



Synthesis and properties of stretched polytetrafluoroethylene–sulfonated polystyrene nanocomposite membranes



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ARTICLE INFO

Article history:

Received 4 August 2015

Received in revised form 25 September 2015

Accepted 6 January 2016

Available online 2 February 2016

Keywords:

Ion exchange membrane

Ionic conductivity

Composite membranes

Water and methanol sorptions

Fuel cells

ABSTRACT

Nanostructured stretched polytetrafluoroethylene–sulfonated polystyrene (strPTFE–sPS) ion-exchange membranes have been synthesized by sulfonation of the nanocomposite strPTFE-implanted PS films. The implantation of the PS (17–76 wt.%) was implemented by the thermal polymerization of styrene, which was absorbed from a styrene–divinylbenzene–toluene solution in the stretched PTFE film at 90 °C. The exchange capacity of the strPTFE–sPS membranes reaches 2.3 mmol g^{−1}. The proton conductivity of the water-saturated samples was 2–2.5 times higher than that of Nafion-115 and MF-4SC. It is found that the synthesized membranes have a methanol diffusion coefficient and permeability that are 1.5 times lower than those for water. Comparative laboratory tests in a hydrogen–air fuel cell at room temperature showed that the current–voltage and power characteristics of the cell with the strPTFE–sPS membrane substantially exceed those with the Nafion-115 membrane.

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1. Introduction

Polymeric ion exchange membranes are an integral part of various electrochemical devices (electrolysers, water treatment systems, electrochemical current sources and sensors), and they must meet various requirements – sufficiently high ionic conductivity, high thermal and chemical stability, and mechanical strength. The perfluorinated membranes of the Nafion (manufactured by Du Pont, USA) and MF-4SC (NPO Plastpolymer, Russia) line are considered to most effectively satisfy these requirements. One of the major drawbacks of these membranes is their high cost due to the complexity of their synthesis and the cost of the starting components [1–3].

The development of alternative cheaper and less complicated ways of preparing of such membranes possessing acceptable properties has attracted much attention. One such approach is to make composite membranes based on fluorinated polymer matrices and to embed therein another polymeric phase containing ion exchange groups. The most straightforward way of solving this problem is to implement the radiation–chemical grafting of a readily sulfonated polymer, usually polystyrene, into a fluoropolymer matrix [1,3]. This approach allows the implementation of various options, but it is complicated by the need to use complex and not widely available radiological equipment, powerful gamma sources, and electron accelerators.

Earlier, we have developed a method of synthesis of nanostructured cation exchange membranes through the thermal polymerization of styrene, absorbed from solution, inside a polymeric film, with subsequent sulfonation of the implanted polystyrene (PS). This route provides a relatively simple pathway for making membranes based on polyvinylidene fluoride (PVDF), polypropylene, or ultra-high-molecular-mass PE films with the properties comparable to those of commercial Nafion and MF-4SC membranes [4–7]. It seems to be a promising approach to obtain membranes based on perfluorinated PTFE matrices possessing high thermal stability, chemical resistance, and mechanical characteristics. However, due to the almost complete absence of sorption of styrene by PTFE films, such a direct route to membranes based on these films is probably impossible.

Recently, through the use of the well-known method of the in situ sorption of liquids in the stretching of polymer films, which is known as “crazing in polymers” [8,9], we succeeded in increasing the sorption of organic solvents by the stretched PTFE films and successfully performed the thermal polymerization of styrene. It was shown that the “stretched PTFE–PS” (strPTFE–PS) nanocomposite with an implanted PS content of 76 wt.% can be obtained by the thermal polymerization of styrene sorbed by a PTFE film stretched in monomer solution. A proposed polymerization model describes the PS accumulation kinetic data with a good accuracy and allows us to assume that the polymerization progresses inside PS nanoinclusions at constant monomer concentration. The formation of polymerization active centers is most efficient on the surface of the PS nanoinclusions, on their contact border

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boundary with the matrix. A heterogeneous change in the sample (greater expansion of thickness and width than length) was observed during the accumulation of the PS in the stretched PTFE films.

The objective of this work was to carry out the synthesis of cation exchange membranes based on the nanocomposite strPTFE–PS films and to study their physicochemical properties as well as perform comparative tests of these obtained membranes in a hydrogen–air fuel cell.

2. Experimental

Cation exchange membranes based on commercial PTFE films (F-4-fluoroplast) were obtained by the sulfonation of nanocomposite strPTFE–PS films. The precursor was obtained by the thermal polymerization of styrene sorbed by a PTFE film undergoing crazing–stretching in a solution of styrene–toluene–divinylbenzene–2,2-azo-di-isobutyric acid (1:1:0.05:0.005). PTFE films (120 or 25 μm) were mounted in a stretching machine, immersed in reaction solution and stretched by 25–200%. Afterwards, the stretched film and reaction solution were placed in a pressurized glass vessel and thermostated at 90 $^{\circ}\text{C}$ for 2 h for the thermal polymerization of the sorbed styrene. The thermal polymerization was repeated several times in freshly prepared reaction solution to accumulate the necessary amount of implanted PS.

The sulfonation of the samples with implanted PS was performed in 0.3 M H_2SO_3 solution in 1,2-dichloroethane at 60 $^{\circ}\text{C}$ for 8 h, followed by storage of the samples in the same solution for one day at room temperature. The ion exchange capacity (IEC) of the synthesized strPTFE–sPS membranes was measured directly using acid–base titration in the presence of 1 M NaCl solution.

Morphology of a strPTFE–sPS membrane was observed by scanning electron microscopy (SEM) using Zeiss LEO SUPRA 25 SEM. The labile protons of the membrane were exchanged with Pb^{2+} by soaking it in a saturated $\text{Pb}(\text{Ac})_2$ solution for 1 day. The stained membrane was rinsed with water and dried under vacuum. A cross-section of the membrane was prepared by the fracturing of the membrane in liquid nitrogen. The membrane samples were sputtered with a thin layer of gold–palladium alloy (5 nm) prior to the SEM observation.

To determine the proportion of the surface of the conducting phase (f_w) in the strPTFE–sPS membranes, we used the well-known relation (1) between the composition of the surface of the mixture and the wetting angles of the individual components of the surface.

$$\cos \theta = \sum_{i=1}^n f_i \cos \theta_i \quad (1)$$

Here, θ is the contact angle with the surface of the mixture, θ_i are the individual contact angles for the components of the mixture, and f_i are the respective fractions of the surface [10]. Assuming that the surface of an strPTFE–sPS membrane is a mixture of pure PTFE with a wetting angle θ_{PTFE} and conductive water-filled pores having zero contact angle, we obtain the surface fraction of the conductive phase f_w as.

$$f_w = (\cos \theta - \cos \theta_{\text{PTFE}}) / (1 - \cos \theta_{\text{PTFE}}). \quad (2)$$

The contact angles θ and θ_{PTFE} were measured with an accuracy of $\pm 5^{\circ}$.

The sorption of aqueous methanol solution into the synthesized membranes was studied using immersion in the solution at room temperature for 5 h. The membranes were then removed and weighed, with the excess solution wiped from the surface with filter paper. The amount of adsorbed solution (m_{sorb}) was defined as the ratio of weight gain during the sorption (Δm) to the weight of the original dry membrane (m_0):

$$m_{\text{sorb}}(\text{wt.}\%) = 100 \times \Delta m / m_0. \quad (3)$$

The diffusion coefficient of water D_w was evaluated using the calculation method for diffusion coefficients employed in the study of the kinetics of penetration of fluids (and solvents) into polymers [11,12]. This approach is also applicable to the transport properties of membranes [13]. As stated in the cited papers, the sorption kinetics for a d -thick film at $R_t > 0.6$ ($R_t = m_{\text{sorb}}/m_{\text{sorb-max}}$) is well described by the relation (4).

$$R_t = 1 - (8/\pi^2) \exp(-t \pi^2 D_w/d^2) \quad (4)$$

In the course of the polymer swelling or water sorption in the dry sorbent, the membrane state constantly changes, and the calculated coefficient D_w is usually called the kinetic constant of diffusion [12]. D_w values obtained using this method can be considered as the average for the state of the membranes from dry to wet. The relative error in the determination of the diffusion coefficients by sorption is less than 10%.

The permeability coefficients of water and methanol, P_w and P_{meth} , for the synthesized membranes were measured using a laboratory two-chamber installation divided by an investigated membrane [4]. Both cells of the two-chamber installation are provided with vertical input tubes for the supply of water and methanol. Those tubes were also used for the observation of the change in their levels h_1 and h_2 and the volumes of the solutions in the cells. During the experiment, the cells' contents were stirred continuously. The methanol concentration C_{meth} in both cells was determined via the refractive index, recorded with an IRF 454B refractometer. The water concentration C_w was determined by the C_w dependence on C_{meth} , calculated based on the changes in the density of the solution.

The values of P_w and P_{meth} were calculated using the Fick equation. The control experiments where C_{meth} was determined using the more sensitive NMR (H^1) showed that the determination of C_{meth} via the refractive index does not noticeably increase the experimental error for the calculated permeability coefficients.

The proton conductivity of the synthesized membranes in water at 25 $^{\circ}\text{C}$ was measured by impedance spectroscopy using a Z-2000 impedance meter (ELINS, Russia) in the frequency range of 100 Hz to 2 MHz in a cell with gold electrodes at a controlled pressure [6].

The dependence of the proton conductivity of the synthesized membranes on the relative humidity RH was determined on sample membranes preincubated for 2 days in a sealed desiccator with a constant pressure of water vapor. To provide the required pressures of water vapor (RH%) saturated aqueous salt solutions of LiCl (12%), MgCl_2 (32%), NaBr (58%), NaCl (75%) as well as 58 wt.% sulfuric acid solution (22%), pure water (100%), and fresh P_2O_5 (0%) were used. The proton conductivity in these experiments was measured in symmetric carbon/membrane/carbon cells at 30 $^{\circ}\text{C}$ using a Z-2000 impedance meter (ELINS, Russia) in the frequency range of 100 Hz to 3 MHz.

The synthesized strPTFE–sPS membranes and Nafion-115 membrane were comparatively tested within hydrogen–air fuel cells (PEMFC) at room temperature with an active electrode area of 5 cm^2 . The electrodes used were the gas diffusion layers (Toray Carbon Paper) with a deposited catalyst Pt/C (25 wt.% Pt) containing 30 wt.% Nafion ionomer. The catalyst load of the electrode was 0.4 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$. When forming the membrane–electrode assemblies, the electrodes were pressed to the membrane at a pressure of 50 kg cm^{-2} for 2 min at 100 $^{\circ}\text{C}$ in the case of composite membranes and at 80 kg cm^{-2} for 3 min at 130 $^{\circ}\text{C}$ in the case of Nafion-115. The relative humidity of the hydrogen and air flows was 100%. The current–voltage and power characteristics of the PEMFCs were measured using a PS-30S (“Ellins”, Russia) potentiostat. Before registration of the stationary load current–voltage characteristics, the PEMFCs were aged for 1 h under a load at $E = 0.5 \text{ V}$, and the current–voltage characteristics were then recorded during stepwise changes in the load, with an exposure at each value of the potential of 5 min.

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