing 13.4 vol% of silica or 26 vol% of PAni or 25 vol% of Ag would fissure during formation.

In conclusion, the ion-exchange membrane conductivity growth during modification by nanoparticles is caused mainly by the dopant influence on pores and channels structure. Semielasticity of walls of the pore model is proposed to explain this phenomenon.

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