Hybrid membranes for fuel cells

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Abstract. Fuel cells are a very efficient, reliable, durable, and environmentally friendly energy source. Membranes for fuel cells were developed based on nitrogen-containing high-molecular compounds and organic–inorganic composites. Their electrical conductivities were measured. The influence of a silicon block of composites on the proton exchange properties of membranes was proved. The comparative characterization of the studied materials was performed.

1. Introduction
The recent studies on the development of fuel cells show the clear trend to the transition from the classic fuel cells with a liquid electrolyte to fuel cells based on a proton exchange polymer membrane (Figure 1).

Figure 1. Proton exchange membrane (PEM) fuel cell.

The main function of a proton exchange membrane is the transfer of a proton formed as a result of the hydrogen ionization on an anode into the cathode region. A number of requirements are imposed
on the proton-conducting membrane. For the efficient work of a fuel cell, the ohmic loss on a membrane must be minimized, which is achieved in case of high proton conductivity of a membrane. The specific conductivity at the level of $10^{-1}$–$10^{-3}$ S/cm is considered sufficient for the use in fuel cells. A membrane must possess significant mechanical strength so that electrodes could be pressed to a membrane. Besides water, highly chemically active hydrogen peroxide can be formed on a cathode as a result of the side reaction, thus, a membrane must possess high chemical resistance to both the oxidation and the hydrolysis. During the operation of a fuel cell, water released on a cathode is partially absorbed by a membrane, which leads to its swelling and, thus, the change in its geometric dimensions. Thus, it is desirable that the degree of swelling of a membrane were as low as possible [1].

Most of these requirements are met by the membranes based on hybrid organic–inorganic polymers [2, 3]. Similar characteristics that determine the prospects of the use in diverse electrochemical devices are typical for membranes based on spatially cross-linked interpolymer complexes synthesized, e.g., by the reaction of epichlorohydrin homopolymers or copolymers of epichlorohydrin and ethylene oxide with poly-4-vinylpyridine. The ionic conductivity of such ammonium interpolymer complexes activated by orthophosphoric acid and additionally moistened in water is $5.5 \times 10^{-3}$ S/cm at room temperature. They are thermally stable (up to 250°C) and possess the conductivity of $10^{-2}$–$10^{-4}$ S/cm at the temperature of 150°C [4, 5].

Compared to the commercial “Nafion” perfluorinated proton exchange membranes [1], products of the sol-gel synthesis with the participation of alkoxysilanes possess a number of advantages [6–10]. The function of the silicon block of such systems is mainly reduced to improving the transport of protons generated by a polymer electrolyte owing to the surface phenomena. These membranes show high proton conductivity both at room temperature and at the temperature higher than the boiling point of water (up to 120–140°C), which is unavailable for polymer membranes. It was shown that the proton conductivity of such membranes in a wide temperature range is provided by silanol groups and functional groups of the organic block doped with mineral acids. The structure of sol-gel synthesis products is determined by the combination of the hydrophobic part and side chains containing ionogenic groups (the hydrophilic part) in their composition. In the presence of water in a polymer, it is localized near ionogenic groups forming the nanosized hydrated region. In this region, besides water, there are different hydrated forms of a proton, which move freely. Thus, the hydrophilic part of the polymer provides the efficient proton transport while the hydrophobic part stabilizes the morphology of membranes providing their mechanical strength.

The described prospects of products of the sol-gel synthesis with the participation of alkoxysilanes and ionogenic organic polymers for creating proton exchange membranes brought us to the study of the transport properties of products based on the synthesized composites.

The aim of the study is to reveal the effect of the silicon block of the composites on the proton exchange properties of the formed membranes. For more correct evaluation of this effect, first, the specific electrical conductivity of the studied polymer systems not containing the silicon block, namely, poly-1-vinylpyrazole (PVP), poly-2-methyl-5-vinylpyridine (PMVP), copolymers of 2-methyl-5-vinylpyridine with vinylchloride (MVP–VC), 2-methyl-5-vinylpyridine with vinylacetate (MVP–VA) and copolymers of 1-vinylpyrazole with vinyltetrahydroindole (VP–VTHI), and 1-vinylpyrazole with vinylacetate (VP–VA), was determined.

2. Experimental
The membrane was formed from solutions of polymers and copolymer in dimethylformamide (DMFA). For increasing the membrane elasticity, a film former (polyvinylbutyral) was added to the initial (co)polymer solution. The films were created by pouring, i.e., by the uniform distribution of homogenized mixtures of (co)polymer solutions with a film former on the glass surface. The surface activation, after drying and heat treatment of films at 110°C, was performed by doping the formed
membranes with orthophosphoric acid solutions. The electrical conductivity of films was measured by
complex impedance under the isothermal mode.

3. Results and discussion
Under doping films with a 9 M H$_3$PO$_4$ solution, for homopolymers of PVP and PMVP and for MVP–
VA copolymer, the destruction of their integrity is observed. Films created using solutions of MVP–
VC copolymer under doping are not destroyed. The same films are characterized by the highest
specific electrical conductivity values (Table 1). Keeping the integrity under doping is also typical for
VP–VTHI–VA copolymers. The results obtained for VP–VTHI copolymers indicate the increase in
the electrical conductivity under the increase in the fraction of the heterocyclic fragment in the
copolymer composition (Table 1). A noticeable increase in the elasticity and electrical conductivity of
films is caused by the introduction of polyvinylacetate (PVA) in the composition of the initial mixture
(the VP–VA copolymer case) as the second film former (Table 1).

Table 1. Proton conductivity of polymer membranes based on homopolymers and
copolymers.

| No | Membrane basis (polymer, copolymer composition) | Specific conductivity, S/cm |
|----|-----------------------------------------------|----------------------------|
| 1. | PVP                                           | 2.8×10$^{-5}$              |
| 2. | PMVP                                          | 6.7×10$^{-5}$              |
| 3. | MVP–VC (80:20 mol %)                          | 9.1×10$^{-3}$              |
| 4. | MVP–VC (90:10 mol %)                          | 6.7×10$^{-3}$              |
| 5. | MVP–VA (67:33 mol %)                          | 5.5×10$^{-5}$              |
| 6. | VP–VTHI (91:9 mol %)                           | 2.17×10$^{-4}$             |
| 7. | VP–VTHI (76:24 mol %)                          | 3.5×10$^{-5}$              |
| 8. | VP–VTHI (14:86 mol %)                          | 3.0×10$^{-5}$              |
| 9. | VP–VA (80:20 mol %)                            | 1.8×10$^{-5}$              |
| 10. | VP–VA (80:20 mol %), PVA                      | 7.65×10$^{-3}$             |

The specific electrical conductivity was measured by the van der Pauw Method four-point probe
technique at the frequency of 500 Hz and the temperature of 25 °C.

The results (Table 1) show that the electrical conductivity of polymer membranes based on
homopolymers and copolymers is insufficiently high. It was assumed that the electrical conductivity of
membranes can be increased by the formation of films based on organic–inorganic composites (Figure
2).

With consideration of the high hydrolysis rate of alkoxy- and chlorosilanes used for the synthesis
of composites, the main goal of the film formation was slowing down the hydrolytic polycondensation
process with the purpose of synthesizing soluble products. The full hydrolysis of these silanes leads to
insoluble products, based on which the formation of elastic films is impossible.

Among the studied polymer systems, only composites based on alkoxyilsilanes proved to be
applicable for it. Regulating the rate of the autocatalytic process of the hydrolytic polycondensation
of trichlorosilanes is a highly complex and, in some cases, insoluble problem.

The initial solutions of composites for the formation of polymer films were synthesized by the
hydrolysis of tetraethoxysilane (TEOS), chloromethyltrithioxysilane (CMTES), and 3-
aminopropyltrithioxysilane (APTES) in the presence of (co)polymers from water–alcohol solutions in
the absence of a catalyst (alkali or acid one). The product of such a process was a soluble hydrolysate,
which was a mixture of polyorganosilsiloxanes, mainly linear-structured ones, containing a significant
number of free silanol groups (scheme 1, the case of homopolymers) [11].
Thus, the scheme of the synthesis of polymer membranes based on composites is described by the following phases:

1. The hydrolysis of alkoxysilanes from water–alcohol solutions in the presence of (co)polymers and in the absence of a catalyst under different silane–organic (co)polymer ratios. The fraction of the silicon block was varied with consideration of the necessary elasticity of the final samples and did not exceed 10 mol %.

2. The introduction of a film former (polyvinylbutyral or PVB) in the resulting hydrolysate in the ratio composite: PVB = 1 : 0.04, the homogenization of the mixture.

3. The application of the mixture of a hydrolysate and a film former on the glass surface.

4. Curing films in the process of drying in air.

5. The heat treatment at 1100°C.

6. The separation from the substrate (glass) and the membrane activation with a 9 M orthophosphoric acid solution.

In accordance with the described scheme, a series of films were created. However, not all the samples were applicable for further operation. Films based on 3-aminopropytriethoxysilane were brittle, and the attempts to dope them with a H₃PO₄ solution led to their full destruction. Also, films based on composites including 1-vinylimidazole were of low quality.
All films based on composites including TEOS and two samples based on CMTES were applicable for the proton conductivity study. The data shown in Table 2 clearly show the total increase in the electrical conductivity of films based on composites compared to films based on homopolymers and copolymers. Higher specific conductivity values are shown by polymer films including MVP fragments. The influence of the number of silanol groups on the transport properties is shown by the comparison of the conductivity of films based on TEOS and CMTES. The CMTES hydrolysis product, because of the presence of chloromethyl substitute, other things being equal, has less silanol groups compared to the analogous TEOS hydrolysis product (scheme 1). This results in a significant decrease in the specific electrical conductivity value (nos. 1, 2 and 3, 4, Table 2).

An indirect proof of the crucial importance of the silicon block for the achievement of the high proton conductivity are the data obtained for a membrane based on TEOS and copolymers of 1-vinylpyrazole and VTHI. Rather high transport activity of these samples (nos. 9, 10, Table 2), in the absence of a clearly marked predominant center, is mainly caused by the presence of the silicon block in its composition. Similar results were shown for samples based on TEOS and copolymers of 1-vinylpyrazole and methyl methacrylate (MMA) (nos. 11, 12, Table 2). However, in this case, the manifestations of the proton exchange activity owing to the hydrolysis of ester group and, thus, the formation of an additional proton generation center cannot be excluded.

The studied membranes are films of the thickness of 40–50 µm characterized by high heat resistance (up to 300°C) and good mechanical properties: the tensile strength is 51.1 ± 2.3 MPa, the relative elongation is 25 ± 5%.

Table 2. Proton conductivity of polymer membranes based on composites.

| No.  | Composite composition (molar ratio of components) | Specific conductivity, S/cm |
|------|---------------------------------------------------|----------------------------|
| 1.   | SiO$_2$ : PVP (1 : 19)                           | $5.6 \times 10^{-3}$         |
| 2.   | SiO$_2$ : PMVP (1 : 19)                          | $2.0 \times 10^{-2}$         |
| 3.   | C$_{1}$CH$_{2}$SiO$_{1.5}$ : PVP (1 : 19)        | $7.6 \times 10^{-4}$         |
| 4.   | C$_{1}$CH$_{2}$SiO$_{1.5}$ : PMVP (1 : 19)       | $3.0 \times 10^{-4}$         |
| 5.   | SiO$_2$ : copolymer MVP–VC (1 : 19)              | $1.2 \times 10^{-3}$         |
| 6.   | SiO$_2$ : copolymer MVP–VC (1 : 13)              | $8.5 \times 10^{-3}$         |
| 7.   | SiO$_2$ : copolymer MVP–VC (1 : 9)               | $4.0 \times 10^{-2}$         |
| 8.   | SiO$_2$ : copolymer MVP–VA (1 : 19)              | $1.0 \times 10^{-2}$         |
| 9.   | SiO$_2$ : copolymer VP–VTHI (1 : 19)             | $1.1 \times 10^{-3}$         |
| 10.  | SiO$_2$ : copolymer VP–VTHI (1 : 13)             | $1.7 \times 10^{-3}$         |
| 11.  | SiO$_2$ : copolymer VP–MMA (1 : 19)              | $7.8 \times 10^{-3}$         |
| 12.  | SiO$_2$ : copolymer VP–MMA (1 : 13)              | $1.4 \times 10^{-3}$         |

4. Summary

Thus, copolymers and composites based on nitrogen-containing heterocyclic compounds are materials that are of interest for the development of proton exchange membranes for hydrogen–air fuel cells, which can compete with the best Russian and foreign analogs in terms of performance characteristics.

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