New Proton-Conductive Membranes for Electromembrane Processes

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Abstract. New hybrid organic-inorganic composites based on sulfur-containing styrene copolymers and allyl glycidyl ether and tetraethoxysilane were obtained by a sol-gel synthesis method. The membranes created on the basis of composites have high proton-conductive properties and are characterized by a higher ion-exchange capacity compared with commercial membranes as Nafion and MF-4 SK. These results alloy to consider composite membranes as perspective materials for fuel cells and another electromembrane processes.

Introduction

In present days the problem of a global energy crisis related with the emission of a huge amount of toxic wastes as a result of energy resources traditional using aggravated in industrialized countries. It affects negatively the environment and causes irreversible climatic changes. The most urgent problem is searching for an alternative way of power production. One of the solutions of this problem is the development of fuel cells based on a polymeric proton-conductive membrane [1].

According to the analysis of studies on polymeric proton-conductive electrolytic membranes developing there are three groups of polymeric systems suitable for the efficient industrial application [2]:

• perfluorinated sulfur-containing polymers;
• condensation polymeric systems;
• hybrid polymeric systems (hydrogels and composites).

In industrial scale, membranes based on perfluorinated sulfur-containing polymers are generally used. They are high tech and characterized by high performance values, but they can only be used at temperatures below 90 °C and, the most important thing is the high cost, because of their production complexity. For example, Nafion membranes consist of a tetrafluorethylene copolymer and a perfluorinated sulfur-containing monomer [3]. Its producing process involves at least five independent technological stages.

Proton-conductive membranes based on condensation systems are, as a rule, formed on the basis of aromatic or heterocyclic high-molecular compounds, for example, based on polybenzimidazole, doped by the phosphoric acid. The advantage of such membranes is a high proton conductivity, considerable heat resistance (up to 600 °C), tolerance to CO and CO₂ impurities, low permeability for different types of fuel, including methanol, high mechanical strength [4]. However membranes based on those polymers are produced now as a pilot project because of the lack of commercial processes of the initial monomers production.

A new type of proton-conductive membranes is composite membranes formed on the based on organic polymers and inorganic additives.

Modification of organic ion-conducting macromolecules with inorganic components is primarily aimed at increasing the water-holding capacity and preventing dehydration of the materials made of this components. Moreover the introduction of inorganic fragments allows increasing the proton conductivity of the final composites. As inorganic additives, silicon and zirconium oxides [5, 6],
cerium oxides [7], carbon materials like nanotubes and fullerenes [8, 9], heteropolyacids such as phosphorus-tungsten or silicon-tungsten [10], poly-antimony acids [11] are widely used.

A promising type of proton-conductive membranes is hybrid composite membranes formed by the method of sol-gel synthesis based on organic polymers and silicon precursors [12]. An organic component, as a rule, contains functional groups providing a proton transport.

The introduction of silicon-containing fragments into the structure of composites can increase their thermal stability and provide additional rise of membrane conductivity due to an increase in porosity, and, consequently, an increase in the volume of channels providing proton transfer [13, 14].

The advantage of hybrid composite membranes based on organic and hetero-organic synthesis products is relative simple production technology and lower cost in comparison with commercial ones.

The purpose of this work was to obtain hybrid organic-inorganic composite materials based on modified styrene (St) and allyl glycidyl ether (AGE) copolymers using tetraethoxysilane (TEOS) as an organic-silicon precursor by sol-gel synthesis method, and to study the main characteristics of polymeric membranes obtained on their basis.

Experimental

St and AGE copolymers were obtained by a suspension free radical copolymerization method according to [15]. To provide a proton conductivity, copolymers were exposed to preliminary sulfonation by the concentrated sulfuric acid \( (p = 1.825 \, g/cm^3) \) in a benzene or toluene solution at the temperature of 60 to 90°С for 1-12 hours. The methods of turbidimetric titration, element analysis (C, H, S weight content), NMR \(^{13}\)C spectroscopy were used to determine the composition and structure of the obtained products. The formation of hybrid composites based on sulfonated copolymers was carried out similarly by sol-gel synthesis method [16]. The composites’ structure was established according to the element analysis (S, N, Si weight content) and infrared spectroscopy. The research of the synthesized samples surface structure was conducted by the scanning electron microscopy method. The impedance spectroscopy method was used to characterize the membranes proton conductivity.

Methods

Turbidimetric titration was carried out at the temperature of 25°С, the initial copolymers solution concentration in cyclohexanone was 0.96 g/100 ml, isopropanol was used as a precipitator. The optical density of solutions was determined by photoelectrocolorimeter KFO-1. The element analysis of copolymers and composites was carried out by Thermo Finnigan Flash EA 1112 Series gas analyzer. Infra-red spectrums of composites were obtained in KBr tablets and in a microlayer using Specord IR-75 spectrometer, and Bruker IFS-25 spectrometer. NMR \(^{13}\)C spectrums of copolymers were registered on VXR- 500S spectrometer “Varian” (with 125,5 MHz operating frequency) with a noise isolation from protons and with a 2,5 sec relaxation delay. The impulse was 90°. Solvents were DMSO-d6 and acetone-d6. Chrome tris-acetylacetonate (0,02 mol/l) was used as a relaxant. The examination of a surface structure of synthesized samples was conducted by the scanning electronic microscopy method using “Philips-525-M apparatus”. Films electroconductivity was measured by a complex impedance technique in isothermal mode in 500000-5000 Hz frequency range using Z-500PX impedancemeter (Elins, Russia).

Results and Discussion

Sulfonated copolymers St and AGE are powdery substances from cream to dark brown color, having a high solubility in benzene and acetone. The degree of copolymers sulfonation was 12 to 95% mol according to the element analysis.

The main active centers for the sulfonation reaction are a reactive AGE oxirane ring and St aromatic fragments. NMR \(^{13}\)C spectroscopy data are evidence of the process both on aromatic ring,
and on epoxy group with the formation of sulfur-aromatic, sulphate and hydroxyl groups in the structure of copolymers.

In spectrums of NMR $^{13}$C of sulfonated copolymers there is a signal in the 154-155 ppm field, which corresponds to a chemical shift of a carbon atom of the aromatic ring bound to a sulfur atom. Simultaneously in spectrums signals in the 65-72 ppm field appear, typical for sulphate and hydroxyl groups as a part of AGE links.

A further formation of hybrid composites represents a process of a hydrolytic condensation of the organic- silicone precursor (TEOS) and St-AGE copolymers and results in the formation of a three-dimensional silsesquioxane structure according to the scheme:

\[
\begin{align*}
\text{R: } & \text{C}_{6}H_{4}-\text{OSO}_{3}H; \\
\text{R': } & \text{CH}_{2}-\text{O-CH}_{2}(\text{OH})-\text{CH}_{2}-\text{OSO}_{3}H.
\end{align*}
\]

R: $\text{C}_{6}H_{4}-\text{OSO}_{3}H$  R': $\text{CH}_{2}-\text{O-CH}_{2}(\text{OH})-\text{CH}_{2}-\text{OSO}_{3}H$.

The obtained composites represent powdery products from a light gray to a brown color, consisting of irregular shaped particles with a typical size from 60 to 100, 200 microns (Fig. 1). In IR spectrums of samples there are absorption bands in the 1000-1200 cm$^{-1}$ field characterizing siloxane bond valent fluctuations and also in the 780-830 cm$^{-1}$ field which can be referred to Si-O-C bond valent fluctuations.

The composites retention of homogeneity and mass after processing by high-boiling organic solvents (xylene, dimethylsulfoxide) and mineral acid water solutions (5 mol/l HCl, 5 mol/l $\text{H}_{2}\text{SO}_{4}$) enables to conclude that these materials, most likely, represent semi-interpenetrating lattices.

Based on the obtained hybrid composite materials durable elastic membranes having a high thermal and chemical stability (thermal-oxidative stability temperature was 220 °C) were created. The membranes proton conductivity was measured at 30, 40, 50, 60, 70 °C temperatures and 75% relative humidity. Measurement results are given in table 1.

<table>
<thead>
<tr>
<th>Name of characteristic</th>
<th>AGE-St-SiO$_2$</th>
<th>Nafion 115</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange capacity, [mg-eq/g]</td>
<td>3,50</td>
<td>0,95</td>
</tr>
<tr>
<td>Specific conductivity, [S/cm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T=303$ K</td>
<td>1,35</td>
<td>1,67</td>
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<tr>
<td>$T=313$ K</td>
<td>2,04</td>
<td>2,25</td>
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<tr>
<td>$T=323$ K</td>
<td>2,93</td>
<td>3,00</td>
</tr>
<tr>
<td>$T=333$ K</td>
<td>3,79</td>
<td>3,75</td>
</tr>
<tr>
<td>$T=343$ K</td>
<td>4,21</td>
<td>4,50</td>
</tr>
<tr>
<td>Activation energy, [kJ/mol]</td>
<td>24,5 ± 0,7</td>
<td>21,6 ± 0,6</td>
</tr>
</tbody>
</table>

Proton conductivity of hybride membranes linearly increase from $1,35\cdot10^{-2}$ до $4,21\cdot10^{-2}$ S/cm in the temperature range from 303 to 353 K (at relative humidity 75 %). The activation energy of proton conductivity of hybrid membranes is $24,5±0,7$ kJ / mol.

Mechanical properties of the synthesized membranes are largely determined by the temperature mode of crosslinking process: with an increase in the crosslinking temperature from 60 to 120 ° C, the Young’s modulus of the membranes increases in almost 19 times (Table 2). In this case, the elasticity of materials decreases, as evidenced by a decrease in the value of the elongation of the samples at break by 37 times.

<table>
<thead>
<tr>
<th>Name of characteristic</th>
<th>Value</th>
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<tbody>
<tr>
<td>Crosslinking temperature, [°C]</td>
<td>60</td>
</tr>
<tr>
<td>Young's modulus, [MPa]</td>
<td>17</td>
</tr>
<tr>
<td>Tensile strength, [MPa]</td>
<td>4</td>
</tr>
<tr>
<td>Elongation at break, [%]</td>
<td>37</td>
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<td>Elongation at break, [%]</td>
<td>37</td>
</tr>
</tbody>
</table>
**Conclusion**

Hybrid membranes prepared by sol-gel synthesis with the participation of TEOS, as well as sulfonated copolymers of styrene and allyl glycidyl ether were studied. The membranes consist of a polymer matrix with particles of silicon dioxide distributed in it. The synthesized membranes are characterized by high proton conductivity, significant ion-exchange capacity and high heat resistance. The activation energy of the proton transfer process in St-AGE-SiO$_2$ membranes is comparable to the activation energy of proton transfer for the commercial Nafion 115 membrane.

The mechanical properties of the membranes can be varied by changing the crosslinking conditions: the tensile modulus of the membranes increases from 17 to 322 MPa, and the elongation at break decreases from 37% to 1% with an increase in the crosslinking temperature from 60 to 120 °C.

The results obtained in this work indicate that the formed hybrid organic-inorganic composite materials can be considered as promising membranes of hydrogen-air fuel cells.

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**References**


