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New generation of nanocomposite materials based on perfluorinated membranes and polyaniline: Intercalation phenomena, morphology and transport properties

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ABSTRACT

This work summarizes results on the synthesis, morphology and transport properties of the new grade of nanocomposite materials based on polyaniline and sulphocationic perfluorinated membranes MF-4SC/Russia.The five types of the intercalation phenomena during the synthesis process of nanocomposite membranes are revealed and discussed. The transport properties and morphology peculiarities are investigated in dependence on the polyaniline distribution in the interior or on the surface of the basic membrane. The materials obtained are perspective for the application in the electrodialysis concentrating of salt solutions, fuel cells and sensor devices.

Keywords: Intercalation phenomena; Nanocomposite membranes; Polyaniline; Transport properties

1. Introduction

Nowadays the preparation and investigation of nanocomposite materials on the base of the perfluorinated sulfocationic membranes and conducting polymers has attracted interest due to the development of fuel cells, sensor and biosensor devices and separation membrane processes.

We present here the results of systematic researches of preparation, morphology, transport behavior and applications of nanocomposite membranes based on the Nafion type membrane MF-4SC (produced in Russia) and polyaniline (MF-4SC/PAni). The aim of this work is to establish the correlation between the preparation conditions, morphological characteristics and transport properties of the MF-4SC/PAni composites, to obtain composite materials with the set of optimal characteristics, to indicate the key role of the intercalation phenomena and morphology transitions in the composites obtained and to propose theoretical approach to the description of macroscopic transport phenomena in the composite membranes.

The cluster morphology of Nafion type membrane is well known and characterized by a number of nanostructural elements from channels with 1–1.5 nm in diameter to the hydrate-ion clusters with 3–5 nm in diameter and phase separation of polar and non-polar regions. Composite MF-4SC/PAni structure is illustrated in Fig. 1 taking into consideration of polyaniline localization places inside cluster zones and near side chains. The role of side segments was noted by [1].

Polyaniline has a specifical unique chemistry and the block structure of the aromatic chains (Fig. 2). One can see the famous transitions of different oxidation

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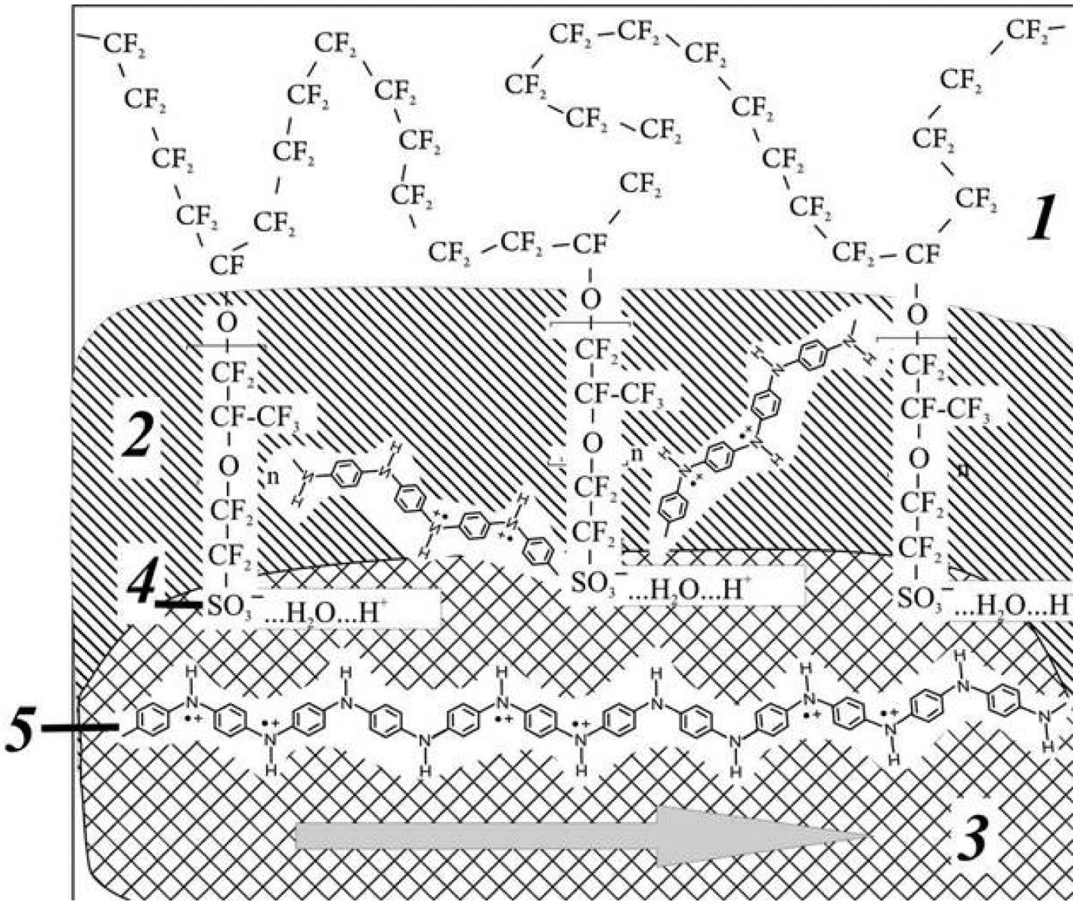

Fig. 1. Schematic presentation of the composite membrane nanostructure. 1-Hydrophobic fluorocarbon backbone and crystallite region; 2-Side chains of fluorovinyl ether with fixed end sulfogroups (''spacers''); 3, 4-Hydrophilic region containing the fixed ions, hydrate water and counterions (ion-dipole associates); 5-Polyaniline chains in cluster zone and between the side chains.

states of polyaniline which are accompanied by the changes of the ability to conduct a current by the delocalized electrons. These peculiarities of polyaniline chemistry call the problems for regulation of the synthesis conditions and electrochemical characteristics of composite membranes.

The five types of these phenomena can be revealed in the process of aniline polymerization, which are presented in Fig. 3:

1. Intercalation of the phenylammonium ions and its distribution in the template matrix (ion exchange with protons and sorption);
2. Growth of the polyaniline chains in the cluster zones;
3. Formation of homogeneous fibrillar morphology in the process of bulk polymerization;
4. Formation of bilayer anisotropic composite in the process of surface modification, morphological transitions from micro- to nanosized inclusions of polyaniline;
5. Formation of microheterogeneous layer on the surface and opening of new ''pores'' and ''channels'' for transport fluxes.

The above-mentioned phenomena results in the multiphase system formation, restructurization of ionic clusters and change of configuration of the side chains in the pristine membranes due to the elastic deformation effects. Thus new structural arrangement is being produced which determine all transport characteristics of composite material.

2. Experimental

Taking into account the different intercalation phenomena and transitions of the oxidation states

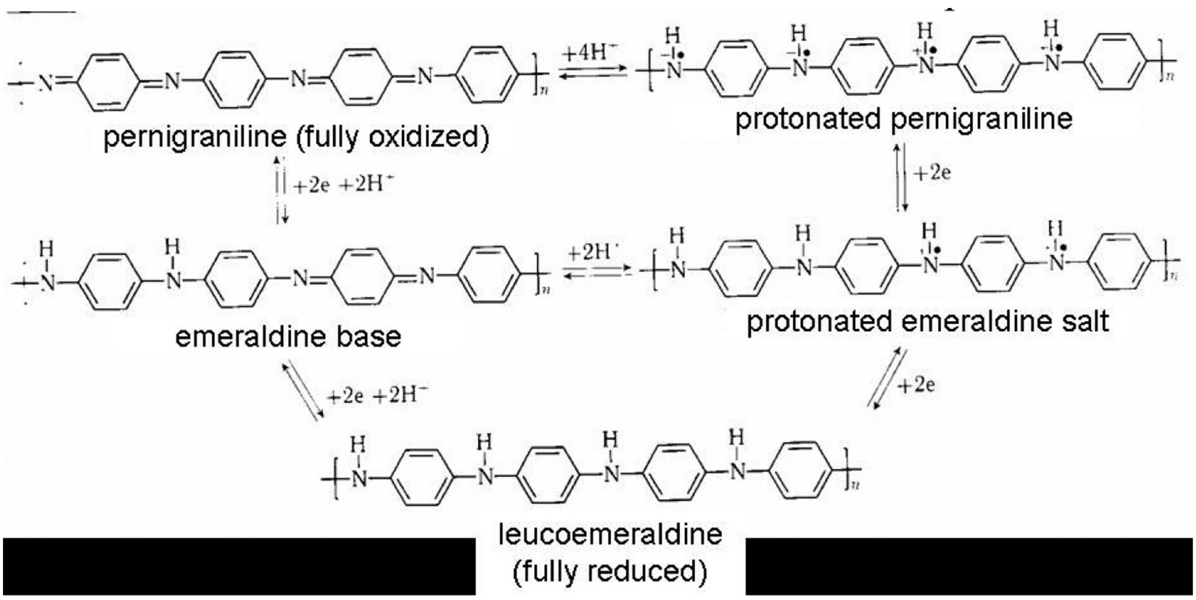

Fig. 2. Molecular structure of different polyaniline forms [2].

of polyaniline we elaborated the next methods of composite preparation by matrix synthesis with variable synthesis parameters [3,4]. These methods permit to prepare the bulk and surface modifications of composite membranes MF-4SC/PAni for different applications.

The set experimental techniques for the morphology and transport properties investigation we used is presented in [3,4].

3. Results and discussion

The comparative study of the morphology peculiarities and transport properties of composite membranes by SEM and AFM techniques was carried out for bulk- and surface-modified samples. It was shown that the homogeneous distribution of polyaniline inside the composite after bulk modification leads to the formation of fibrillose nanosize polyaniline assembles, which stabilize the conducting and selectivity properties. In the case of surface-modified anisotropic composites the morphological transition from the nano- to the microsize of polyaniline inclusions were revealed (Figs. 3 and 4).

The investigation of transport properties of polyaniline/MF-4SC composite membranes after bulk modification – conductivity, diffusion and electro-osmotic permeability, proton permselectivity was carried out as functions of aniline polymerization parameters and acid concentration. High values of the ''true'' transport numbers of composites were obtained and discussed. The dynamic hydration numbers of protons and chloride co-ions were estimated using the ''true'' transport numbers of protons and the electro-osmotic coefficients of composites [4–6].

The method of bulk modification permits to obtain the composite with the electroconductivity k_m = 3.15 S/m that is 25% greater then for the basic MF-4SC. In the bare membrane the proton is transferred on the proton-hydrate clusters chains. The appearance of polyaniline intercalations leads to the conductivity increase due to the contribution of delocalized electrons transfer on the polyconjugated bonds. This effect is confirmed by the electroconductivity measurements of the membranes dried at 80°C up to the constant weight. For composite membranes it is equal to k_m = 0.15 S/m and for the pristine MF-4SC – $k_m = 0.57 \times 10^{-3}$ S/m. The diffusion permeability coefficients were investigated. Comparison of these values for the composites and basic membranes shows that in the firs case it's about 40% lower. The polyaniline intercalations hinder co-ions transfer through the transport channels of the membrane [7].

Surface investigation (by SEM) of the composite membranes shows that even after 1 h of synthesis (under above-mentioned conditions) the polyaniline chains pass throughout membrane thickness up to the other side surface, which was in contact with water during the synthesis (Fig. 5). As a result, the gradient distribution of polyaniline leads to the anisotropic structure composite; however, a distinct interface between the polyaniline layers was not observed. The thickness of polyaniline layers after 1 h of synthesis is about 10% of membrane thickness. These data are

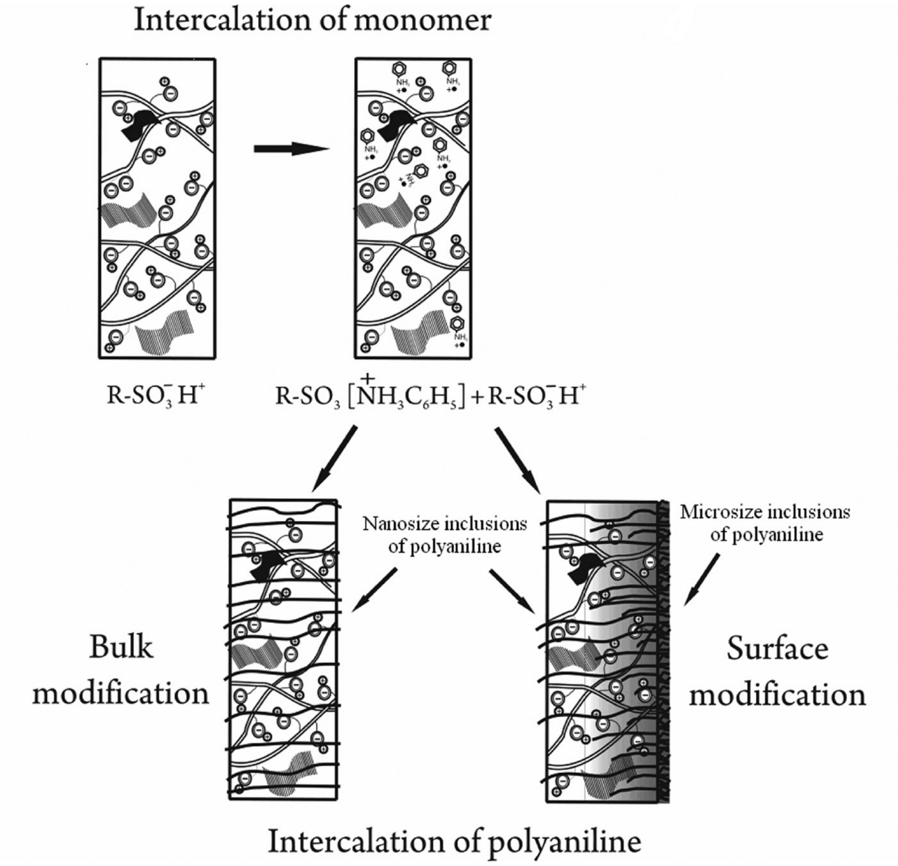

Fig. 3. Intercalation phenomena in the process of the composite MF-4SC/polyaniline preparation.

coincided with results of the detailed investigations obtained in [8]. SEM images in Fig. 5 show the morphological transitions of polyaniline from microsize coatings (1–2 μm) to the nanosized inclusions of polyaniline fibrils (30–80 nm) on the other side.

The dependencies of dimensionless transport properties of composite membranes on the aniline polymerization time are presented in Fig. 3. The dimensionless parameters Y were calculated as ratios of composite transport characteristics (water transport number t_w, integral coefficient of diffusion permeability P, specific conductivity κ_m) and corresponding characteristics of the base membrane. The dependencies obtained demonstrate an extreme character. The lowest values of the transport characteristics were observed for the membrane after 1 h of PAni synthesis: electro-osmotic permeability decreases by 70%, diffusion permeability by 40%, while specific conductivity drops by one order of magnitude. The electro-osmotic permeability decreases significantly due to the deformation of hydration ion shells in the transport channels of the composites (Fig. 6, curves 3, 4). At the same time, asymmetry of integral coefficient of diffusion permeability was observed: in the case when the modifying layer is turned towards water, the diffusion permeability is higher than in the case of the layer orientation towards the electrolyte solution (Fig. 6, curves. 1, 2).

4. Application

The composite after 1 h of synthesis was chosen for the test as it has the most pronounced capability to decrease ion and water fluxes. The properties of the obtained MF-4SC/PAni sample on the concentration of NaCl solutions were compared to those of the initial membrane MF-4SC and MC-40, which is usually used in the industrial electrodialysis devices. The modification of the membrane MC-40 by polyaniline in the same experimental conditions leads to decrease of the diffusion permeability on 15–20%, but electro-osmotic permeability does not change in compare with the original sample. This may be explained by the presence of large pores and inert filler polyethylene in the structure of the electrodialysis membrane MC-40. All the cation-exchange membranes were investigated under the same experimental conditions (current density, temperature,

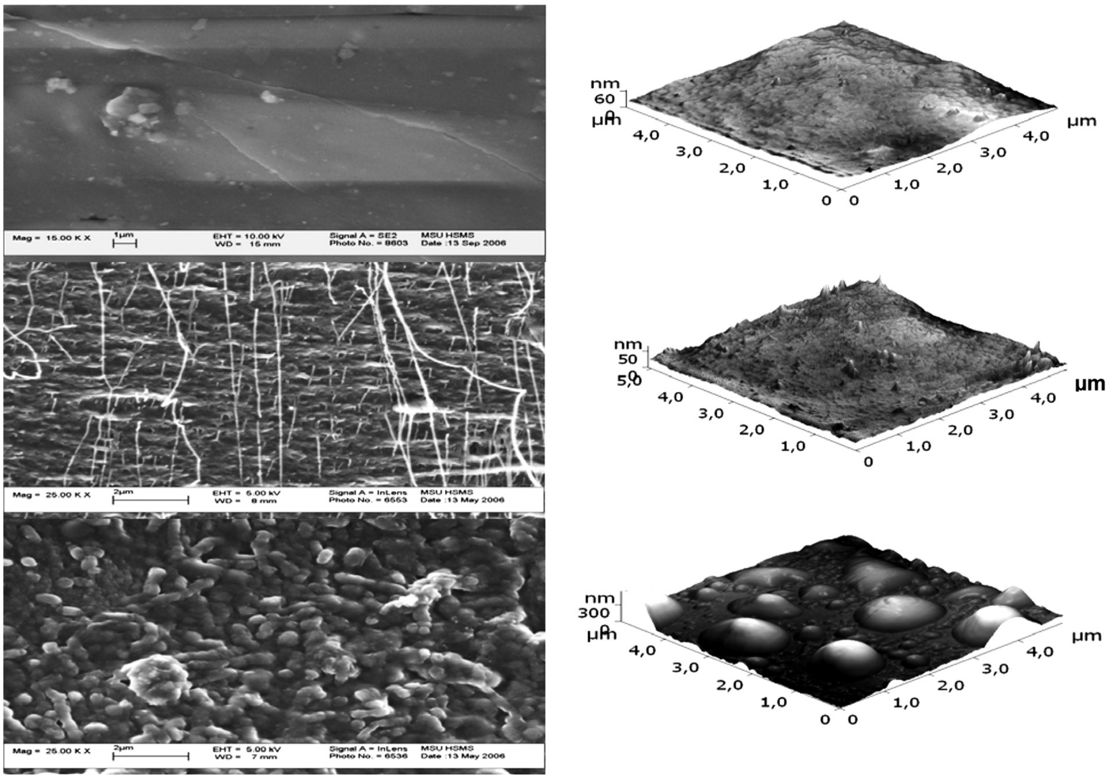

Fig. 4. SEM and AFM micrographs of MF-4SC membranes and composite membranes MF-4SC/PAni (bulk modification). 1 - MF-4SC; 2 and 3 - MF-4SC/PAni after 5 h and 30 days synthesis.

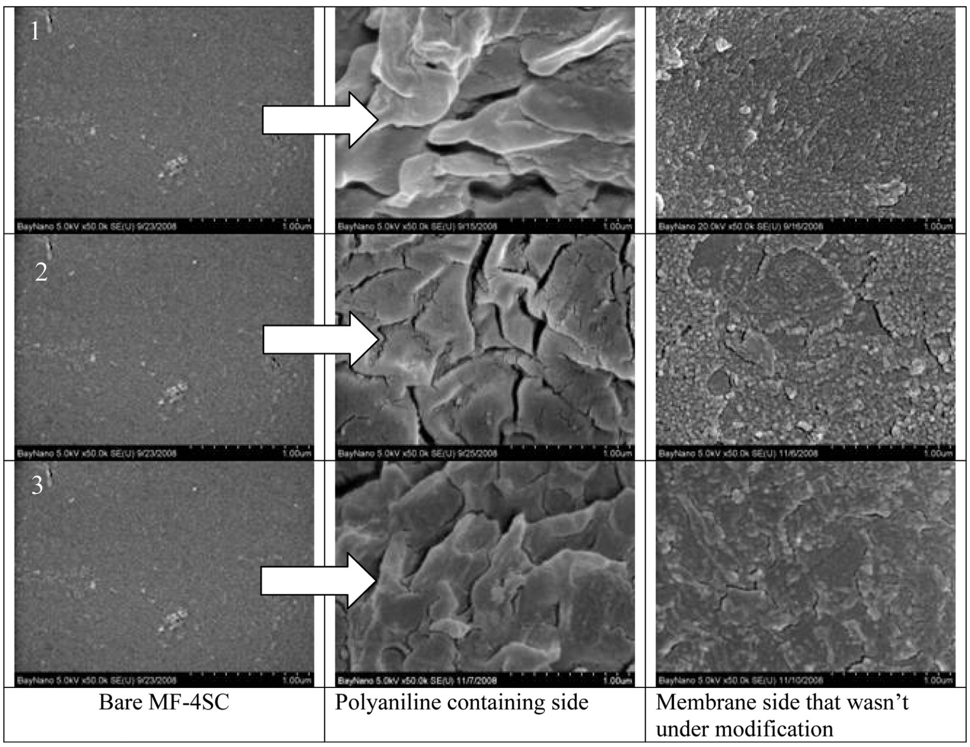

Fig. 5. SEM pictures of surface modified composites. 1,2,3 – 1,2,3 h of polymerization correspondingly.

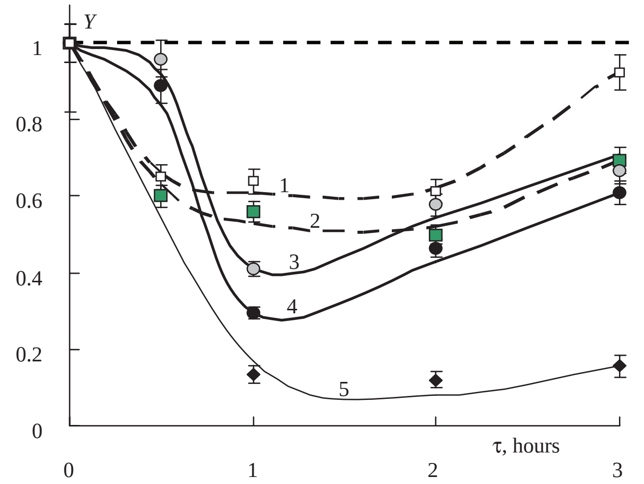

Fig. 6. Dimensionless transport properties of composites MF-4SC/PAni depending on the synthesis time: the diffusion permeability of the 0.5 M HCl solution depending on the orientation towards the electrolyte (1 – non-modified, 2 – modified side of the membrane), 3, 4 – the water transport numbers in the 0.5 M LiCl and 0.5 M NaCl solution, respectively, 5 – the specific conductivity of membranes in the 0.5 M HCl solution.

solution flow rates). Dependences of the NaCl solution concentration in the CC of the electrodialysis cell on the current density (*i*) are shown in [9].

The application of composite membranes MF-4SC/PAni, which have lower values of t_w during electrodialysis of salt solutions, the concentration of NaCl increases by 40% compared to membrane MF-4SC and by 15–20% compared with MC-40. Therefore the composites obtained are perspective for the enhancement of solution concentrating in the electromembrane processes: electrodialysis and membrane electrolysis.

5. Conclusions

Nanocomposite polymer materials of new generation on the base of MF4-SC membranes manufactured in Russia having physicochemical characteristics optimized by polyaniline were created.

Comparative analysis of morphology peculiarities and transport properties of the bulk and surface modified MF4-SC/Pani composites was carried out and perspectives of applications in electromembrane systems were revealed.

The bulk-modificated materials obtained can be recommended as solid polymer electrolytes in fuel cells and sensor devices. The surface-modificated membranes MF4-SC/Pan was used in the process of electro dialytic concentrating of electrolyte solutions.

The development of nanocomposite membranes which was exposed at International Hi-Tech Fair in China, at Shenzhen Convention and Exhibition Center (CHTF-2008) and at V International Exhibition of Nanoindustry <<NTMEX-2008>> in Russia has been rewarded by diploma and medal.

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