NOVEL BI-LAYER HYBRID MEMBRANES: DEVELOPMENT AND TRANSPORT ASYMMETRY RESEARCH

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Introduction

Ion-exchange membranes are intensively used in fuel cells [1], as well as in electrolysis, dialysis, electrodialysis and other membrane methods for obtaining, separating and purifying various mixtures, in sensors and transducers during gas transportation [2]. It is well-known that American cation-exchange perfluorinated membrane Nafion-117® (DuPont de Nemours, USA) and its Russian analogue MF-4SC (LTD Plastpolymer, Russia) are the most extensively applied materials for such membrane type. To change ion and molecular transport, incorporation of different inorganic dopants can be realized. Polyaniline, nanoparticles of noble metals, oxides of zirconium and silicon [3], carbon nanotubes and other materials can improve efficiency of transport properties. One of the membrane modifiers can be alumosilicate nanotubes (halloysite) and their variations, which are ecologically safe, obtainable and cheap [4]. Due to its tubule form halloysite can be as a container for the delivery of metallic nanoparticles inside the membrane matrix. To achieve the best quality for use in fuel cells and membrane switches (membrane relays or diodes) the novel bilayer hybrid membranes based on MF-4SC and halloysite nanotubes were synthesized and studied.

Experiments

Development of bi-layer membranes was carried out by means of a novel approach that included two steps. At first, the polymer solution was placed into a glass former with flat bottom and kept at least 2 h to ensure uniform distribution over the surface and removal of air bubbles (2-nd layer). Then, the polymer solution was dried at a temperature 65 °C until completely solvent evaporation (about 1.5–2 h). The second step was coating of the 2-nd warmed up layer by the polymer solution with non- and modified nanotubes (1-st layer) by means of airbrush. Spraying was carrying out gradually to prevent dissolution of the 2-nd layer by new portions of the suspension solvent at a pressure 3 atm. Further, the 1-st membrane layer was dried at a temperature of 80 °C to remove residual solvent. After that, the film was neatly removed from the glass surface. The membrane was visually homogeneous over the entire area of both the sample surfaces. The ratio of the layers' thicknesses 2 to 1 was 4:1, and the total thickness of the obtained membranes was approximately 160–220 μm. The content of the halloysite nanotubes was 4 wt % of the 2-nd membrane layer. The content of the modifying metal was 2 wt % of the nanotubes' mass. The obtained membranes and modifier were investigated by transmission and scanning electron microscopy, optical microscopy. Transport characteristics (integral diffusion permeability and current–voltage curves) were measured in two-chamber cell equipped with platinized platinum electrodes and two magnetic stirrers based on the experimental determination of the diffusion rate of an electrolyte through a membrane into water by the conductometric method. These experiments were performed at the department of Physical Chemistry, Kuban State University (laboratory of Prof. N.A. Kononenko).

Results and Discussion

Composition of three bi-layer membranes is given in Table 1. To confirm bi-layer structure of synthesized composites, we used micrography of the normal cut-off of membrane No. 1 (Figure 1). It is seen that there is a modified layer having a different structure (at the bottom of the film) which is approximately four times thinner than non-modified layer. The contrast of two membranes layers can be seen clearly in Figure 1b, which is a photo made using optical microscope.

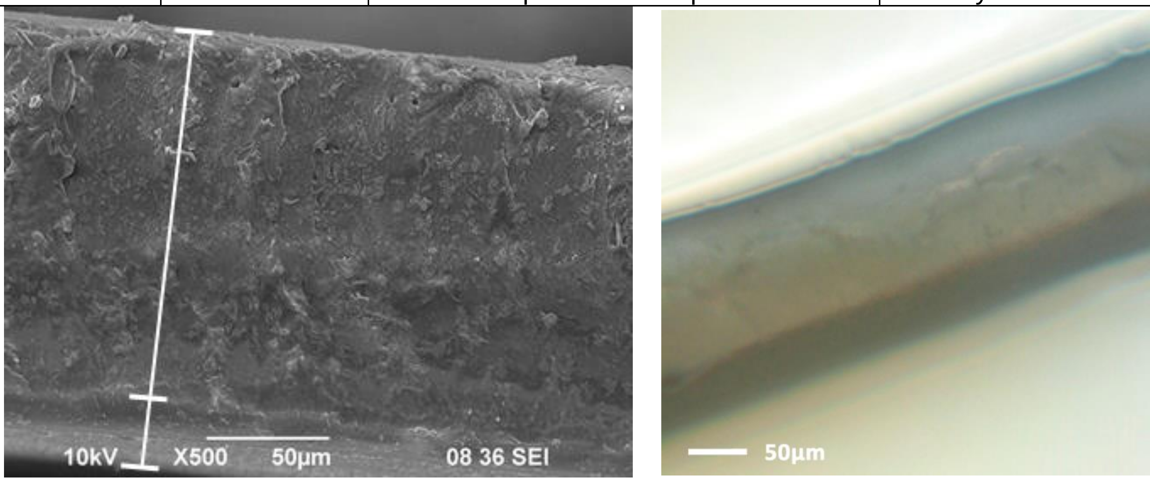
Measurements of the integral coefficient of diffusion permeability were performed in solutions of sodium chloride in the concentration range 0.1–1.0 M and results are placed in Table 2. Subscript "*s*" means orientation of the first (modified and thinner) layer towards electrolyte solution (s-orientation) and subscript "*w*" means orientation of the first layer towards the chamber with pure water (w-orientation). It is shown that membranes are characterised by low values of integral diffusion coefficients P_s and P_w.

It was found that the less asymmetry of the current–voltage curve (CVC) is observed for the membrane No. 1, and the largest for the membrane No. 2, which also has more pronounced diffusion permeability asymmetry. Introduction of 4 wt % halloysite nanotubes in one layer of perfluorinated matrix MF-4SC increases the limiting current density and leads to asymmetry of CVC, while the addition of halloysite nanotubes functionalized with platinum partly compensates for the effect of halloysite adding. The addition of platinum nanoparticles to the external surface of halloysite nanotubes leads to a reduction in the plateau of the limiting current by 25%–50%, which is more significant in the case of the w-orientation of the membrane (a modified layer is turned to the cathode). The shortening of the plateau of the limiting current can be connected with the catalytic action of platinum on the process of water splitting, which leads to the appearance of additional charge carriers—protons and hydroxyl ions [5].

Due to asymmetry effects of the current–voltage curves of bi-layer hybrid membranes on the base of MF-4SC, halloysite nanotubes, and platinum nanoparticles, it is prospective to assemble membrane switches (membrane relays or diodes) with predictable transport properties.

Table 1: Composition of synthesized bi-layer membranes

Bi-Layer Membrane	Thickness, *h*, μm	Thin Layer (1)	Thick Layer (2)
No. 1	221	MF-4SC modified with 4 wt % of halloysite nanotubes encapsulated by 2 wt % platinum nanoparticles	Pristine MF-4SC membrane
No. 2	181	MF-4SC modified with 4 wt % of halloysite nanotubes	Pristine MF-4SC membrane
No. 3	166	MF-4SC modified with 4 wt % of halloysite nanotubes encapsulated by 2 wt % platinum nanoparticles	MF-4SC membrane modified with 4 wt % of halloysite nanotubes



(a) *(b)*

Figure 1. SEM micrography (a) and optical microscope image; (b) of the normal cross-section of the bi-layer membrane No. 1.

Table 2: Experimental diffusion permeability in NaCl solution for three bi-layer hybrid membranes based on MF-4SC

C_0 M	P_s/P_w, μm^2/s, Bi-Layer Membrane No. 1	P_s/P_w, μm^2/s, Bi-Layer Membrane No. 2	P_s/P_w, μm^2/s, Bi-Layer Membrane No. 3
0.1	5.92/6.30	5.84/5.23	4.38/5.13
0.25	9.73/10.9	9.12/11.0	8.69/8.40
0.5	15.5/14.4	15.8/16.5	13.8/13.5
0.75	17.8/19.7	17.3/19.2	14.7/15.5
1.0	20.8/21.9	20.4/19.7	16.9/17.7

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