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Ion Transport in Hybrid Membranes Based on Perfluorosulfonic Polymers

A. K. Osipov[a, b, *], **I. A. Prikhno**[a, b], **and A. B. Yaroslavtsev**[a, b]
[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
**e-mail: osipov.aleksander.k@gmail.com*

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Abstract—A comparative study of the transport characteristics of Nafion and Aquivion perfluorinated membranes and hybrid membranes on their basis has been carried out. It has been shown that the modification of membranes of both types with acid salts of heteropoly acids and silica significantly increases their proton conductivity. In the case of high humidity, the best conductivity is achieved when they are doped with salts of heteropoly acids. The highest improvement in the membrane conductivity is achieved at low humidity for membranes doped with SiO_2; in this case, the conductivity is increased by almost an order of magnitude.

Keywords: perfluorinated membranes, hybrid membranes, salts of heteropoly acids, Nafion, Aquivion, proton conductivity, diffusion permeability

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INTRODUCTION

The interest of researchers in materials on the basis of perfluorinated sulfonic membranes is determined by a set of unique properties, due to which they can find application in various technologies. Such membranes are used as a solid electrolyte in fuel cells and other electrochemical power generators, electrolyzers, water purification systems, sensors, as well as catalysis and gas separation [1–3]. The replacement of internal combustion engines by fuel cells on the basis of such membranes will make it possible to decrease the harmful effect of transport vehicles on the environment [4, 5]. Nafion proton-conducting sulfonated cation-exchange membranes (DuPont, United States) are of greatest interest for this application. These membranes have been the most well studied to date [6–8]. But, despite its multiple advantages, Nafion has a number of disadvantages as well [9], which prompts researchers to search for ways of improving its properties. The introduction of various inorganic dopants into membranes can improve their transport properties [1–12].

An alternative approach is the development of membranes with a sulfonated side chain shorter than in Nafion membranes [13–19]. Solvay commercialized a material under the brand name Aquivion, which has a structure similar to that of Nafion and differs by a short side chain. Recently, we described the transport properties of these membranes [20]; however, there is currently almost no published information about the properties of hybrid membranes on the basis of Aquivion.

In this connection, the aim of this work was to do a comparative study of the transport properties of Aquivion and Nafion membranes doped with hydrated silica and acid cesium salts of phosphotungstic and silicotungstic heteropoly acids.

EXPERIMENTAL

Chemicals and Materials

Nafion 212 (Du Pont, the equivalent weight of 1100) and Aquivion 87 (Solvay, the equivalent weight of 879) membranes, tetraethoxysilane (Fluka, ≥98%,), phosphotungstic ($H_3PW_{12}O_{40} \cdot xH_2O$, Merck) and silicotungstic ($H_4SiW_{12}O_{40} \cdot xH_2O$, Aldrich) heteropoly acids, cesium carbonate (Aldrich, 99.9%), reagent grade hydrochloric acid (Khimmed), reagent grade aqueous ammonia (Khimmed), reagent grade 30% solution of hydrogen peroxide (Khimmed), reagent grade isopropyl alcohol (Khimmed), and deionized water (the specific resistance of 18.2 MΩ/cm) were used in this work.

Preparation of Hybrid Membranes

Hybrid membranes were synthesized in situ in the pores of a ready-to-use membrane. To obtain membranes doped with the salts of heteropoly acids, they were successively treated with solutions of heteropoly acids and cesium carbonate after swelling in isopropa-

Table 1. The water uptake by the test membranes at different relative humidities

Sample	Water uptake at RH = 95%, %	Water uptake at RH = 32%, %
Nafion	14 ± 1	3 ± 1
Nafion + SiO_2	15 ± 1	2 ± 1
Nafion + CsHPWA	20 ± 1	4 ± 1
Nafion + CsHSiWA	19 ± 1	5 ± 1
Aquivion	17 ± 1	5 ± 1
Aquivion + SiO_2	22 ± 1	5 ± 1
Aquivion + CsHPWA	26 ± 2	8 ± 2
Aquivion + CsHSiWA	24 ± 2	7 ± 2

nol. For the modification by silica, the membranes were treated with a tetraethoxysilane solution in methanol after their swelling in a methanol–water mixture. After this, tetraethoxysilane was hydrolyzed by treating the membranes with an ammonia solution. After rinsing, the membranes were conditioned according to a procedure described in [21].

Investigation Techniques

The water uptake of hybrid membranes at various relative air humidities (RHs) were determined by the difference in the weights of the samples exposed at a controlled RH before and after annealing at 150°C. To set the required humidity, saturated solutions of Na_2HPO_4 and $CaCl_2$ (95 and 32%, respectively) were used.

The proton conductivity of the membranes was measured both in contact with water and in air at an RH of 30%. To set the required humidity and temperature, a Binder MKF115 climate chamber with stationary conditions (the accuracy of humidity setting of ±2.5%) was used. The resistance was measured by impedance spectroscopy using the two-electrode technique with carbon electrodes having an active surface area of ~0.5 cm and a 2V-1 ac bridge in the frequency range of 10 kHz–2 MHz. The value of conductivity was calculated from the resistance found by from the intercept of the impedance hodograph on the active resistance axis.

To determine the diffusion permeability, a sample was placed into a cell consisting of two compartment with a volume of 32 cm^3 each. One of them contained a 0.1 M HCl solution, and the other contained deionized water stirred at a constant rate. The change in pH in the compartment that initially contained water was recorded using an Ekspert-001 pH meter every 3 s. The time of completion of the experiment was determined by the pH of the solution reaching a constant value. The diffusion permeability was determined using the equation $P = \frac{dc}{dt}\frac{Vh}{S\Delta c}$, where V is the volume of the solution, cm^3; h is the membrane thickness, cm; Δc is the concentration gradient, mol/cm^3; and t is the time, s (the error in the determination of P was less than 1%). The rate of concentration change $\frac{dc}{dt}$ was determined as the change in the concentration of H^+ ions in the cell that initially contained water over the set time interval.

RESULTS AND DISCUSSION

Water Uptake

Under equivalent conditions, the water uptake turns out to be higher for all the modified membranes than that of the unmodified membrane; this difference is associated with the hydrophilicity of dopant particles, which retain additional water molecules. The water uptake at different relative humidities is higher in the case of modified membranes (Table 1). Note that the water uptakes of the Aquivion-based membranes turns out to be even higher than that of the Nafion due to the higher concentration of hydrophilic sulfo groups per unit volume in the membrane with a shorter side chain.

Proton Conductivity in Contact with Water

For all the dopants, the modification leads to a growth in the conductivity of the hybrid materials under study (Fig. 1); this is associated with pore widening due to the occurrence of dopant particles in the pores [22] with the proton-donating properties of the dopants themselves. For the samples containing acid salts of heteropoly acids, the conductivity is higher than for the samples doped with hydrated silica. The conductivity in the case of modification increases as a result of membrane pore widening by entering dopant particles with a size of 2–5 nm, which retain additional water and, as a consequence, broadening of the pore-connecting channels which limit proton transport [22]. In additional, acid salts of heteropoly acids are characterized by high acidity and conductivity [23], which explains the substantially higher conductivity of the membranes modified by these salts relative to that of the silica-modified membranes. The higher conductivity of the membranes obtained on the basis of Aquivion also seems to be due to the higher concentration of sulfo groups, which are directly involved in the proton transport. A less pronounced effect of silica on the conductivity of Aquivion membranes in comparison with Nafion membranes is presumably due to the more perfect porous structure of this membrane.

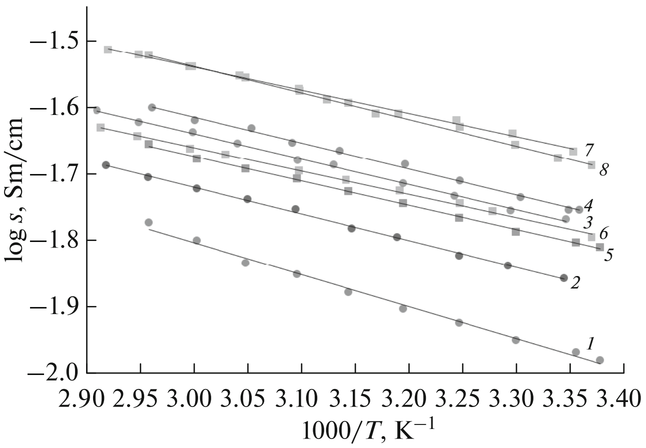

Fig. 1. The proton conductivity of the (*1*) Nafion, (*2*) Nafion + SiO_2, (*3*) Nafion + CsHSiWA, (*4*) Nafion + CsHPWA, (*5*) Aquivion, (*6*) Aquivion + SiO_2, (*7*) Aquivion + CsHSiWA, and (*8*) Aquivion + CsHPWA membranes under study in contact with water.

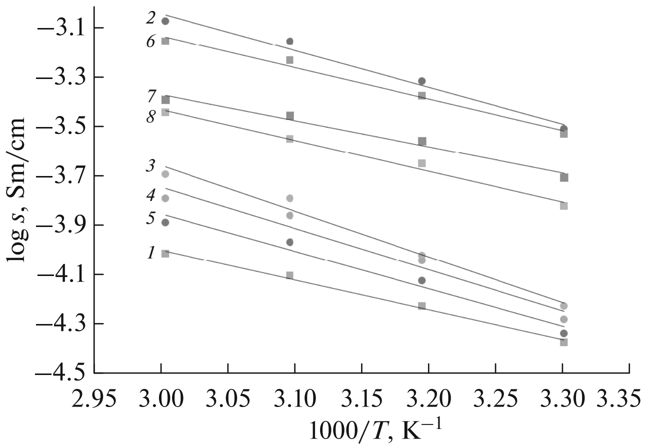

Fig. 2. The proton conductivity of the (*1*) Nafion, (*2*) Nafion + SiO_2, (*3*) Nafion + CsHSiWA, (*4*) Nafion + CsHPWA, (*5*) Aquivion, (*6*) Aquivion + SiO_2, (*7*) Aquivion + CsHSiWA, and (*8*) Aquivion + CsHPWA membranes under study measured at RH = 32%.

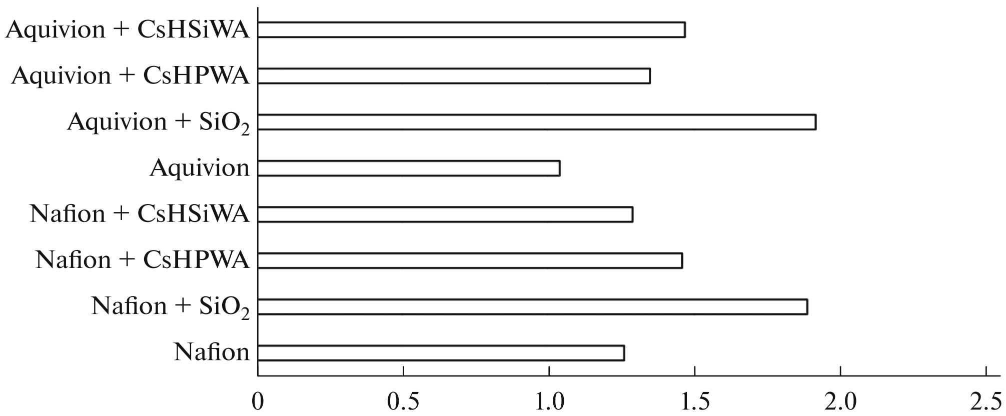

Fig. 3. The diffusion permeability of HCl through the membranes under study, $P \times 10^7$, cm^2/s.

Proton Conductivity at Low Humidity

At a relative air humidity of 32%, the conductivity of all the membranes substantially decreases (Fig. 2). In this case, the modification results in an increase in the membrane conductivity, the increment being sharper than that at a high relative humidity.

At a low relative humidity, proton conductivity is determined by proton hopping over oxygen-containing sites of the membrane walls and dopant particles [24]. Therefore, it is the presence in the membrane of a dopant with the surface containing additional proton transport sites that leads to the increase in the conductivity of hybrid membranes.

Diffusion Permeability

As a result of the modification, the rate of the diffusion of HCl through a membrane increases for all the hybrid membranes. However, the diffusion permeability takes nearly equal values for the hybrid membranes of both types, whereas that of the initial Aquivion membrane is lower as compared to Nafion (Fig. 3).

The rate of diffusion of an acid is determined by the diffusion of the anions through membranes, since the concentration of protons and the rate of their transport are much higher. To provide electrical neutrality, the transport of an equivalent number of anions is required, which occurs only through the free solution inside a pore and turns out to be more impeded. The formation of dopant nanoparticles in membrane pores leads to their widening and, as a consequence, broadening of the pore-connecting channels which limit the rate of ion transport. In addition, as a result of the modification, the water uptake of the membranes grows, which is accompanied by an increase in the volume of the pores and electroneutral solution through which the anion transport occurs. This leads to an increase in the diffusion permeability of the hybrid membranes.

CONCLUSIONS

It has been shown that the high proton conductivity of Aquivion 87 perfluorinated membranes with a short side chain can be additionally improved by doping with silica and acid cesium salts of heteropoly acids. In that case, it turns out to be significantly higher than for a Nafion 212 membrane. At the same time, the modification results in some increase in the diffusion permeability of the hybrid membranes.

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