Perfluorinated Nanocomposite Membranes Modified by Polyaniline: Electrotransport Phenomena and Morphology

A.A.-R. Sytcheva[1], S.A. Shkirskaya[2], N.P. Berezina[2]

1. BAY-NANO Research Institute for Nanotechnology, Department of Nanometrology, Miskolc-Egyetemvaros, Miskolc, Hungary, 3515
2. Kuban State University, Department of Physical Chemistry, 149, Stavropolskaya St., Krasnodar, Russia, 350040

sytcheva@bznano.hu
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The synthesis of composite ion-exchange materials and investigation of their functional properties are relatively new research area in membrane electrochemistry and high-molecular chemistry. The investigation of composites based on ion-exchange membranes and polyaniline (PAni) in a "free standing" state is of special interest because such composite materials can be used to promote the efficiency of electromembrane separation processes. Most often such materials are obtained by chemical template synthesis, where various redox systems are electron acceptors during the oxidative polymerization of aniline.

PAni was obtained in nanosized cavities of the cluster structure of perfluorinated sulfocationic MF-4SC membranes (Plastpolymer, Russia). Chemical synthesis was performed by methods of counter diffusion and successive diffusion (to water) of aniline solution and different initiators of polymerization at room and reduced temperatures. The mechanism of composite template synthesis has been investigated and features of the multistage process of aniline polymerization are revealed, taking into account the protonization of aniline in equilibrium solution and self-assembling effects in the membrane phase. The methods of synthesis of bulk and surface PAni modified membranes with stable physicochemical characteristics have been elaborated [1].

The atomic force microscopy images testify to a morphological transition from the nano- to the microsize of PAni intercalates with increasing the aniline polymerization time for bulk-modified composites (Fig. 1). It can be seen that after 5 hours of synthesis PAni forms particles on the membrane surface of a height below 20-30 nm and diameter below 40-100 nm. PAni microdomens in the form of granules or hemispheres with a diameter of 200 nm up to 1.4 μm and a height of up to 300 nm are characteristic of the membrane PAni/MF-4SC surface after 30 days of synthesis. Surface investigation (by scanning electron microscopy) of the surface-modified composite membranes shows that even after 1 hour of synthesis the PAni chains formed penetrate the membrane and outcrop to the surface which was in contact with water during the synthesis. As a result, the gradient distribution of PAni leads to the anisotropic structure composite; however, a distinct interface between the PAni layers was not observed. SEM images in Fig. 2 show transition from microsized coating (1-2 μm) (modifying solution side) to the nanosized inclusions of PAni (30-80 nm) on the other side.

Transport properties of PAni/MF-4SC composite membranes (after bulk and surface modification) – conductivity, diffusion, electroosmotic permeability and proton permselectivity – have been investigated as functions of aniline polymerization parameters

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and acid concentration. It was revealed that proton transport is the dominant contributor to the overall conductivity of the composites obtained since PAni does not form percolation path for polaron conductivity. It has been shown that water is transferred with proton as hydronium structures $[H_5O_2]^+$ and $[H_9O_4]^+$ by the migration mechanism, whose contribution to the total proton transfer is about 30%. It has been determined that under electric field 15-30% of the total water content of the membrane is transferred along with protons. High values of the "true" proton transport numbers of composites are obtained and discussed. The dynamic hydration numbers of protons and chloride co-ions were estimated using the "true" transport numbers of protons and the electroosmotic coefficients of composites.

It has been shown that PAni intercalates allow to optimize the structure and properties of composite membranes.

1. N.P. Berezina et al., Electrochim. Acta **54** (2009) p2342.
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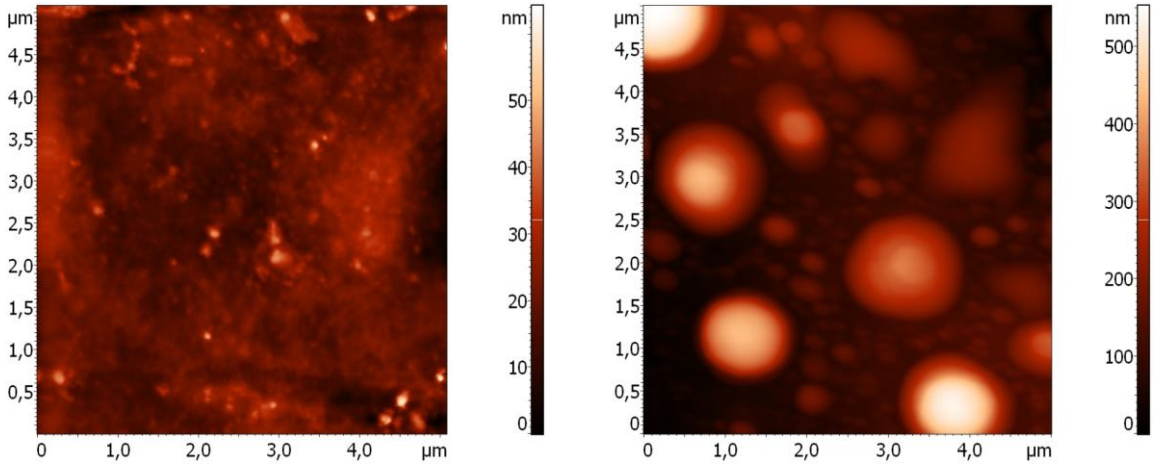
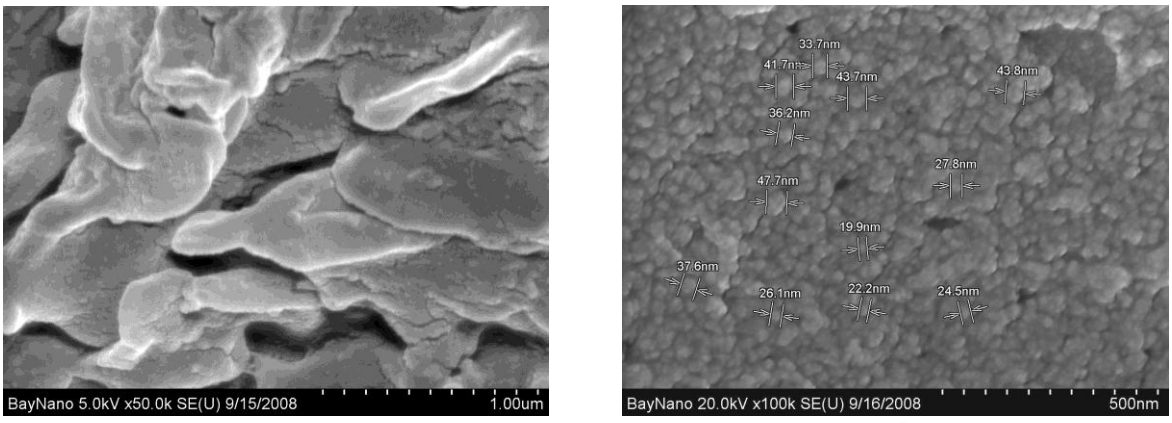


a *b*

Figure 1. AFM images of PAni/MF-4SC bulk-modified composite membranes after 5 hours (a) and 30 days (b) of synthesis



a *b*

Figure 2. SEM images of surface-modified composite membrane PAni/MF-4SC after 1 hour of synthesis: (a) the side with PAni layer on it and (b) the opposite side (magnification: 50 000x and 100 000x)

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