

# Effects of mixed conductivity of nanocomposite membranes MF-4SC/PANI

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**Abstract** Changes in the conducting and hydrophilic properties of composites MF-4SC/polyaniline (PANI) under conditions of prolonged synthesis have been studied. A maximum of PANi content of about 0.20 by weight, which can be incorporated into the matrix of MF-4SC under these conditions of synthesis, is determined. Percolation behavior of electrical conductivity of the composites after drying was observed. The conductivity of PANi salt inside MF-4SC was estimated within the frames of the percolation model. Using the fibrous cluster model of the membrane and the conductivity data on individual PANi, theoretical assessment of the electrical conductivity of nanocomposite MF-4SC/PANI has been performed. Reasons for a significant reduction in the conductivity of PANi during its integration into the structure of the initial matrix were discussed. A scale of membrane conductivity, reflecting changes in the electrical conductivity of composites at various stages of synthesis, was drawn.

**Keywords** Perfluorinated sulfocationic membrane · PANi · Composite · Electrical conductivity · Theory of percolation · Fibrous cluster model

## Introduction

Modification of membranes is currently one of the most quickly developing areas within the synthesis of composite nanomaterials. In order to obtain samples with improved structural organization and a wider range of functional properties, intensive search for approaches to the creation of composite membranes is performed. A number of publications appeared during the last years, which deal with modification of membranes by incorporating polyaniline (PANI) into them. The advantages of PANi application to the modification of base membranes are simplicity of synthesis in the matrix of sulfocationite polymers, the capability to transfer current due to delocalized electrons, presence of electrochromic effects, and stabilization of water at the internal phase boundaries. According to [1], there were approximately 5,000 papers published in 2010 on conducting polymers; the total number of scientific publications on this topic in the ScienceDirect database is 49,615, out of which 48% is dedicated to PANi.

In a number of papers [2–6], methods of synthesis of bulk- and surface-modified composites based on perfluorinated sulfocationite polymers MF-4SC and PANi have been developed and morphological and transport properties of such composites have been studied. It has been established that nanocomposites MF-4SC/PANI can be used as polymer electrolytes in fuel cells to improve their performance [7, 8]. Application of these composites leads to an increase in the degree of concentration of salt solutions by electro-dialysis [9] compared to the unmodified MF-4SC membrane. Also, they may act as carriers of metal catalysts such as platinum [10].

The variety of chemical forms of PANi leaves open the problem of measuring the dependence of conductive properties of such composites upon the synthesis conditions

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and distribution character of PANi in the base matrix. It is difficult to determine the conductive properties of such materials since the composite formation is referred to as a “self-assembling” process. PANi aromatic chains undergo dynamic changes of oxidation state and morphological transitions from fibrous to grainy nanoparticles during the synthesis. The effect of these phenomena on the conductive properties of material with variable water content and water energy state is still unclear. So, the aim of this paper is to study the dependence of conductivity and hydrophilic properties of composite membranes under prolonged synthesis conditions to reveal the contributions of different conductive mechanisms to the total conductivity of the material.

## Experimental

### Objects and methods of investigation

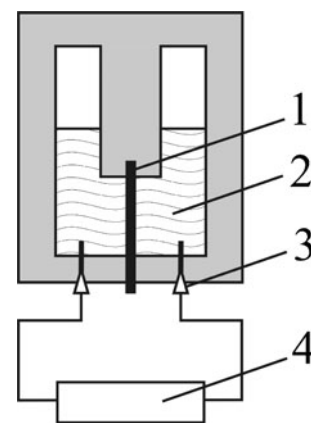
Perfluorinated sulfocationite membranes MF-4SC (Plastpolymer Plc., St. Petersburg, Russia) were used as a basic membrane for the matrix synthesis of PANi. The physicochemical characteristics of the protonated forms of these membranes (thickness in the swollen and dry state ( $l_{sw}$ ,  $l_{dry}$ , m), ion exchange capacity in the swollen and dry state ( $Q_{sw}$ , mol  $\text{SO}_3^-/\text{g}_{sw}$ ;  $Q_{dry}$ , mol  $\text{SO}_3^-/\text{g}_{dry}$ ), weight fraction of water in the swollen state ( $W$ , g  $\text{H}_2\text{O}/\text{g}_{sw}$ ), and water capacity ( $n$ , mol  $\text{H}_2\text{O}/\text{mol SO}_3^-$ ) are shown in Table 1.

Experimental techniques described earlier [3, 11] were used for determining thickness and the hydrophilic properties of the membranes (the uncertainty of these techniques being below 5%).

The conductivity ( $\kappa$ ) of the membranes was determined from the value of membrane resistance measured as active component of the membrane impedance at 100 kHz AC. The sample was placed between chambers of a two-compartment cell filled with mercury (Fig. 1). The membrane surface being in contact with mercury was  $0.785 \text{ cm}^2$ . This technique provides ideal contact between the electrodes and a membrane sample [3, 11].

The morphology of the membranes was characterized using an atomic force microscope (AFM) Ntegra Spectra (by NT-MDT Co., Russia). Images were recorded in the tapping mode applying high-resolution non-contact silicon

**Fig. 1** Schematic of the cell for conductivity measurements: (1) membrane, (2) mercury, (3) measuring electrodes, (4) impedance meter



gold-coated tips. Before the measurements, the membranes were conditioned in a 0.5 M  $\text{H}_2\text{SO}_4$  solution with subsequent rinsing in distilled water and drying for at least 24 h at a temperature of 110 °C.

The following reagents were used for the experiment: aniline (distilled twice),  $\text{H}_2\text{SO}_4$  (ultra pure), HCl (reagent grade), KCl (reagent grade),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (reagent grade), KOH (reagent grade).

### Matrix synthesis of polyaniline

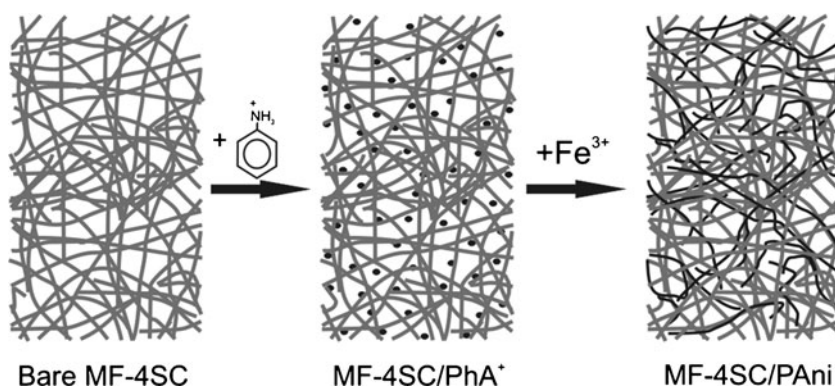
The matrix synthesis of PANi in a MF-4SC membrane was carried out under static conditions (the synthesis scheme is shown in Fig. 2). For this purpose, samples of perfluorinated membranes of the same area in the  $\text{H}^+$  form were kept for 24 h in a mixture of 0.01 M aniline and 0.5 M  $\text{H}_2\text{SO}_4$  (one sample of MF-4SC was left as a reference). It is known that in acidic environment aniline exists in the protonated form of phenylammonium ions ( $\text{PhA}^+$ ), which are the counterions for sulfocationite membrane MF-4SC. Thus, the monomer easily enters the bulk of the membrane and accumulates by ion exchange with the protons of sulfonic groups and by non-exchange sorption in the vicinity of the ether groups of lateral chains of the fluoroethylene matrix [12]. This process is accompanied by desorption of water from the bulk of the membrane, which leads to a reduction of its water capacity [13].

The samples were placed then in a mixture of polymerizing solutions 0.01 M  $\text{FeCl}_3$ , 0.01 M aniline, and 0.5 M  $\text{H}_2\text{SO}_4$ , where they were kept for different time intervals: 5

**Table 1** Physicochemical characteristics of initial MF-4SC samples

$l_{sw} \times 10^4$ , m	$l_{dry} \times 10^4$ , m	$Q_{sw} \times 10^4$ , mol $\text{SO}_3^-/\text{g}_{sw}$	$Q_{dry} \times 10^4$ , mol $\text{SO}_3^-/\text{g}_{dry}$	$W$ , g $\text{H}_2\text{O}/\text{g}_{sw}$	$n$ , mol $\text{H}_2\text{O}/\text{mol SO}_3^-$
1.59	1.54	6.9	9.3	0.26	20.6
0.75	0.65	7.3	9.3	0.21	16.9

**Fig. 2** Scheme of synthesis of PANi in the matrix of MF-4SC membrane



and 24 h and 10, 20, or 30 days. Every third day, the solution above the membrane was replaced by a fresh one. Under the action of an oxidant ( $\text{FeCl}_3$ ), the colorless MF-4SC film being saturated by phenylammonium ions becomes emerald green, which is characteristic of the emeraldine salt. Samples prepared by this method are bulk-modified composites [4].

In order to determine the physicochemical properties of the samples obtained, the samples after synthesis were washed with water; the electrical resistance of water being above the membrane was controlled and the samples were equilibrated with working solutions. In order to measure the electrical conductivity of composites in the dry state, they were dried in vacuum at a temperature of 110 °C.

**Results and discussion**

Hydrate characteristics of composites

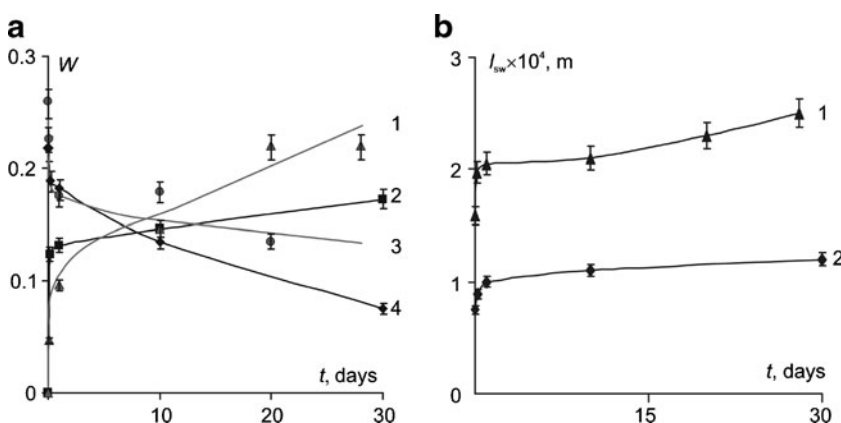
Figure 3a shows the dependence of water content ( $W$ ) and of PANi content ( $W_{\text{PAni}}$ ) in the composites upon the time of synthesis. The PANi content in the samples was determined gravimetrically. To this end, samples with PANi and MF-4SC reference were dried and weighed. Sample weighing

was carried out in a weighing bottle to avoid moisture uptake; the accuracy of weighing was up to four decimal digits. The weight fraction of PANi,  $W_{\text{PAni}}$ , was calculated by the following equation:

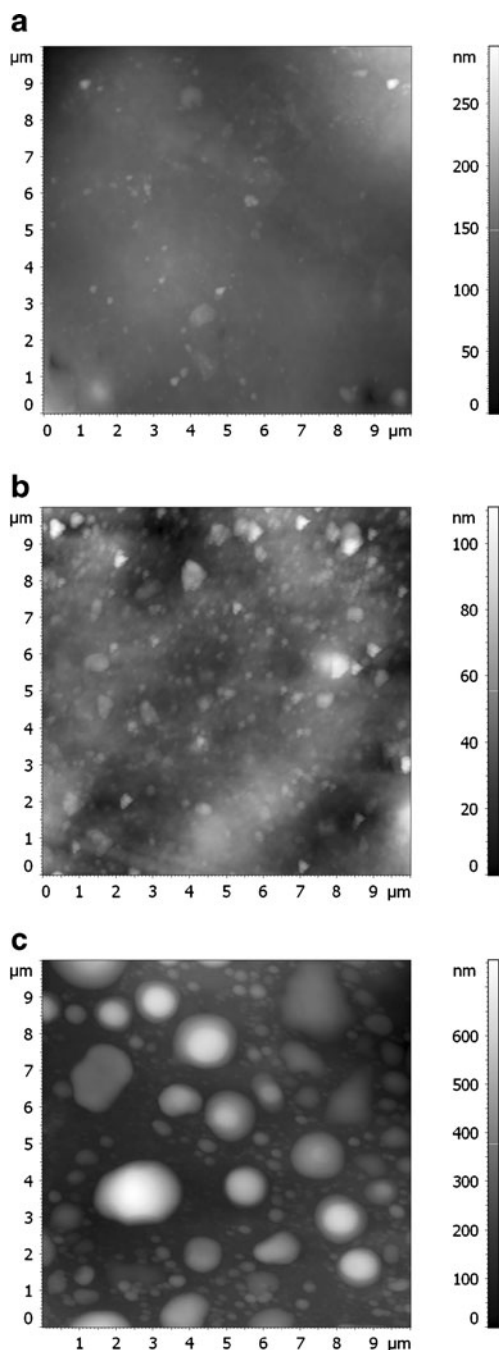
$$W_{\text{PAni}} = \frac{m_{\text{MF-4SC/PAni}} - m_{\text{MF-4SC}}}{m_{\text{MF-4SC/PAni}}} \quad (1)$$

where  $m_{\text{MF-4SC/PAni}}$  is weight of the composite and  $m_{\text{MF-4SC}}$  is weight of the initial reference membrane. It can be seen from Fig. 3a that increasing the synthesis time leads to an increase in the weight fraction of PANi in the composite membrane; the maximum weight fraction is 0.172 for the “thin” ( $l=7.5 \times 10^{-5}$  m) and 0.22 for the “thick” ( $l=1.5 \times 10^{-4}$  m) membranes. These values correspond to a similar effect of hydrophilicity decrease of the composite membranes (50–60% on average). The water content of the “thin” membrane after 30 days of the synthesis of PANi is 0.076 g  $\text{H}_2\text{O}/\text{g}_{\text{sw}}$ , while that of the “thick” one is 0.135 g  $\text{H}_2\text{O}/\text{g}_{\text{sw}}$ . The data presented in Fig. 3a show that the introduction of PANi in the initial membrane changes its hydrophilic–hydrophobic balance due to the displacement of water from the water cluster zones. In this case, the cluster areas of the membrane are expanded by the intercalated polymer chains, leading to an increase in the thickness of the composite membranes by approximately 60% (Fig. 3b). Studies of surface morphology of the

**Fig. 3** Influence of PANi synthesis time on: **a** PANi content ( $W_{\text{PAni}}$ ) and water content ( $W$ ) of the composites; **b** thickness of composites; 1, 3: MF-4SC thickness of  $1.59 \times 10^{-4}$  m; 2, 4: MF-4SC thickness of  $7.5 \times 10^{-5}$  m



composites obtained under similar synthesis conditions, by the methods of AFM (Fig. 4a–c) and standard porosimetry [4], showed that PANi is also localized in the surface layers of the membrane. This leads to “fouling” of the composite film with a porous PANi layer (the pore diameter is up to approximately 10  $\mu\text{m}$ ) during the 30 days of synthesis. The surface morphology is defined by PANi microdomains with a diameter from 300 nm up to 1.4  $\mu\text{m}$  and a height of up to 300 nm.



**Fig. 4** AFM images of MF-4SC (a), PANi/MF-4SC after 5 h (b), and 30 days (c) of synthesis. Scan size,  $10 \times 10 \mu\text{m}$

### Conductivity of composites

The results of measurements of composite membrane conductivity (thickness  $7.5 \times 10^{-5} \text{ m}$ ) in a 0.1 M HCl solution as a function of the synthesis time are shown in Fig. 5a. It can be seen that the synthesis of PANi for 24 h leads to an increase in the conductivity of the samples by 5–6%, which corresponds to a weight fraction of PANi of approximately 0.13. In the initial MF-4SC membrane, the proton is transferred along a chain of proton hydrate clusters. The appearance of emeraldine inclusions leads to an increase in the electrical conductivity due to the contribution of current transfer by delocalized electrons along a chain of polyconjugated bonds (polaron conductance) [6] and by proton conductivity of polyemeraldine [10, 14]. Further increase of the synthesis time leads to a decrease in electrical conductivity of the composite. We suggest that this effect is caused by two reasons: the supplanting of protons, which neutralize sulfo-groups of basic matrix, with positive-charged nitrogen atoms of PANi (Fig. 5a, inset) and water content reduction because of placement of PANi chains in structural cavities of the membrane.

The authors of [15] processed experimental data on the ion exchange capacity and water capacity of perfluorinated membranes within the frameworks of percolation theory and determined the critical volume fraction of conducting phase,  $\varphi_{\text{cr}}=0.15$ , which corresponds to the transition from non-conducting to conducting state. The volume fraction of conducting phase  $\varphi$  in the membrane can be calculated by the following equation:

$$\varphi = QM + W \quad (2)$$

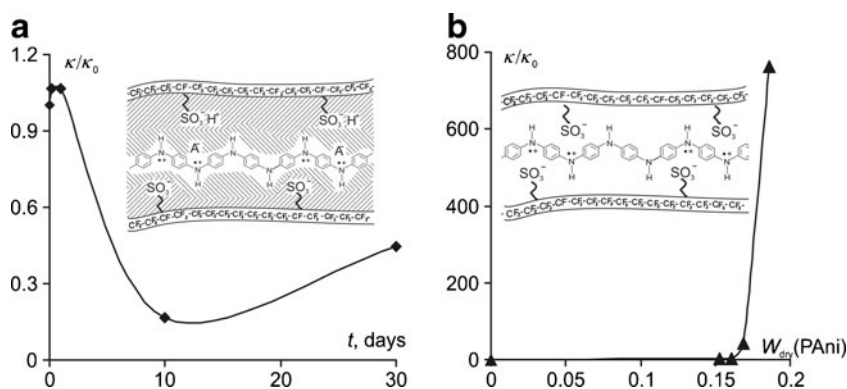
where  $M$  is the molar weight of ionic groups (g/mol),  $Q$  is ion exchange capacity (mol/g<sub>sw</sub>), and  $W$  is water content of the material (g H<sub>2</sub>O/g<sub>sw</sub>).

Using the approach proposed in [15], we can calculate the critical water content of the membrane ( $W_{\text{cr}}$ , g H<sub>2</sub>O/g<sub>sw</sub>) at which it becomes non-conductive. Applying the previously obtained value of  $\varphi_{\text{cr}}=0.15$  and knowing the ion exchange capacity of the sample,  $Q_{\text{sw}}=7.3 \times 10^{-4} \text{ mol SO}_3^-/\text{g}_{\text{sw}}$ , we get  $W_{\text{cr}}=0.095 \text{ g H}_2\text{O}/\text{g}_{\text{sw}}$ . It can be seen that for the “thin” membrane, the synthesis of PANi for 30 days leads to a decrease in water capacity below the threshold value ( $W=0.076 \text{ g H}_2\text{O}/\text{g}_{\text{sw}}$ ), while the membrane retains quite a high value of conductivity ( $\kappa=0.69 \text{ S/m}$ ). We can assume that the electrical conductivity of such samples is provided by residual HCl solution and conductivity of PANi.

Figure 5b shows the relative conductivity of composite membranes (thickness  $7.5 \times 10^{-5} \text{ m}$ ), washed with water and vacuum-dried, as a function of PANi content. It can be seen that, for the given series of dry samples, a stepwise increase of electrical conductivity is observed at 10 days of



**Fig. 5** Dependencies of relative conductivity  $\kappa/\kappa_0$  of swollen composites MF-4SC/PAni in a 0.1-M HCl on the synthesis time (a) and those of  $\kappa/\kappa_0$  of dried MF-4SC/PAni after washing with water on the content of PAni (b); insets show the structures of interpolymer complex MF-4SC/PAni in the swollen and dry states, respectively



synthesis, which corresponds to a PAni content of 0.17 (calculated with reference to the dried sample). Compared to the initial membrane, the conductivity of composite obtained by 30-days synthesis increases by three orders of magnitude and equals  $0.25 \pm 0.03$  S/m. This is caused by the accumulation of PAni in the MF-4SC matrix, of which conductivity becomes more significant. Also, the electron conductivity of PAni in dried samples is not screened by the ion conductivity of the initial matrix and that of the electrolyte solution.

Parameters of the percolation model for nanocomposites MF-4SC/PAni

It is known that dispersions of PAni in an inert medium of glycerol [16] as well as in poorly conductive epoxy resin [17] form conductive aggregates. Such systems could be described in terms of the percolation theory. In the composites that we studied in the dry state, there is dispersion of PAni particles of complex geometric shape in an inert environment. The particles are located mainly in cavities and channels of the membrane matrix. To estimate the electrical conductivity of PAni clusters located in the dried composites, data on the conductivity of samples were processed within the frameworks of percolation theory [18], the basic equation of which is as follows:

$$\log \kappa = \log \kappa^0 + \tau \log(\varphi - \varphi_{cr}) \tag{3}$$

where  $\kappa$  is the measured value of conductivity,  $\kappa^0$  is a factor, the value of which is of the same order of magnitude as that of the conductivity of conductive particles,  $\varphi$  and  $\varphi_{cr}$  are the volume fraction of conductive particles and the critical value of this parameter, where an abrupt change in conductivity is observed, and  $\tau$  is the critical index of conductivity, which characterizes the distribution of conductive particles in the matrix and depends upon their shape [19].

PAni is the only conductive phase of the composite after vacuum drying. Thus, for the calculation of parameters of the percolation model, it is necessary to determine the

volume fraction of PAni, which obviously can be found using the following equation:

$$\varphi = \frac{V'}{V} = \frac{V'}{V' + V''} \tag{4}$$

where  $V$ ,  $V''$ , and  $V'$  are the total volume, volume of the perfluorinated matrix, and volume of PAni, respectively. As

$$V' = \frac{P'}{d'} = \frac{W_{PAni}P}{d'} \tag{5}$$

$$V'' = \frac{P''}{d''} = \frac{(1 - W_{PAni})P}{d''} \tag{6}$$

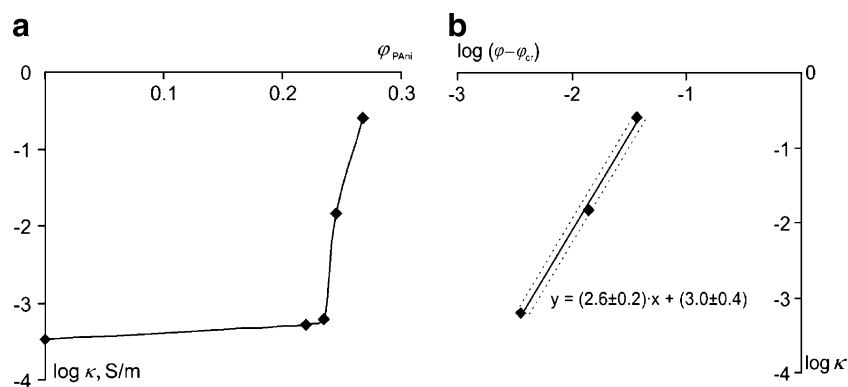
where  $P$ ,  $P'$ , and  $P''$  are the weight of ion exchange material, of PAni, and the conducting phase of the perfluorinated matrix, respectively;  $d'$ ,  $d''$ , and  $d$  are the density of the conductive phase, of the perfluorinated membrane in the dry state, and of the ion exchange material, respectively;  $W_{PAni}$  is the weight fraction of PAni in the composite; after simple transformations, the following expression for the volume fraction of PAni in the dry composite is obtained:

$$\varphi = \frac{W_{PAni}d''}{W_{PAni}d'' + (1 - W_{PAni})d'} \tag{7}$$

We assumed that the density of PAni doped with hydrochloric and perfluorinated sulfuric acids in the MF-4SC matrix is the same as the density of PAni hydrochloride ( $d=1.33 \text{ gcm}^{-3}$ ) [20]. The density of dry MF-4SC is  $d=2.13 \text{ gcm}^{-3}$  [21].

Figure 6a shows the dependence of conductivity of the composite,  $\kappa$ , upon the volume fraction of PAni,  $\varphi$ , i.e., upon the volume fraction of conductive particles. The value of  $\varphi_{cr}$  was determined from the abovementioned dependence by the tangent method. After that, the dependence was plotted in coordinates  $\log(\kappa) - \log(\varphi - \varphi_{cr})$  (Fig. 6b). Linear approximation of this dependence allowed us to determine parameters  $\kappa^0$  and  $\tau$  from the point of intersection with the vertical axis and the

**Fig. 6** Dependencies of  $\log \kappa$  on  $\varphi$  (a) and  $\log \kappa$  on  $\log (\varphi - \varphi_c)$  (b) for composites MF-4SC/PAni



slope. It is important to note that the values of parameters of Eq. 3 calculated by us are close to theoretical ones ( $\varphi_{cr}=0.15\pm 0.03$ ,  $\tau=1.6\pm 0.1$ ), although they are higher:  $\varphi_{cr}=0.23\pm 0.01$ ,  $\tau=2.6\pm 0.2$ .

Let us denote factors that may cause the deviation of experimental percolation parameters from theoretical ones for the composites investigated. First of all, according to SEM and AFM, it is known [4] that filamentary and granular particle geometry is characteristic of PAni inside the membrane; intermediate particle geometries are also present. Apart from that, the calculation of the volume fraction of PAni was carried out with the assumption that the density of PAni incorporated into the MF-4SC is the same as the density of PAni hydrochloride taken from [20].

Thus, the higher values of parameters may be due to the complex geometry of particles of the conducting phase in the composites studied. For particles of complex geometry, higher values of percolation parameters were also obtained, for example, in [11, 22] where the increase in the values was also attributed to anisotropy of particle arrangement in the membrane. Let us also note that, in [16], the volume fraction of PAni in its dispersion in glycerol, at which the percolation transition was observed, was found to be 20–35%.

The calculation of  $\kappa^0$  showed that it was  $(10\pm 1)\times 10^2$  S/m, which, in principle, corresponds to the conductivity of the emeraldine salt dispersed in a dry non-conductive matrix MF-4SC. For example, the average value of the conductivity of PAni hydrochloride, according to [19], is  $(4.4\pm 1.7)\times 10^2$  S/m, which is in agreement with the data of [23] as well. It should be noted that, in literature, a rather large scatter of the conductivity of pure PAni is observed, which depends both upon the synthesis conditions and the method of conductivity measurement. In this regard, a calibration of the electrical conductivity of pressed PAni powder obtained in different European laboratories was performed [20] (grant IUPAC). The value given above is obtained as an average for

59 samples synthesized under the same experimental conditions. The respective value of conductivity of deprotonated PAni is  $1.4\times 10^{-6}$  S/m. Let us also note that, according to [24], the electrical conductivity of PAni nanotubes may be up to  $5\times 10^3$  S/m.

The value of  $\kappa^0$  calculated by us is of the same order of magnitude as the above experimental data but is slightly higher. The discrepancy between the data may be due to measurement errors as well.

If PAni is distributed in the matrix MF-4SC and is in the form of emeraldine salt, the total conductivity of the composite may be as low as  $\kappa=0.25\pm 0.03$  S/m. This value is in agreement with the one obtained by us earlier for bulk-modified MF-4SC/PAni composite synthesized by sequential diffusion: the conductivity of the composite in the dry state was found to be  $\kappa=0.15\pm 0.02$  S/m [25].

The conductivity of PAni is an important characteristic, but experiments to determine the conductivity of PAni in a nanocomposite are very complicated. At the same time, there are a number of papers on the electrical conductivity of nanocomposite membranes based on MF-4SC (or Nafion) and PAni [2, 8, 26]. However, the data on the conductivity of PAni contained in those papers are practically useless since the conductivity of PAni strongly depends upon the conditions of its matrix synthesis and the distribution of PAni in the matrix.

Estimation of the total conductivity of nanocomposites using parameters of the fibrous cluster model

In [3], a fibrous cluster model of the conductivity of composite membranes was developed. Within the model composite MF-4SC/PAni consists of four structural elements, which are grouped in two pseudophases: fibrous inclusions of PAni are merged with cluster zones and non-conductive crystallites of the perfluorinated matrix into a pseudophase I with a mixed (electron ion) type of

conductance. Inclusions of internal electrically neutral solution in structural cavities of the composite membrane form pseudophase II with bipolar conductivity. A set of transport and structural parameters for a series of membranes was also calculated: initial MF-4SC, MF-4SC/PAni after 5 h and 30 days of synthesis with FeCl<sub>3</sub> as initiator of polymerization. A significant change in model parameters was observed for the sample, of which synthesis lasted 30 days. For example, parameter  $f_2$  corresponding to the volume fraction of internal solution in the pores increased twofold compared to the initial membrane ( $f_2=0.16$ ); the value of parameter  $\alpha$  reflecting the reciprocal orientation of structural fragments changed from 0.3 (for the initial MF-4SC) to 0.1. Thus, the introduction of PAni chains in the initial matrix leads to a more random distribution of the conducting phases.

We used a micro-heterogeneous model to calculate the total conductivity of the composite membrane,  $\kappa$ , taking into account the conductive properties of its structural fragments [11, 27], which is given by:

$$\kappa^\alpha = f_1 \kappa_1^\alpha + f_2 \kappa_2^\alpha, \tag{8}$$

where  $f_1$  is the volume fraction of polymer framework with sulfonic groups at the ends of the lateral segments (pseudophase I),  $f_2 = 1 - f_1$  is the volume fraction of conductive pseudophase II within the matrix, and  $\kappa_1, \kappa_2$  are the conductivity of pseudophase I and pseudophase II, respectively (S/m). We assumed that during 30 days of synthesis, a limiting PAni content is achieved in the membrane sample under consideration and that the entire free solution is replaced by the PAni chains. This follows from the antibatic character of desorption curves of the solution and the PAni content (Fig. 3a). Thus, pseudophase II consists only of PAni fibrils, while pseudophase I contains cluster zones and fluoroethylene chains of the perfluorinated matrix. It can be assumed that the conductivity of PAni ( $\kappa_2$ ) is between 440 and 1,000 S/m, according to the experimental data of [19] and estimation of  $\kappa^0$  made above. The value of the electrical conductivity of pseudophase I,  $\kappa_1$ , was taken from the data [3] on the conductivity of MF-4SC/PAni (30 days of synthesis) membrane in a H<sub>2</sub>SO<sub>4</sub> solution at the iso-conductivity point ( $\kappa_1=1.14$  S/m). The calculation of  $\kappa$  by Eq. 8 shows that the resulting

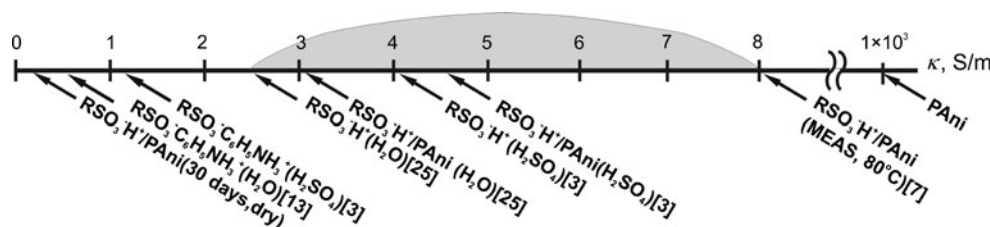
value of conductivity of the nanocomposite is between 3.7 S/m (if  $\kappa_2=440$  S/m) and 4.8 S/m (if  $\kappa_2=10^3$  S/m). These data are in good agreement with results of measurements of the electrical conductivity of nanocomposites based on Nafion or MF-4SC and PAni [2, 8, 27].

Evolution of membrane conductivity at different stages of MF-4SC/PAni composite formation

Figure 7 shows the scale of electrical conductivity of the initial MF-4SC membrane, of composites MF-4SC/PAni, and of PAni. Analysis of the given data shows that the conductivity of the composites is between the PAni hydrochloride  $(4.4 \pm 1.7) \times 10^2$  S/m (electron conductivity) and a value of 3–5 S/m (average conductivity of the proton form of MF-4SC in an acid solution). Under these conditions, the composite membrane has the sum of the proton and electron conductivities, which, however, is two orders of magnitude as low as the electron conductivity of PAni. Thus, the PAni chains lose their capability to transfer delocalized electrons within the “labyrinth” of the basic matrix and the proton conductivity of the basic matrix becomes dominant in acid solutions. An additional weakening of the delocalized electron transfer of PAni may be associated with the electrostatic repulsion of PAni chains by the negatively charged sulfo groups. This phenomenon presumably refers to the properties of polymer composite systems. It has been shown in [17], which studied the electrical conductivity of nanocomposites based on PAni introduced in a liquid epoxy resin matrix by dispersive polymerization, that the electrical conductivity of the system decreases by four orders of magnitude compared to individual PAni ( $10.9 \times 10^2$  S/m) but increased by two orders of magnitude compared to the conductivity of the base matrix ( $10^{-2}$  S/m).

Transfer of the membrane from the proton form to the mixed form of H<sup>+</sup>/PhA<sup>+</sup> [3, 13] during the synthesis of composites MF-4SC/PAni leads to a decrease in ion conductivity by a factor of 4–5. The saturation degree of membrane by PhA<sup>+</sup> ions does not exceed 17–22%. We assume that polymerization of PhA<sup>+</sup> ions under the action of initiators proceeds almost completely to form rigid aromatic chains of PAni, which is accompanied by an

Fig. 7 The scale of conducting properties of polymer materials with ion (MF-4SC), electron (PAni), and mixed (MF-4SC/PAni) conductivity



increase in electrical conductivity of the membrane. Within the range of 10-day synthesis, the chemical state of PANi corresponds to its emeraldine salt, which provides higher conductivity of the composite [3]. The effect of conductivity increase depends on the acidity of the medium, exposure time, and concentration of the initiator. The conductivity of the composite both in an acid solution and washed state is higher than that of the initial MF-4SC membrane under similar conditions by 20–30%. Increasing the synthesis time above 24 h decreases the electrical conductivity of the membrane. The block structure of PANi, the so-called redox heterogeneity of aromatic chains, and partial deprotonation due to a long synthesis time decrease the effect of polaron conductivity. The latter can be observed in a dry state or during the formation of emeraldine under the action of oxidant on the transition of the membrane from mixed form  $H^+/PhA^+$  to composite MF-4SC/PANi [3]. It should be noted that the values of  $\kappa$  calculated within the frames of the fibrous cluster model are in agreement with experimental data on the conductivity of composites highlighted in the scale (Fig. 7).

## Conclusions

A series of composite membranes MF-4SC/PANi with the synthesis time varying from 3 h to 30 days has been obtained. A maximum PANi quantity being about 0.20 (by weight), which can be incorporated into the MF-4SC matrix under the actual synthesis conditions, has been determined. It was found that the appearance of intercalated polymer chains in the bulk of the basic matrix leads to an increase in membrane thickness by 60% and reduces the water capacity of the membrane by 50–60%. During the drying process of the composite, a transition from mixed-ion electron conductor to pure electron conductor is observed. A typical effect of electrical percolation was observed for the composites after drying: a slight change in the electrical conductivity at volume fractions of PANi below 0.23 and its rapid increase in the range of volume fractions 0.23–0.27. Data analysis within the frames of the percolation transition allowed us to determine the parameters of percolation transition and to estimate the electrical conductivity of PANi salt inside the MF-4SC being  $\kappa^0 = 1 \times 10^3$  S/m. Evaluation of the electrical conductivity of nanocomposite MF-4SC/PANi has been performed using the parameters of the fibrous cluster model of membrane and data on the electrical conductivity of “pure” PANi. The electrical conductivity of composites in equilibrium acid solutions is two orders of magnitude as low as the conductivity of individual PANi, regardless of the method of synthesis. A scale of membrane conductivity, reflecting evolution of the electrical conductivity of composites at various stages of synthesis, was drawn.

## Symbols

Subscript dry	characteristic of membrane in dry state
Subscript sw	characteristic of membrane in swollen state
$l$	thickness of membrane (m)
$Q$	ion exchange capacity of membrane (mol $SO_3^-/g_{sw}$ )
$W$	weight fraction of water in membrane (g $H_2O/g_{sw}$ )
$n$	water capacity of membrane (mol $H_2O/mol SO_3^-$ )
$W_{PANi}$	weight fraction of polyaniline in membrane (g PANi/ $g_{sw}$ )
$m_{MF-4SC}$	weight of MF-4SC membrane (g)
$m_{MF-4SC/PANi}$	weight of composite MF-4SC/PANi (g)
$\varphi$	volume fraction of conductive particles
$\varphi_{cr}$	critical volume fraction of conductive particles
$M$	molar weight of ionic groups (g/mol)
$W_{cr}$	critical water content of membrane (g $H_2O/g_{sw}$ )
$\kappa$	specific AC conductivity of membrane (S/m)
$\kappa_0$	specific AC conductivity of unmodified membrane (S/m)
$\kappa^0$	factor of the same order of magnitude as that of the conductivity of conductive particles
$\tau$	index characterizing the distribution and shape of conductive particles in basic matrix
$V$	total volume of material ( $m^3$ )
$V'$	volume of polyaniline ( $m^3$ )
$V''$	volume of dry perfluorinated matrix ( $m^3$ )
$P$	total weight of material (g)
$P'$	weight of polyaniline (g)
$P''$	weight of dry perfluorinated matrix (g)
$d$	density of material in dry state ( $g/cm^3$ )
$D'$	density of polyaniline ( $g/cm^3$ )
$d''$	density of dry perfluorinated matrix ( $g/cm^3$ )
$f_1$	volume fraction of pseudophase I
$f_2$	volume fraction of pseudophase II
$\alpha$	parameter characterizing the space orientation of pseudophases in membrane
$\kappa_1$	AC conductivity of pseudophase I (S/m)
$\kappa_2$	AC conductivity of pseudophase II (S/m)

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## References

1. Inzelt G (2011) Rise and rise of conducting polymers. *J Solid State Electrochem* 15:1711–1718
2. Tan S, Belanger D (2005) *J Phys Chem B* 109:23480–23490
3. Berezina NP, Kubaisy AA-R, Timofeev SV, Karpenko LV (2007) *J Solid State Electrochem* 11:378–389
4. Berezina NP, Kononenko NA, Sytcheva AA-R, Loza NV, Shkirskaya SA, Hegman N, Pungor A (2009) *Electrochim Acta* 54:2342–2352
5. Pud A, Ogurtsov N, Korzhenko A, Shapoval G (2003) *Prog Polym Sci* 28:1701–1753
6. Bhadra S, Khastgir D, Singha NK, Lee JH (2009) *Prog Polym Sci* 34:783–810
7. Compan V, Molla S, Sytcheva AA-R, Berezina NP, Suarez K, Solorza O, Riande E (2009) *ECS Trans* 25:645–658
8. Peighambaroust SJ, Rowshanzamir S, Amjadi M (2010) *Int J Hydrogen Energy* 35:9349–9384
9. Protasov KV, Shkirskaya SA, Berezina NP, Zabolotskii VI (2010) *Russ J Electrochem* 46:1131–1140
10. Sapurina IYU, Kompan ME, Malyshkin VV, Rosanov VV, Stejskal J (2009) *Russ J Electrochem* 45:697–706
11. Berezina NP, Kononenko NA, Dyomina OA, Gnusin NP (2008) *Adv Colloid Interf Sci* 139:3–28
12. Ogumi Z, Toyama K, Takehara Z (1992) *J Membr Sci* 65:205–212
13. Sycheva AA-R, Falina IV, Berezina NP (2009) *Russ J Electrochem* 45:108–115
14. Nekrasov AA, Ivanov VF, Vannikov AV (2001) *Electrochim Acta* 46:3301–3307
15. Berezina NP, Karpenko LV (2000) *Colloid J* 62:749–757
16. Aoki K, Kawaguchi F, Nishiumi T, Chen J (2008) *Electrochim Acta* 53:3798–3802
17. Jang J, Bae J, Lee K (2005) *Polymer* 46:3677–3684
18. Kirkpatrick S (1971) *Phys Rev Lett* 27:1722–1725
19. McLachlan DS, Blaszkiewicz M, Newnham RE (1990) *J Am Ceram Soc* 73:2187–2203
20. Stejskal J (2002) *Pure Appl Chem* 74:857–867
21. Berezina NP, Chernyaeva MA, Kononenko NA, Dolgoplov SV (2011) *Membr Membr Technol* 1:37–45, in Russian
22. Scher H, Zallen R (1970) *J Chem Phys* 53:3759–3761
23. Hsu C-H (1991) *Synth Met* 41–43:671–674
24. Jackowska K, Bieguński AT, Tagowska M (2008) *J Solid State Electrochem* 12:437–443
25. Falina IV, Berezina NP (2010) *Polymer Sci B* 52:244–251
26. Huang QM, Zhanga QL, Huang HL, Li WS, Huang YJ, Luoc JL (2008) *J Power Sources* 184:338–343
27. Gnusin NP, Berezina NP, Kononenko NA, Dyomina OA (2004) *J Membr Sci* 243:301–310