Development of composite membrane materials for fuel cells

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Abstract. This study is devoted to the development and investigation of composite membrane materials for fuel cells. Proton conductive membranes consisting of silica and various low- and high-molecular organic compounds have been prepared by the sol-gel method. The synthesized membranes are characterized by proton conductivity (up to 10^{-2} S/cm), ion-exchange capacity (1.84-3.5 meq/g), thermal stability (260 – 400 °C), and tensile modulus (128 - 322 MPa).

1.　　　Introduction

Membrane methods are currently considered among the most promising techniques due to their high efficiency, low energy consumption, scale-up possibility and modular design [1]. They can be applied in a wide variety of areas [2-4], such as water treatment, chemical and petrochemical industry (separation of mixtures of high-molecular and low-molecular compounds, azeotropic mixtures, recovery helium from hydrogen or natural gas), food industry (pasteurization of beer, wine stabilization, producing of dairy products, juice concentration), environmental protection (control of various pollutants in water, wastewater treatment); microbiology and medicine (purification and fractionation of biologically active substances and drugs, enzymes, purification of blood, biosensors and tissues of artificial organs). In recent years there has been a dramatic increase of interests in membrane development and application for alternative energy sources – fuel cells.

Nowadays, one of the most promising types of fuel cells is polymer electrolyte membrane (PEM FC) based on proton conductive membranes. Unlike traditional energy sources, there is a direct conversion of fuel energy into electrical energy bypassing ineffective combustion processes in PEM FC. Therefore, this device is twice as efficient as, for example, internal combustion engines. In addition, during PEM FC operation, there is no release of harmful substances into the atmosphere, producing pure water as a by-product [5].

A key component of PEM fuel cells is a proton conducting membrane. There are a number of requirements to the proton conductive membrane for fuel cell operation. The membrane must conduct hydrogen ions (protons) but not electrons. It must separate the gas or fuel flows on the anode and cathode. Finally, the membrane must be chemically stable and compatible with the structure of catalyst and gas diffusion layers, providing the lowest losses at the interface boundaries and do not "poisoning" of catalysts over the range of operating temperatures and humidity [6].

Commercial membranes, such as Nafion (Du Pont, USA), possess high proton conductivity, chemical and mechanical resistance. However their high cost and several technological disadvantages (such as very low conductivities at low relative humidity or temperatures above 80ºC) limit their practical application [7, 8]. Therefore the development of new membrane materials for PEM fuel cells is nowadays an important task of both science and technology.

A number of advantages in comparison with perfluorinated Nafion-type membranes have organic-silicon composite membranes prepared by the sol-gel method. Organic-silicon composite materials combine the desired characteristics of polymers (e.g., flexibility, ductility, and processability) and inorganic supplements (e.g., heat resistance, retention of mechanical properties at high temperature, and low thermal expansion) [9,10].

Organic-silicon compounds are often used in the sol-gel process for preparation of hybrid organic-inorganic materials for practical application as effective adsorption, ion exchange and proton-conducting membranes [11-12]. Improving in physical and chemical properties of composite membranes is achieved by creating of additional cross-linked structures by introduction of organosilicon monomers - alkoxysilanes.

The aim of this work was to develop the proton-conducting organic-silicon composite membranes by the sol-gel method and to study their characteristics.

2.   Materials and methods

4-Vinylpyridine (4-VP), 2-hydroxyethyl methacrylate (HEMA), 3-pyridinesulfonic acid (PSA), 2-phenyl-5-benzimidazole sulfonic acid (FBISA), allyl glycidyl ether (AGE) (99.0%, Sigma Aldrich, styrene (ST) (99.98%, Angarsk Polymer Plant), polyvinylbutyral were used for the synthesis of membranes. Concentrated sulfuric acid (GOST 14262-78, Reaktiv) was used for sulfonation of St–AGE copolymers. Orthophosphoric acid (Reaktiv) 7 mol/L solution was used for doping of membranes based on copolymers (4-VP- HEMA). Tetraethyl orthosilicate (TEOS) (Reaktiv) was used as the precursor for the preparation of hybrid membranes.

4-VP – HEMA copolymers were prepared under conditions of free radical initiation at 60 °C by the action of azobisisobutyronitrile in dimethylformamide. Copolymers ST – AGE were obtained by suspension radical copolymerization according to a procedure described in [13]. The copolymers ST – AGE were sulfonated with concentrated sulfuric acid in benzene or toluene solution at a temperature from 60 to 90°C for 2 h. The copolymer/sulfuric acid molar ratio was 1 : 8.

The formation of ion exchange membranes was carried out by the sol–gel method similar to [14]. A mixture of copolymer solutions or heteroaromatic sulfonic acids in ethanol with TEOS was homogenized with a magnetic stirrer at 50°C for 1 h. After this, the mixture was cooled to room temperature and coated on polyethylene terephthalate surface to form thin membrane. The solvent removal and membrane structuring were performed by drying in air followed by thermal treatment at temperatures of 60, 80, and 120°C for 30 min.

Membranes based on 4-VP – HEMA copolymers were doped by immersion in 9 mol/L phosphoric acid solution for 24 hours.

The elemental analysis of the synthesis products was performed on a Thermo Finnigan gas analyzer. The IR spectra of copolymers and composites were obtained on a Specord IR-75 spectrometer in KBr tablets. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 204F1.

Proton conductivity of membranes was determined by impedance spectroscopy at temperature range of 303–343 K and 75% relative humidity on a Z-3000 instrument (Elins, Russia) using a two probe method. The measurements were conducted within the frequency range of 500–5 kHz.

The ion exchange capacity was determined by titration. Membrane samples were preliminarily held in 0.05 M sodium hydroxide solution for 24 h and subsequently titrated with 0.05 M hydrochloric acid solution.

The mechanical properties of the membranes were studied on a Shimadzu AGS-X testing machine. Test specimens were prepared in the form of a rectangle of a 25×60 mm size. The specimens were conditioned prior to testing at 23°C and 50% relative humidity for 24 h. The tests were conducted at a crosshead speed of 1 mm/min. The continuous measurement of the load and elongation of the specimens was performed in automated mode. The modulus of elasticity and elongation at break were determined using the dedicated software. The breaking strength (σ_r, MPa) was calculated according to the formula:

$$\sigma_r = \frac{F_r}{A_0},$$

where F_r is the tensile load at the time of break, N, and A_0 is the initial cross section of the sample, mm^2 (it is determined by the average values of the thickness and width).

The relative elongation at break (E, %) was calculated according to the formula:

$$E = \frac{\Delta l_{or}}{l_0} 100,$$

where l_0 is the initial gauge length of the sample, mm, and Δl_{or} is the change in the gauge length of the sample at the moment of break, mm.

3. Results and discussing

Hybrid ion-exchange membranes based on silica were prepared by sol-gel reaction of TEOS in the presence of various functional organic compounds. The subsequent thermal treatment of the membranes at 60–120°C results in the formation of semi-interpenetrating polymer networks (SIPN) consisting of silica, the three-dimensional structure of which contains intercalated macromolecules of low and high molecular compounds.
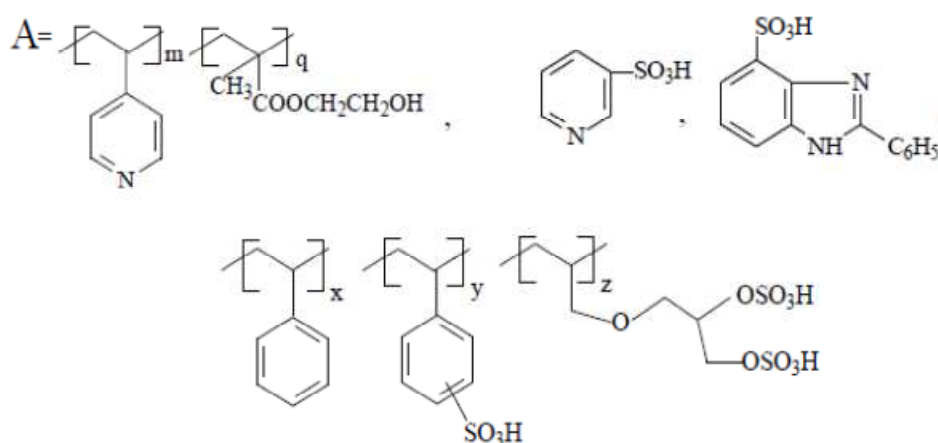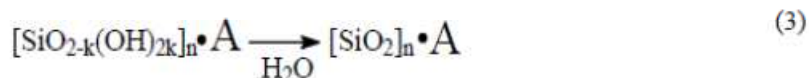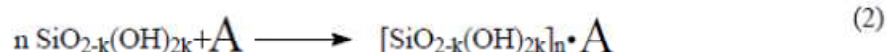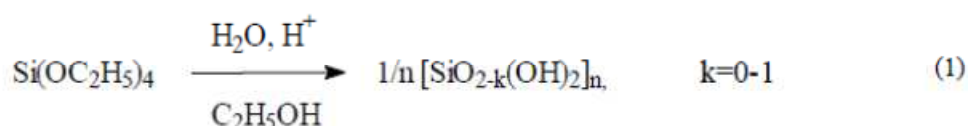
Composite synthesis by the mechanism of SIPN formation of organic and inorganic polymers opens wide possibilities for the functionalization of hybrid structures by diverse functional groups and substituents.

The structure of sol-gel synthesis products is determined by the combination of the hydrophobic part and side chains containing ionogenic groups (hydrophilic part) in their composition. The hydrophilic part of the polymer provides effective proton transport, while the hydrophobic part stabilizes the morphology of membranes and improves their mechanical strength.

There are three approaches to proton conducting membranes development in this study:
1. Preparation of hybrid membranes by sol-gel method based on nitrogen-containing high-molecular weight compounds doped with orthophosphoric acid.
2. Preparation of hybrid membranes by sol-gel method based on sulfonated copolymers of ST-AGE.
3. Introduction of low-molecular compounds in the sol-gel synthesis phase.

Formation of hybrid membranes by the sol-gel method with the participation of copolymers 4-VP-HEMA, TEOS and orthophosphoric acid (1st approach), sulfonated copolymers ST-AGE and TEOS (2d approach), as well as heteroaromatic sulfonic acids (2-phenyl-5-benzimidazole sulfonic acid (PBISA), 3-pyridinesulfonic acid (PSA), TEOS, orthophosphoric acid and polyvinyl butyral as a film former (3rd approach) can be represented with following schemes (1-3):

Membranes are gels consisting of silica particles which are uniformly distributed in the polymer matrix forming three-dimensional structure. Heteroaromatic sulfonic acids or molecules of copolymers are mechanically coupled and incorporated in the network membrane structure.

Synthesized membranes possess high thermal stability (260 - 400 °C) due to the presence of silica in their composition, which has a three-dimensional structure (Fig. 1).
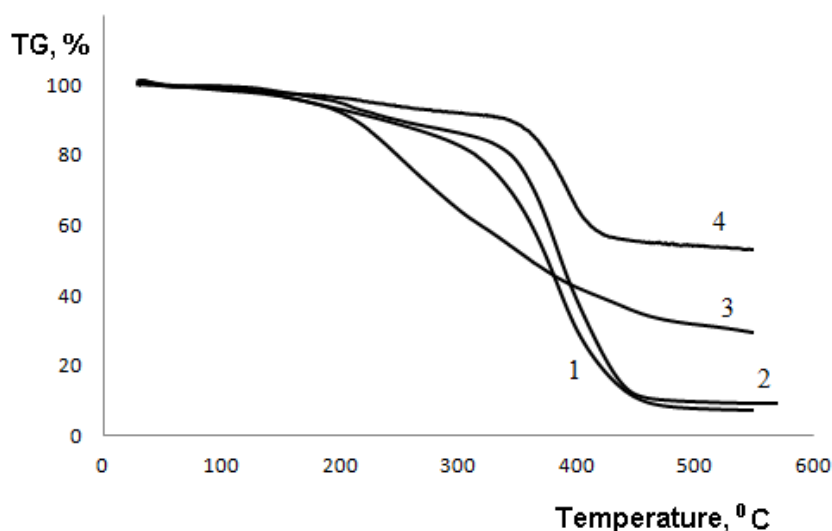

Figure 1. Thermogravimetric curves: 1 - 4-VP-HEMA-SiO_2; 2 - ST-AGE-SiO_2, 3-FBISA-SiO_2; 4 - PSA-SiO_2

The dynamic analysis data of mechanical properties and differential scanning calorimetry support the formation of SIPN. The study of the dynamics of the change in mechanical properties makes it possible to obtain information on temperature transitions and compatibility of components in investigated systems. The temperature dependence of shear modulus (E) and mechanical loss angle tangent (tan δ) has one temperature transition peak indicating the absence of phase separation and compatibility of the components in SIPN (Fig. 2).
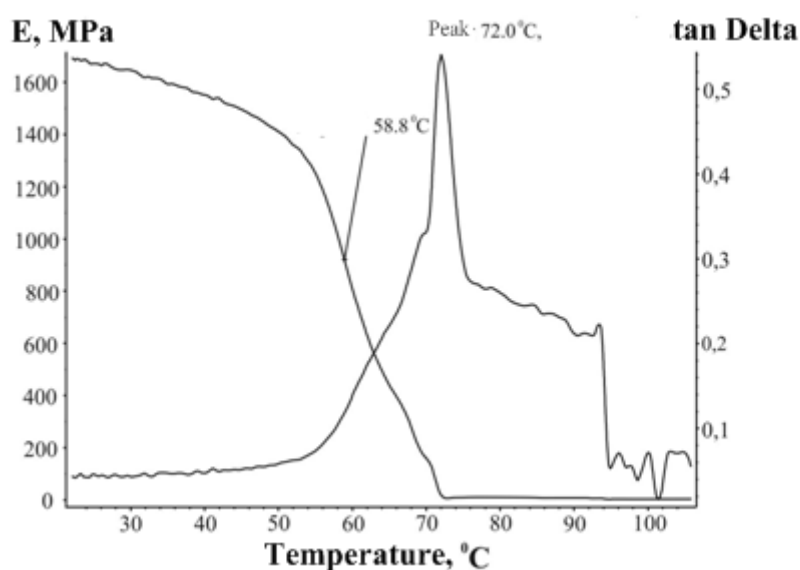

Figure 2. Temperature dependence of shear modulus (E) and mechanical loss angle tangent (tan δ) of 4-VP-GEMA-SiO_2 membrane.

Physical and technical characteristics of synthesized membranes are presented in table 1.

Table 1. Physical and technical characteristics of synthesized membranes

Parameter		Membrane			
		4-VP-HEMA-SiO$_2$	3-FBISA-SiO$_2$	PSA-SiO$_2$	ST-AGE-SiO$_2$
Ion exchange capacity, meq/g		2.1	2.7	1.84	3.5
Activation energy, E$_A$, KJ/mol K		12	21.7	24.9	25.2
Tensile modulus Ep, MPa		134	128	191	322
Heat resistance, °C		190	350	300	130
Tensile strength, σr, MPa		55	6	4	106
Ion conductivity, σ, (S/cm)·10^2	T=303 K	0.91	0.03	0.12	1.35
	T=318 K	1.20	0.04	0.19	2.04
	T=338 K	1.60	0.08	0.34	3.79
	T=353 K	1.90	0.10	0.55	4.21

4. Conclusion

Synthesized membranes are characterized by proton conductivity of the order of 10^{-2} S/ cm, ion exchange capacity 1.84-3.5 meq /g, and thermal stability from 260 to 400 ° C. The activation energy values of the proton transfer process of membranes are 12-25.2 kJ / mol·K. The mechanical properties of membranes can be varied by changing the conditions of crosslinking: tensile modulus of membranes increases from 128 to 322 MPa. Thus membranes developed in this study can be considered as prospective new materials for hydrogen fuel cells.

5. Acknowledgments

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