ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 8, pp. 1976–1977. © Pleiades Publishing, Ltd., 2015.
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LETTERS TO THE EDITOR

Modifiation of Perfluorosulfonic Membranes with Sodium Tungstate

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Received March 23, 2015

Keywords: perfluorosulfonic memdrane, sodium tungstate, polymer form, absorption spectra

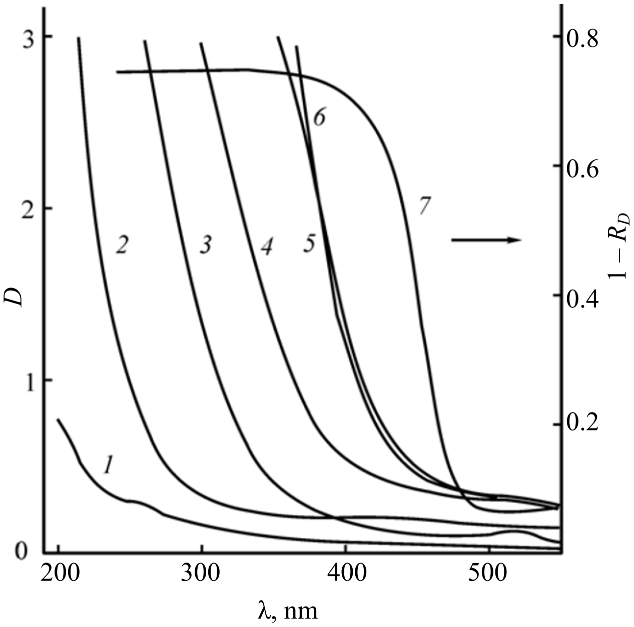
DOI: 10.1134/S1070363215080307

Perfluorosulfonic membranes are widely used as solid electrolytes; however, its complex spatial structure has not been yet resolved [1–6]. In general it is clear that a system of pores with walls covered with sulfonate groups is formed inside fluorocarbon matrix of perfluorosulfonic membranes. The most widely accepted model of the membrane structure suggested in [1] states that spherical voids of about 4 nm in diameter are connected by narrow channels with cross-section of about 1 nm. Additional evidence in favor of this model can be obtained by comparison of the membrane parameters with sizes of species that can be incorporated inside it. Herein we discuss the results of direct impregnating of perfluorosulfonic membranes with aqueous solutions of sodium tungstate. Besides this, the proposed membrane modification could enhance its sensitivity to the near-ultraviolet radiation in view of the photocatalysis applications.

Noteworthily, the membrane high transparency in the UV region was completely retained irrespectively of concentration and pH of aqueous Na_2WO_4 solutions as well as time of the dry membrane incubation in the solution. Indeed, tungstate ions exist in the polymeric form in the aqueous solution, and the size of even the smallest one ($W_4O_{13}^{2-}$) [7] exceeds the diameter of the membrane channels. However, the salt was not found in the perfluorosulfonic membranes treated even with diluted impregnating solutions containing a noticeable fraction of the monomeric WO_4^{2-} ions [7]. That could be a result of condensation of the tungstate ions induced by sulfonic groups located at the membrane channels inlet. The assumption was confirmed by the long-wave shift of the absorption bands of Na_2WO_4 solutions in contact with the membrane. Apparently, the formed polytungstate anionic species are fairly stable, so that they were retained in the surrounding solution, whereas the transparency of the membrane in the UV region was completely retained due to the channels locking.

The impregnation of the membrane with Na_2WO_4 solution could not be realized at the studied pH and concentrations even after conversion of the membrane into the sodium salt form [8]. Likely, the salt exclusion was a result of high alkalinity of the membrane pore space and the appearance of pH gradient at the channels inlets. The highest absorption of the salt (0.022 g per 1 g of the membrane) was reached after prolonged incubation of the membranes in the alkaline solution of Na_2WO_4 (pH = 9.2 mol/L of tungstate) at 60°C; those conditions favored depolymerization of polytungstate anions [7]. The absorbed amount of the salt corresponded to 18% of the membrane theoretical absorption capacity of 0.120 g per 1 g of the membrane (the latter value was estimated assuming complete filling of the membrane pores volume V_C of 0.204 cm^3/g with the 2 mol/L salt solution).

In spite of the steric hindrance, modification of the membrane resulted in significant spectral changes. Judging from the initial position of the absorption band (see the figure), the monomers WO_4^{2-} were predominantly incorporated in the pores space, as expected. Their further condensation could occur in the acidic medium [7]. In order to verify the assumption, a sample containing 0.022 g of the salt per 1 g of the membrane material was exposed in vapors of wet



Absorption spectra of pristine membrane (*1*), of the membranes containing 0.022 g of Na_2WO_4 per 1 g of membrane before (*2*) and after its incubation in HCl vapor during 5 (*3*), 10 (*4*), 15 (*5*), and 20 min (*6*); and of polycrystalline WO_3 (*7*). R_D is the diffuse reflection coefficient.

hydrogen chloride till the highest long-wave shift of the spectrum was attained (see the figure). In the course of the treatment, the charge transfer band approached the position typical of polycrystalline WO_3 (see the figure), thus evidencing about the condensation of the oxoanionic tungsten(VI) species in the perfluorosulfonic membrane. We estimated the amount of the Na_2WO_4 salt incorporated in the membrane: if the membrane thickness was of 0.05 cm, the total volume of the specimen was of 0.1 cm^3, and the specimen mass equaled 0.1 g, then the effective salt concentration in the membrane was of $c \approx 0.07$ mol/L. Since the membrane absorbance was of $D > 3$ (see the figure), the molar absorptivity at the long-wave band ε was of 103 L mol^{-1} cm^{-1}.

Condensation of WO_4^{2-} ions into the polynuclear hydroxide forms was accompanied by the proportional increase in the number of available system states, and the donor 2*p* orbitals of oxygen and 5*d* acceptor orbitals of tungsten approached each other. The increase in the effective negative charge at oxygen atoms of the W–O–W bonds due to the condensation of WO_4^{2-} monomers could provide an alternative explanation of the observed band shift. Indeed, the resulting destabilization of the system of oxygen donor *2p* orbitals and the enhanced splitting of tungsten(VI) acceptor *5d* states decreases the energy of the $2p^n(O) \rightarrow 5d(W)$ transitions.

It is important to note that the condensed oxoanionic tungsten(VI) species incorporated inside the perfluorosulfonic membranes were locked in the pore space, not being washed away during the prolonged contact with water. This opens a possibility for further studies of photocatalytic activity of the modified membranes in the processes of water purification of organic impurities.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Education and Science of Russian Federation within the frame of the basic part of the governmental contract.

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