Electrotransport phenomena and hydration effects of nanocomposites based on Nafion membrane and silica

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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. There are a number of electrochemical processes which need advanced materials for the formation not only of electrodes but also separation films. This problem attracts the interest of researchers due to the development of fuel cells, sensor and electrodialysis devices. Application of perfluorinated sulfocationic membranes in fuel cells is limited because of significant loss in proton conductivity at high temperatures and low-wet conditions due to dehydration. Therefore one of the aims of production of composite materials is stabilization of water content and improvement of their conducting characteristics. A wide row of researches are focused on Nafion membranes modified by silica because these materials are prospective for using in fuel cells [1].

Present work describes features of hydrophilic and transport properties of the composites Nafion/SiO_2. The influence of Nafion 115 membrane modified by silica on ionic selectivity, proton conductivity and electroosmotic permeability was studied experimentally. Water distribution curves on the effective pore radii were obtained also for different membranes. Water transport numbers of composite membranes in acid and salt solutions were investigated in dependence on solution concentration by the volumetric method in a two-chamber cell with reversible silver chloride electrodes. Modification of perfluorinated membranes by silica leads to increase electroosmotic permeability as compared to the initial membrane for the concentration range of 0.1 – 0.5 M. On the base of the microheterogeneous model it is possible to calculate characteristics of the static hydrate structure in the gel phase. The analysis of the conductivity concentration dependencies in the framework of the extended three-wire model of conduction permits to estimate current-flow channels and to evaluate the volume fraction of the inner solution in a membrane before and after modification. Such investigations are useful to solve the problem concerning the modificator localization and degree of change in configuration of polymer matrix segments.

The theoretical estimation of “true” transport numbers was carried out using two approaches [2]. The concentration dependences of conductivity of Nafion and Nafion/SiO_2 membranes were used to calculate the transport numbers of counter-ions on the base of three-wire model of conductivity of ion-exchange materials [3]. For the second approach, the Scatchard’s equation taking into account electroosmotic transfer of water and potentiometric transport numbers counter-ions was used. The analysis of interrelation between water-transport numbers and ion-transport numbers provides the opportunity to estimate dynamic hydration parameters of the counter-ions and co-ions in the membrane system.

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