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Synthesis and transport properties of membrane materials with incorporated metal nanoparticles

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The size distribution of copper and silver nanoparticles obtained on MF-4SC perfluorinated sulfocation membrane and the effect of metal nanoparticles on the membrane transport properties are reported.

Synthesis of nanoparticles is one of the most important challenges in materials science. The main problem is to prevent the particles formed from aggregation that results in an increase in the particle sizes and loss of many unique properties. Synthesis in a porous matrix is one of the most promising methods for the preparation of nanoparticles.[1] This method allows the particles formed to be isolated from each other. Moreover, it decreases surface tension that is the main force driving the nanoparticle aggregation processes. One of the commonly used techniques involves synthesis of nanoparticles in nanoporous oxides and in micelles with surfaces coated by surfactants.[2] The effect of the size of copper nanoparticles embedded in KU-23 and KU-2 ion-exchange materials on their electrode properties was studied.[3,4] Perfluorinated sulfocation membranes can be considered as promising matrices for the synthesis of metal nanoparticles. Microphase separation processes result in the formation of an extensive system of nanopores connected by channels in a polymer membrane.[5,6] This kind of structure makes the membrane an ideal 'nanoreactor' for the synthesis of nanoparticles. This approach has been used to synthesise nanoparticles with special magnetic properties.[7]

According to published data,[8–10] certain additives affect significantly the transport properties of proton-conducting polymer materials, such as diffusion permeability, transport numbers of different ions and ionic conductivity. Thus, studies on the synthesis of metal particles can be of considerable interest for modifying membrane materials.

The purpose of this work was to synthesise silver and copper nanoparticles in an MF-4SC membrane matrix and to study the effect of these particles on the transport properties of the membrane. Copper and silver nanoparticles were obtained directly in the pores of a perfluorinated MF-4SC membrane (Plastpolymer, St. Petersburg) similarly to the synthesis in KU-2 ion-exchange resins as described previously.[11] Silver and copper cations were incorporated in the membrane matrix by ion exchange. Cations incorporated in MF-4SC were reduced to the metals by treatment with an alkaline $Na_2S_2O_4$ solution. The number of membrane treatment cycles was varied to give composite materials containing 6%, 10% and 12% Ag, as well as 3%, 6% and 8% Cu.

All the composite membranes are visually homogeneous. Incorporation of inorganic solids results in a change in the membrane colour. Incorporation of silver gives a grey 'metallic' or black colour. In the case of copper, the composite materials become reddish-brown and later greenish-grey due to oxidation.

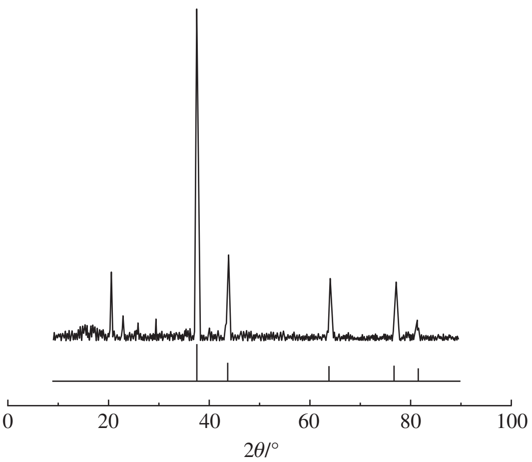

Figure 1 X-Ray pattern of MF-4SC composite membrane containing 6% Ag.

X-Ray data show that crystalline silver particles are formed during the synthesis (Figure 1). The average particle size assessed from X-ray data amounts to 20 nm. However, the formed copper is amorphous according to X-ray data.

Transmission electron microscopy shows that isolated metal nanoparticles with a bimodal size distribution are formed in the membrane matrix. The majority of particles with sizes of about 3–5 nm are produced within the polymer matrix [Figure 2(*a*)]. In addition, a small number of large particles (20–50 nm) are also found in these membranes. Their sizes are much larger than the pore size. So we assumed that they were formed on the membrane surface where no size limitations exist [Figure 2(b)].

In order to prove our assumption, the next experiment was carried out. The membrane surface was treated mechanically and chemically (by concentrated HNO_3) to remove the outer layer and transmission electron micrographs were again recorded. As shown in Figure 2(*c*),(*d*), the number of large particles decreases considerably in comparison with that before mechanical treatment. After chemical treatment of the surface, we can only observe particles with sizes of about 3–5 nm [Figure 2(*e*)]. This fact confirms our assumption that particles with sizes of about 20–50 nm are located on the membrane surface only. The surface layer was removed after a short acidic treatment. Due to diffusion limitations, the acid fails to reach the particles with sizes of about 3–5 nm located in the membrane matrix and to dissolve them within this short period of time. Note that after removal of

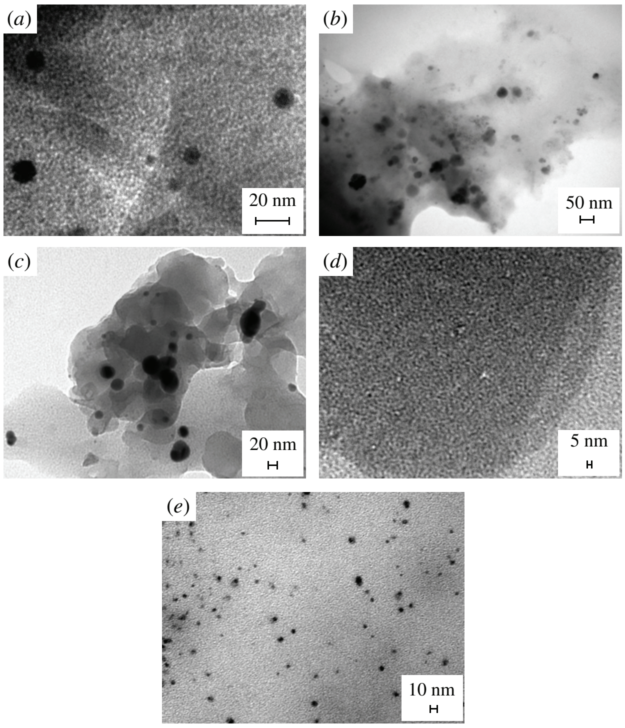

Figure 2 TEM images of (*a*), (*b*) MF-4SC composite membrane containing 6% Ag; (*c*), (*d*) MF-4SC composite membrane containing 6% Ag after mechanical surface treatment; (*e*) MF-4SC composite membrane containing 6% Ag after surface treatment by conc. HNO_3.

the upper modifying layer, the membranes lose the dark grey colour with metallic lustre and become slightly turbid.

It is important to note that the difference in the nanoparticle sizes determined from X-ray data and by transmission electron microscopy is very typical. We believe it to be due to a fast decrease in X-ray reflection intensity with a decrease in the particle size owing to dispersion of reflection with a decrease in the number of structure layers. The change in interlayer distances on nanoparticle surfaces due to 'relaxation effects' is also very important. So, the contribution of small nanoparticles to the resulting X-ray signal is negligible in comparison with that of larger particles located on the membrane surface. For this reason, we can find only a broad X-ray signal of very small intensity after chemical treatment of the surface of membrane modified by silver.

Proton conductivity data for membranes in contact with water are shown in Figures 3 and 4. Incorporation of metal nanoparticles (6% Ag and 3% Cu) results in a decrease in membrane conductivity because of partial blocking of membrane channels by the embedded metal and partial exchange of SO_3H group

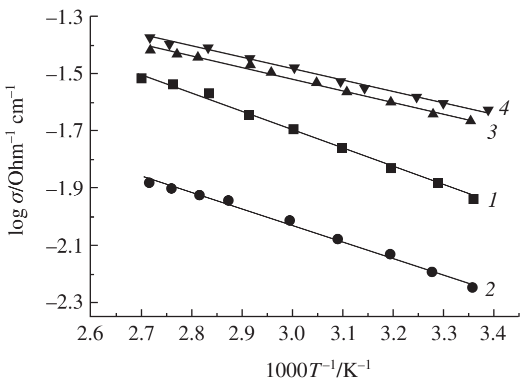

Figure 3 Arrhenius plots of proton conductivity for MF-4SC membranes with different Ag content: (*1*) pure, (*2*) 6% Ag, (*3*) 10% Ag and (*4*) 12% Ag.

Table 1 Sorption exchange capacity for the membranes obtained.

Membrane	SEC, mg-equiv./g
MF-4SC	0.66
MF-4SC (6% Ag)	0.28
MF-4SC (3% Cu)	0.31

Table 2 Activation energy of proton conductivity for some composite membranes.

Membrane	E_{act}/kJ mol^{-1}
MF-4SC	16.8
MF-4SC (6% Ag)	12.4
MF-4SC (3% Cu)	11.5

Table 3 Water uptake for the membranes obtained.

Membrane	*W* (%)
MF-4SC	24.5
MF-4SC (6% Ag)	12.3
MF-4SC (10% Ag)	17.0
MF-4SC (12% Ag)	18.9
MF-4SC (3% Cu)	7.8
MF-4SC (6% Cu)	9.1
MF-4SC (8% Cu)	18.6

Table 4 Diffusion permeability of 1 M NaCl solution for some composite membranes.

Membrane	P/cm^2 s^{-1}
MF-4SC	3.2×10^{-7}
MF-4SC (6% Ag)	3.1×10^{-7}
MF-4SC (10% Ag)	2.8×10^{-7}
MF-4SC (12% Ag)	2.1×10^{-7}
MF-4SC (3% Cu)	2.4×10^{-7}
MF-4SC (6% Cu)	2.2×10^{-7}
MF-4SC (8% Cu)	1.1×10^{-7}

protons for cations. This is confirmed by a decrease in the sorption exchange capacity (Table 1). An increase in the metal concentration leads to an increase in the membrane conductivity. The activation energy of composite membranes (Table 2) appears to be lower than that of the original MF-4SC. This fact can be explained by a partial charge transfer through metal particles. Meantime, the electron contribution remains low and amounts to 0.1–0.2% for membranes with silver and 0.08–0.15% for membranes with copper. The conductivity increase for composite membranes with an increase in metal content may also be attributed to a widening of membrane channels. Intercalation of metal nanoparticles widens both pores and channels connected by pores. Our assumption is indirectly confirmed by a growth of the water uptake with a growth of the metal content (Table 3). Membrane modification by a small number of metal particles leads to a decrease in water uptake due to hydrophobicity of the surface of metal nanoparticles and partial replacement of SO_3H protons for cations resulting in a decrease in the number of hydrated protons. Yet another reason is that metal nanoparticles exclude a certain fraction of the pore volume from the transport processes. However, an increase in the metal content results in rising the water uptake due to the widening of pores and channels.

Membrane modification results in a decrease in its diffusion permeability (Table 4). The concentration of cations (counterions) in cation-exchange membranes (such as MF-4SC) is higher than that of anions. Thus, the diffusion coefficient of cations is by an order of magnitude higher than that of anions.[6] Therefore, the NaCl diffusion rate is controlled by the slower diffusion of anions and the lowering of the diffusion permeability is caused by partial blocking of membrane channels by metal particles.

It is necessary to mention that, according to conductivity data, the modification leads to an increase in the proton con-

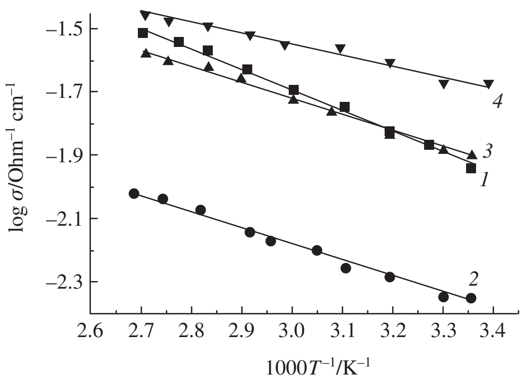

Figure 4 Arrhenius plots of proton conductivity for MF-4SC membranes with different Cu content: (*a*) pure; (*2*) 3% Cu; (*3*) 6% Cu and (*4*) 8% Cu.

ductivity and a decrease in the anion diffusion after membrane treatment (10% Ag, 6% Cu). This suggests that the transport number of anions diminishes after the modification. So, we can conclude that composite membranes with metal nanoparticles become more selective for cation migration.

In conclusion, it has been shown that the MF-4SC membrane is a suitable matrix for the synthesis of metal nanoparticles. The nanoparticles formed are characterized by a bimodal distribution. Metal nanoparticles with sizes of about 3–5 nm are formed within the polymer matrix without agglomeration. A small number of large particles (20–50 nm) are formed on the membrane surface. The modification makes the membranes more selective.

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