Nanocomposite Membrane Materials Based on Nafion and Cesium Acid Salt of Phosphotungstic Heteropolyacid

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This paper is devoted to the study of the composite (hybrid) Nafion membranes doped by different concentrations of cesium acid salt of phosphotungstic heteropolyacid. The conductivity of the membranes was studied as a function of temperature (at 100 % relative humidity, RH) and RH (at t = 25 °C). Due to the membrane modification, the conductivity increases. At 100% RH, the dependence of conductivity on the dopant concentration passes the maximum at 3 wt.%. Conductivity of hybrid membranes is by 15-20% higher than that of Nafion. Conductivity of the membranes containing ≥ 7 wt.% of $Cs_xH_{3-x}PW_{12}O_{40}$ is lower as compared with that of the initial Nafion. Due to the introduction of $Cs_xH_{3-x}PW_{12}O_{40}$, conductivity markedly increases at low RH for all concentrations. At RH = 32 %, the maximum conductivity is observed for the membrane containing 5 wt.% of the dopant ($2.7 \cdot 10^{-3}$ S/cm) and this value is three times higher as compared with Nafion.

Permeability of electrolyte solutions through the membranes is studied. The presence of the dopant with acidic properties decreases the HCl permeability; the higher is $Cs_xH_{3-x}PW_{12}O_{40}$ concentration in the membrane, the lower is the diffusion permeability. Hence, the presence of the dopant prevents the diffusion of anions and increases selectivity.

The effect of $Cs_xH_{3-x}PW_{12}O_{40}$ on the membrane transport characteristics was explained according to the model of the limited elasticity of membrane pores and channels. Hybrid membranes containing minor amounts of $Cs_xH_{3-x}PW_{12}O_{40}$ can be considered as promising electrolytes for proton exchange membrane fuel cells due to their high conductivity at low RH and high selectivity.

1. Introduction

According to The fuel cell industry review (2013), commercial fuel cells are primarily based on a proton-exchange polymer membrane as a solid electrolyte (PEMFC). This technology offers a number of advantages: the design of small-sized systems with a capacity varying from several watts to megawatts and low operating temperatures which ensure their fast start-up. The benefits of PEMFC have encouraged intensive research and development both in academic and commercial directions (Arpornwichanop et al., 2014). The main efforts were focused on the improvement of performance and lifetime of FC and on the reduction in the energy costs. Perfluorosulfonic cation-exchange membranes such as Nafion® are often used in the PEMFCs production (Chandan et al, 2013). The advantages of the Nafion® membranes are related to their high chemical and thermal stability, high proton conductivity, and strength (Ramkumar J., 2011). However, their use in PEMFC is limited by the following drawbacks: reduced conductivity at low RH, relatively high gas permeability (10^{-11}-10^{-10} mol·cm^{-1}·s^{-1}) and permeability of methanol (10^{-6} cm^2/s), and high cost (Li et al., 2003). Their performance at low RH can be improved by their modification with different dopants such as silica, zirconia, and heteropolyacids (including phosphotungstic acid $H_3PW_{12}O_{40}$, PWA) (Ahmad et al, 2010; Tripathi and Shahi, 2011; Yaroslavtsev et al., 2012a). One of the most promising procedures for the modification of the Nafion-type membranes is concerned with the incorporation of silica nanoparticles with heteropolyacids

(Mahreni et al., 2009) and their insoluble acid salts (Prikhno et al., 2014) or only insoluble acid salts of heteropolyacids (Xiang et al.,2011) into the parent membrane matrix. The presence of cesium acid salt of PWA in the membrane was shown to promote the catalytic reactions at the FC electrodes (Gerasimova et al. 2012). The concentration and distribution of dopants in the host membrane are known to exert a marked effect on the characteristics of the hybrid membranes.

From this viewpoint, in situ modification of the membranes by the introduction of a dopant into the parent membrane matrix makes it possible to achieve a uniform distribution of dopant particles with dimensions of 3-5 nm in the membrane matrix. However, this method suffers from evident drawbacks (for example, it does not allow controlled introduction of the prescribed amounts of dopants) and can hardly be commercialized. The more promising approach is related to the introduction of dopant nanoparticles into polymer solutions and subsequent casting.

The objective of this work is concerned with the synthesis and characterization of the transport characterisrics of the hybrid materials composed of the Nafion-based membranes and cesium acid salt of PWA. The materials are prepared by casting from polymer solutions containing dopant nanoparticles.

2. Experimental

2.1 Materials

In this work, we used the solution of Nafion® membranes (Aldrich, perfluorinated resin solution, 5 wt.% in lower aliphatic alcohols and water). As chemical reagents, we used phosphotungstic heteropolyacid hydrate $H_3PW_{12}O_{40} \cdot 44H_2O$ (Acros), cesium carbonate Cs_2CO_3 (Khimmed, Russian Federation), hydrochloric acid (a 36% water solution), nitric acid (a 70% water solution) and hydrogen peroxide (Khimmed Russian Federation). In all experiments, deionized water with a resistance of 18.2 MΩ•cm was used.

2.2 Synthesis of caesium acid salt

Cesium acid salt of PWA was synthesised according to the procedure described by Yaroslavtsev et al. (1994). Basic salt $Cs_3PW_{12}O_{40}$ was obtained from the solutions of cesium carbonate and PWA. Then it was treated by the dilute solution of nitric acid in order to obtain the acid salt. A white precipitate was washed in deionized water and dried at 110°C in air.

2.3 Preparation of Nafion / $Cs_xH_{3-x}PW_{12}O_{40}$ membranes

Composite membranes were prepared by casting from polymer solutions containing the calculated amounts of $Cs_xH_{3-x}PW_{12}O_{40}$ (CsPWA). The mixture was stirred in the ultrasonic bath for 1 h. Then the solutions were cast into a Petri dish and dried in air at 25°C for 12 h and at 60°C for 12 h to remove the solvent. The recast membranes were detached from the Petri dish by the addition of deionized water. Then, the excessive water was removed with the filter paper and the membranes were hot-pressed at 110 °C and 60 bar for 3 min to improve their mechanical strength. All membranes were treated gradually by 10 % H_2O_2, HCl solutions and deionized water at 80 °C for 2 h. The CsPWA concentration was ranged from 0 to 15 wt.%.

2.4 Instruments and methods

Crystalline structure was characterized by the X-ray diffraction (XRD) with CuK_α radiation on a Rigaku D/MAX 2200 diffractometer. The XRD data were analyzed using the Rigaku Application Data Processing software. Microstructure of the materials were examined by scanning electron microscopy (SEM) on a Carl Zeiss NVision 40 (SEM images were obtained at a 1-kV acceleration voltage) and by transmission electron microscopy (TEM) on a JEOL JEM-1011 (TEM images were obtained at a 100-kV acceleration voltage). Prior to TEM measurements, the membranes were ultrasonically dispersed in methanol and supported onto carbon-coated Cu grids.

Thermal analysis of the samples was performed on a Netzsch-TG 209 F1 instrument under an argon atmosphere in platinum crucibles in the temperature range of 25-150°C and 25 – 700 °C for membranes and CsPWA powder, respectively (heating rate was 10°C/min). Water uptake was determined as the difference between the initial weight of the sample and its weight after drying at 150 °C.

Proton conductivity was measured in the temperature interval from 20 to 90 °C (measurements in contact with deionized water, 100 % RH) and at different RH (measurements at t = 25 °C). To prepare the samples with different water uptake, the membranes were conditioned at different RH maintained by the saturated solutions of the following salts (RH given in parentheses): $MgCl_2$ (32 %), NaBr (58 %), NaCl (75 %) and Na_2HPO_4 (95

%). The conductivity was measured by the impedance spectroscopy in a frequency range from 10 Hz to 2 MHz using a 2B-1 impedance analyzer. Carbon sheets were used to improve the contact between the membrane and the electrodes. Conductivity was calculated from the impedance plots as the intercept on the resistance axis.

The diffusion permeability was measured in a two-chamber cell with the effective surface area S = 3.9 cm^2. The electrolyte (0.1M HCl) was transferred through the membrane into a chamber filled with deionized water. The volume of liquids in each chamber (V, cm^3) was the same. Changes in pH were measured every 3 s during the experimental runs using a pH-meter Expert-001 ("Ekoniks-expert", Russia) in the water-filled chamber. The pH-meter was calibrated using standard buffer solutions. The diffusion permeability is calculated as:

$$P = \frac{dC}{dt} \cdot \frac{Vh}{S\Delta C},$$

(1)

where h is the membrane thickness, cm; ΔC is the concentration drop, mol/cm^3; and t is time, s. The rate of concentration changes (dc/dt) was determined as the change in the proton concentration in the water-filled chamber (the accuracy in P is below 1%).

3. Results and discussion

The XRD pattern of the $Cs_xH_{3-x}PW_{12}O_{40}$ powder corresponds to the cubic modification of $Cs_{1.7}H_{1.3}PW_{12}O_{40} \cdot 3H_2O$ (Figure 1b). The unit cell parameters of crystal lattice change is 11.835±0.008 Å. SEM images show that the $Cs_xH_{3-x}PW_{12}O_{40}$ powder is composed of the aggregates with the dimensions up to 2 µm. According to the thermal analysis data, the total weight loss of $Cs_xH_{3-x}PW_{12}O_{40}$ in the temperature range of 25-700°C is 2.66 wt.%. The principal weight loss takes place at t<100°C and corresponds to dehydration process.

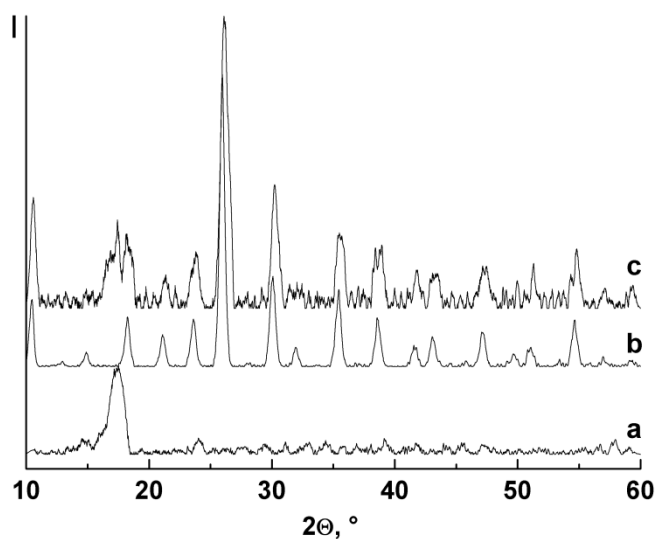Figure 1: The XRD patterns of Nafion (a), $Cs_xH_{3-x}PW_{12}O_{40}$ (b), and Nafion + 10 wt.%$Cs_xH_{3-x}PW_{12}O_{40}$ (c).

The XRD pattern of the composite membrane presents the superposition of XRD the patterns corresponding to unmodified Nafion membrane and $Cs_xH_{3-x}PW_{12}O_{40}$ powder (Figure 1). According to the XRD data, the mean size of the X-ray coherent scattering regions for $Cs_xH_{3-x}PW_{12}O_{40}$ particles within the membrane is about 30 nm. According to the TEM data, the average size of the particles in the composite membranes is about 10 nm, but bigger particles with dimensions up to 40 nm are also observed (Figure 2). The dimensions of the particles are independent of the CsPWA concentration in the membrane. Since the dopant concentration has no effect on the dimensions of the particles, one can conclude that the number of pores, where the particles are located, increases with increasing CsPWA concentration. The presence of smaller $Cs_xH_{3-x}PW_{12}O_{40}$ particles in the membrane is a result of both ultrasonic treatment and prevented aggregation of nanoparticles due to the reduced surface tension in the Nafion solution.
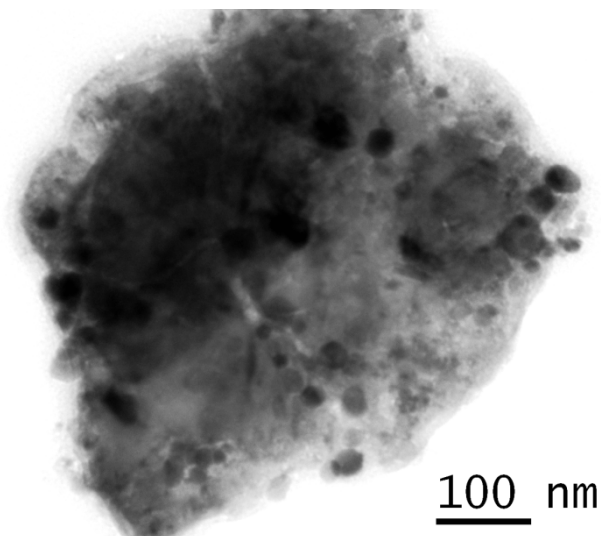
Figure 2: TEM image of the hybrid membrane based on Nafion+1.5 wt.% CsPWA.

The presence of CsPWA nanoparticles in the membrane matrix influences on proton conductivity both at high and low relative humidities. The dependence of conductivity at 100% RH on the dopant content shows the maximum at 3 wt.%. When the dopant concentration is higher than 5 wt.%, the conductivity of hybrid membranes is lower than that of the initial Nafion (Figure 3). However, the difference between the conductivities of the initial and the hybrid membranes is low and does not exceed 15 %. The decrease in RH is accompanied by the increase in the difference between the conductivities of the hybrid membranes and the initial Nafion (Figure 4). The maximum conductivity at low RH is observed for the Nafion+5 wt.% CsPWA membrane and this value is $2.7 \cdot 10^{-3}$ S/cm at RH=32% and t=25°C. This value is three times higher as compared with the conductivity of initial Nafion.
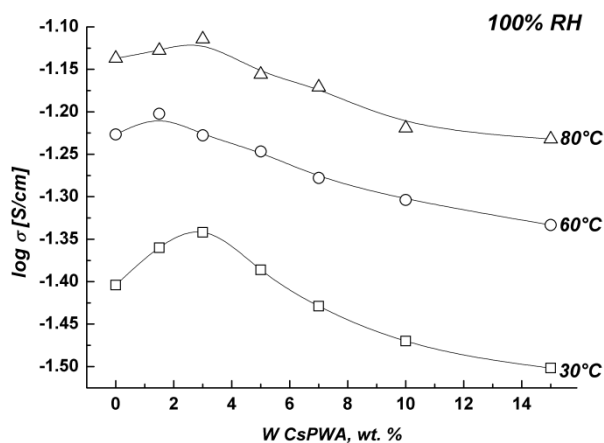

Figure 3: Proton conductivity at 100 % RH in contact with water as a function of CsPWA concentration in the membrane.
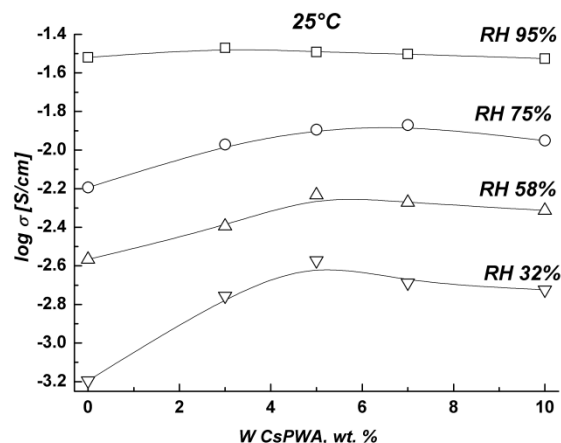
Figure 4: The dependence of proton conductivity on CsPWA concentration in the membrane at 25 °C and at different RH.

The increased conductivity of hybrid membranes can be determined by the increased number of acidic protons which serve as the current carriers. When conductivity is controlled only by the concentration of protons, the corresponding dependence on the dopant concentration is linear. However, the conductivity of the samples with high dopant concentrations is lower as compared with the conductivity of the initial Nafion membrane. This dependence of conductivity on the CsPWA concentration at 100 % RH (Figure 3) can be explained according to the model of the limited elasticity of membrane pores and channels (Novikova et al., 2010). Proton transfer in the Nafion-type membranes proceeds via the system of pores and channels (Kreuer, 2003). At RH=100%, all functional –SO$_3$H groups of membrane are fully dissociated, the concentration of

water molecules in the pores is high, and protons are transferred by hopping between water molecules (Grotthus mechanism). As a result, a double electrical layer is formed near the pore walls and protons are mostly localized within the thin Debye layer with a width of 1 nm. The proton transfer rate is controlled by the proton migration in narrow membrane channels where their mobility is a minimum. Hydrophilic functional – SO_3H groups in the Nafion solution are localized near the surface of CsPWA particles. As a result, the particle appears to be incorporated within the hydrophilic pore of the cast membrane, the dimensions of the particles and the channels connecting the pores become bigger. However, the possibility of unhampered deformation of membrane pores and channels system is limited and further increase in the dopant concentration leads to the decrease in the conductivity (Novikova et al., 2010).

When RH decreases, the Nafion membranes experience dehydration and the mechanism of proton transfer is changed. Upon dehydration at low RH, the distance between two neighbouring oxygen atoms increases and the activation energy of proton hopping increases whereas the hopping frequency decreases. At low RH, the CsPWA particles are involved in the proton transfer via its oxygen atoms. Therefore, the composite effect is more pronounced at low RH. Noteworthy is that conductivity of the hybrid membranes with high CsPWA concentration is higher than that of initial Nafion.

Table 1 shows the diffusion permeability of HCl solution through the hybrid membranes. Due to the presence of CsPWA nanoparticles in the membrane matrix, permeability of electrolyte decreases. The higher is the dopant concentration, the lower is the diffusion permeability. The diffusion permeability of Nafion+10 wt.% CsPWA membrane is five times lower than that of the virgin Nafion membrane.

Table 1: Diffusion permeability (P, cm^2/sec) of 0.1 M HCl solution for Nafion+CsPWA membranes

W CsPWA, %	0	1.5	3	5	7	10
P	$3.72 \cdot 10^{-7}$	$1.02 \cdot 10^{-7}$	$1.93 \cdot 10^{-7}$	$9.3 \cdot 10^{-8}$	$8.9 \cdot 10^{-8}$	$7.4 \cdot 10^{-8}$

A simultaneous transfer of cations and anions through the membrane takes place (transfer of only cations or only anions should be accompanied by charge separation which requires marked energy consumption). The driving force of diffusion permeability of the electrolyte solution through the membrane is the gradient of ion concentrations, and the rate of ion transfer in the membrane is controlled by the carrier concentration. Concentration of cations in the Nafion membranes is significantly higher than the concentration of anions. Hence, the rate of diffusion of anions is much higher. As a result, the rate of HCl diffusion through the membrane is determined by the anions diffusion. The protons are primarily transferred along the walls of membrane pores and channels within the limits of the thin Debye layer formed by dissociated –SO_3H functional groups and counter ions (protons or metal ions). Anions are displaced from this region and their transfer proceeds through the electrically neutral solution ("free solution") in the central part of the pore (Yaroslavtsev, 2012b). In the initial and in the composite membranes, the Debye layer along the pore walls is nearly the same. In this case, the incorporated dopant particle displaces a certain volume of the free solution where the anions are transferred. As a result, the rate of anionic transfer decreases. Furthermore due to the dissociation on the CsPWA surface, the second double (Debye) layer is formed, thus additionally hindering and slowing down the diffusion of anions.

Hence, incorporation of nanoparticles containing acidic protons decreases the diffusion rate of anions and nonpolar molecules. Since conductivity of the composite membranes containing ≤5 wt.% of CsPWA is not lower than that of the initial Nafion membrane (Figure 3), modification provides the increased selectivity of the cation transfer.

4. Conclusions

In this work, the effect of cesium acid salt of PWA on the transport characteristics of the Nafion membranes was studied. Due to modification, proton conductivity of the membranes increases. The best pronounced composite effect was observed at low RH: conductivity of the hybrid membranes appears to be three times higher than that of the initial Nafion membrane. The incorporation of CsPWA is accompanied by the retarded diffusion of anions through the membrane. The reasons behind changes in the transport characteristics of the hybrid membranes with varying ambient conditions and dopant concentrations are discussed.

The experimental data show that the membranes are characterized by higher conductivity at low RH and the cation selectivity in the hybrid Nafion+$Cs_xH_{3-x}PW_{12}O_{40}$ membranes is improved. These materials can be used as promising electrolytes for low-temperature PEMFC.

Acknowledgments

References

Ahmad H., Kamarudin S.K., Hasran U.A., Daud W.R.W., 2010, Overview of hybrid membranes for direct-methanol fuel-cell applications, Int. J. Hydr. En., 35, 2160 – 2175.

Arpornwichanop A., Suwanmanee U., Saebea D., Patcharaworachot Y., Authayanun S., 2014, Study on a proton exchange membrane fuel cell system fuelled by a mixture of bio-ethanol and methane, Chemical Engineering Transactions, 39, 1033-1038 DOI:10.3303/CET1439173.

Chandan A., Hattenberger M., Elkharouf A., Du S., Dhir A., Self V., G. Pollet B., Ingram A. Bujalski W., 2013, High temperature (HT) polymer electrolyte membrane fuel cells (PEMFC). A review, J. Power Sources 231, 264-278.

Gerasimova E.V., Safronova E.Yu., Volodin A.A., Ukshe A.E., Dobrovolsky Yu.A., Yaroslavtsev A.B., 2012, Electrocatalytic properties of the nanostructured electrodes and membranes in hydrogen-air fuel cells, Cat. Today 193, 81-86.

Kreuer, K. D., 2003, Handbook of Fuel Cells Fundamentals, Technology and Applications; Vielstich, W., Lamm, A., Gasteiger, H. A., Eds.; John Wiley & Sons Ltd: Chichester, U.K.

Li Q.F., He R.H., Jensen J.O., Bjerrum N.J., 2003, Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100°C, Chem. Mater. 15, 4896-4915.

Mahreni A., Mohamad A.B., Kadhum A.A.H., Daud W.R.W., Iyuke S.E., 2009, Nafion/silicon oxide/phosphotungstic acid nanocomposite membrane with enhanced proton conductivity, J. Membr. Sci. 327, 32-40.

Novikova S.A., Safronova E.Yu., Lysova A.A., Yaroslavtsev A.B., 2010, Influence of incorporated nanoparticles on MF-4SC membrane ion conductivity, Mend. Comm. 20, 156-157.

Prikhno I.A., Safronova E.Yu., Yaroslavtsev A.B., Wu W., 2014, Synthesis and study of hybrid materials based on the membranes of Nafion, hydrated silica, phosphotungstic heteropoly acid and its acid salts, Petrol. Chem. 54, 556-561.

Ramkumar J., 2011, Nafion perfluorosulphonate membrane: unique properties and various applications. Ch. 13. in book: Functional Materials. Elsevier, Amsterdam, The Netherlands.

Tripathi B.P., Shahi V.K., 2011, Organic-inorganic nanocomposite polymer electrolyte membranes for fuel cell applications, Prog. Pol. Sci. 36, 945-949.

Xiang Y., Yang M., Zhang J., Lan F., Lu S., 2011, Phosphotungstic acid (HPW) molecules anchored in the bulk of Nafion as methanol-blocking membrane for direct methanol fuel cells, J. Membr. Sci. 368, 241-245.

Yaroslavtsev A.B., Yaroslavtseva E.M., Chuvaev V.F., 1994, Structure, composition and electroconductivity of potassium, rubidium and cesium 12-tungstenophosphates, Zhurnl. Neorg. Khimii, 39, 948-950 (in Russian).

Yaroslavtsev A.B., Dobrovolsky Yu.A., Frolova L.A., Gerasimova E.V., Sanginov E.A., Shaglaeva N.S., 2012a, Nanostructured materials for low-temperature fuel cells, Rus. Chem. Rev. 81 191-220.

Yaroslavtsev A.B., 2012b, Correlation between the properties of hybrid ion-exchange membranes and the nature and dimensions of dopant particles, Nanotech. Russ. 7, 437–451.

The fuel cell industry review, 2013. Prepared by Johnson Matthey PLC trading <www.fuelcelltoday.com> accessed 27.02.2015.