Preparation of MF-4SC Composite Membranes with the Anisotropic Distribution of Polyaniline and Ion-Transport Asymmetry

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Abstract—A method of preparing MF-4SK membranes with the anisotropic distribution of aniline over the thickness is developed. The processes of aniline polymerization in the matrix of the MF-4SC sulfocationite membrane are investigated via electronic-absorption and IR spectroscopy. The processes of ion transport in the obtained composite membranes are studied via impedance spectroscopy, voltammetry, and potentiometry.

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Ion-exchange membranes are commonly used in modern technologies [1]. In the past years, perfluorinated sulfonic acid proton-conducting membranes of the Nafion type (the Russian analog, MF-4SC) have been mostly employed in electrochemical synthesis and fuel-cell production. These membranes are based on the product of copolymerization of perfluorinated vinyl ether with tetrafluoroethylene. Nevertheless, growing practical demands dictate the search for new materials with improved characteristics.

Polyaniline (PANI) attracts the attention of researchers because of its optical and electrochemical properties and high chemical resistance [2, 3]. Certain cation-exchange materials with PANI surface layers feature an increased selectivity of transfer [4]. To prepare the conducting form of PANI, it is doped with different acids. It is of interest to use polyacid solutions or the related films as matrices for the polymerization of aniline [5].

In our study, the MF-4SC membrane was used as a matrix for the polymerization of aniline. The as-prepared materials may possess an increased conductivity and improved transport characteristics due to formation of hydrogen bonds between nitrogen atoms of PANI and protons of MF-4SC sulfo groups, in which a proton is shifted toward a nitrogen atom [5]. As a result, the concentration of defects, which play the role of electric-current carriers in proton conductivity, increases [6]. It is of interest to prepare membranes with a nonuniform distribution of various dopant particles over the membrane thickness. Such composite materials may exhibit asymmetry of transport properties [7]. This phenomenon is significant for creation of systems for water purification and ion separation. The use of PANI, which is distinguished from the earlier used inorganic dopants by increased alkalinity, makes it possible to ensure a high gradient of proton concentration; a high degree of hydration of membranes; and, hence, the highest asymmetry of transport properties.

The goals of this study were to investigate the processes of matrix polymerization of aniline, to obtain materials with an anisotropic PANI distribution; and to investigate their transport characteristics.

EXPERIMENTAL

As starting materials, MF-4SC extrusion membranes (OAO Plastpolimer; \( d = 80–90 \mu m \) and an exchange capacity of 0.9 mg-equiv/g), ammonium persulfate (98%, Riedel-deHaen, Germany), and aniline hydrochloride (>99%, Merck, Germany) were used. The synthesis of membranes with the anisotropic PANI distribution was performed through the polymerization of aniline directly in the MF-4SC membrane matrix. In the first case, the membrane was preliminary kept in an ammonium persulfate solution for 2 h (method 1), whereas in the second case, the membrane was kept for 2 h in a solution of aniline hydrochloride (method 2). Then, one of the membrane surfaces was treated with the solution of the second
reagent. In this case, PANI particles directly formed in the membrane matrix, as evidenced by a change in the color of the polymer to emerald green. The time of membrane treatment with each reagent was 2–5 min. The concentration of solutions was varied in the range 0.005–1 mol/l. The prepared composite membranes were aged according to a standard technique [8].

The thickness of the membranes was measured with a Mitutoyo digital micrometer with an error of 1 µm. Electronic absorption spectra in visible and UV regions were registered on a Cary 100 spectrophotometer (Varian, United States) in 2-mm-thick quartz cuvettes. The IR spectra of the studied compounds in the form of films were measured on a Nexus IR-FT spectrometer (Nicolet, United States) equipped with a MATIR attachment. The conductometric measurements of the membranes were conducted in deionized water with a 2V-1 ac bridge in the frequency range 10–6 × 10^6 Hz at temperatures varying from 20 to 100°C. The ionic conductivity at every temperature was found through extrapolation of impedance hodographs to the axis of active resistances. Volt–ampere curves were measured as described in [9, 10].

To determine the diffusion permeability, HCl or NaCl solutions of different concentrations and deionized water were placed into vessels separated with a membrane [11]. In the study of interdiffusion of H+/Na+ cations driven by the chemical-potential gradient, solutions of NaCl and HCl (HCl + NaCl) with the equivalent anion concentration were used. In all experiments, the values of pH and electric conductivity of NaCl solutions were measured (with a step of 3 s) with an Ekspert-001 pH meter and an Ekspert-002 conductometer (Ekoniks-ekspert, Russia) in one of the vessels. The pH meter was calibrated relative to standard buffer solutions. The conductometer was calibrated with the use of standard NaCl solutions. The time of the experiments was defined by attainment of constant pH values of solution or by the moment when the time dependence of conductivity ceased to be linear. Before every experiment, the membrane was transformed into the hydrogen form. To this end, it was kept in a 5% HCl solution and washed with deionized water to remove chloride ions.

RESULTS AND DISCUSSION

To study the kinetics of aniline polymerization in the MF-4SC membrane matrix (in situ), the electronic-absorption spectra were measured. The dependences of absorption-band intensity on the time of aniline polymerization show the induction period. The duration of this period significantly depends on the concentration of solutions, the ratio of reagents, and the sequence of contacts between solutions and a membrane.

The polymerization of aniline is accompanied by a change in the color of the membrane from colorless to blue-green and by an increase in the optical density of absorption bands at 350 and 740 nm in the electronic spectrum of the membrane (Fig. 1). The band at 350 nm is attributed to electronic transitions in amine fragments of PANI chains, whereas the band at 740 nm is associated with localized polarons that arise from intermolecular donor–acceptor interaction between quinoneimine (acceptor) and amine (donor) fragments [4]. Note that the band at 350 nm has a small shoulder at 420 nm due to the formation of cation radicals that results from intermolecular interactions. Note that the band at 740 nm appears immediately in the case of aniline polymerization in the membrane matrix, in contrast to the process proceeding in the MF-4SC solution. In the latter case, the first thing to form is pernigraniline (the absorption maximum at 650 nm), which is reduced with aniline to yield emeraldine, and the absorption maximum shifts toward the longwave region [4].

In the polymerization of aniline in the membrane, which was preliminarily kept in a solution of aniline hydrochloride, the reaction proceeded even at very small concentrations of aniline (0.005 mol/l) (Fig. 2a). It was shown that an increase in the concentration of the oxidant leads to a sharp reduction in the time of reaction. Thus, when the concentration of ammonium persulfate was increased by a factor of 10 (from 0.1 to 1 mol/l), the time of reaction became shorter by a factor of 3 (Fig. 2a).

For membranes preliminary kept in the oxidant solution, the polymerization occurred only at high oxidant concentrations. When the concentration of (NH₄)₂S₂O₈ was less than 0.1 mol/l, no reaction proceeded, while at a concentration of 1 mol/l, a higher concentration of aniline (0.05 mol/l) is required than that in the opposite case. At a concentration of ammonium persulfate solution of 0.125 mol/l, the minimum concentration of aniline hydrochloride at which the color changes is 0.1 mol/l.

Figure 2b depicts comparative time dependences of the intensities of absorption bands at 360 and 710–740 nm for the membranes kept in aniline and in the oxidant in the following sequence: (i) first in aniline hydrochloride and then in ammonium persulfate (curves 1, 2) and (ii) first in ammonium persulfate and then in aniline hydrochloride (curves 3, 4). Even at equal solution concentrations, the sequence of membrane treatment plays the decisive role. Thus, if the membrane was preliminary kept in aniline, the intensity of the absorption bands was two orders of magnitude higher than that in the opposite case. In addition, the duration of the induction period and the time of the whole reaction noticeably shortened. For exam-