

## Ion Exchange Membranes Based on Silica and Sulfonated Copolymers of Styrene with Allyl Glycidyl Ether

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**Abstract**—Proton-conducting membranes have been obtained by sol–gel synthesis involving tetraethyl orthosilicate and sulfonated suspension copolymers of styrene with allyl glycidyl ether. The membranes are gels consisting of a polymer matrix, in which silica particles are uniformly distributed. The synthesized membranes are characterized by the proton conductivity of up to  $4.21 \times 10^{-2}$  S/cm at 343 K and 75% humidity, an ion exchange capacity of 3.5 meq/g, a proton-transfer activation energy of  $25.2 \pm 2.6$  kJ/mol, thermal stability of up to 130°C, and mechanical strength (tensile modulus of elasticity, 322 MPa).

**Keywords:** sol–gel synthesis, tetraethyl orthosilicate, sulfonated copolymers of styrene and allyl glycidyl ether, proton exchange membrane, ion exchange capacity

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Preparation methods and properties of hybrid organic–inorganic materials are the subject of many studies aimed at, among other things, the creation of effective polymer electrolyte membranes for fuel cells [1–3]. The presence of small amounts of hydrophobic additives in the composition of such materials leads to a change in ionic conductivity, gas permeability, thermal stability, and selectivity as compared to membranes made from base polymers. The increase in the ionic conductivity in hybrid membranes is usually associated not only with the widening of pores and ion transport channels, but also with the presence of nanoparticles possessing significant affinity for mobile electrolyte ions, which can be adsorbed by the particles [1, 4].

The main function of the proton exchange membrane of a hydrogen–air fuel cell is the proton transfer to the cathode region. Most frequently, sulfo groups act as acidic proton-generating groups. Sulfo groups can be introduced into the composition of an ion exchange membrane using several techniques, such as the sulfonation of a finished polymer and polymerization (polycondensation) of sulfonated monomers; in the case of hybrid membranes, the introduction of sulfo-containing components can be performed at the composite formation stage [5, 6].

Thus, a series of copolymers with different combinations of sulfonated units was obtained via copolycondensation of terephthalic and 4,4'-oxydibenzoic acids in the presence of hydrazine sulfate and oleum. Introducing sulfonated fragments into copolymer molecules makes it possible to obtain materials with high values of ion exchange capacity (1.5 mmol/g) and water absorption (110%), while the strength and thermal stability remain at the level of base copolymers [7]. A sulfo-containing proton-conducting polymer membrane for fuel cells was obtained from a hybrid electrolyte on the basis of a polyvinyl alcohol/chitosan/polystyrene sulfonic acid/montmorillonite nanocomposite. It was shown that the methanol permeability and water absorption capacity of the composite membrane were better than those of Nafion 117. The proton conductivity was  $10^{-2}$  S/cm at room temperature and 70% relative humidity [8].

Organic–inorganic nanostructured membranes, in which an oligo(ethylene oxide) component is the proton-conducting phase and sulfonated derivatives of octahedral oligo(silsesquioxane) are proton-donating dopants, were proposed. These dopants were synthesized via the reaction of octa(aminopropyl)oligo(silsesquioxane) with 2-sulfobenzoic acid cyclic anhydride at their various ratios and contained sulfo groups alone or sulfo groups together with amino

groups in their organic framework. The synthesized membranes are stable to temperatures above 200°C. Their conductivity associated with the segmental mobility of oligo(oxyethylene) blocks (Grotthuss mechanism) is determined by the number of charge carriers and membrane structure. The maximum conductivity is  $1.03 \times 10^{-4}$  S/cm at 120°C under anhydrous conditions [9].

Composite proton-conducting membranes were also obtained in the form of interpolymer films from ethylene glycol polyvinyl glycidyl ether modified with a sulfonic acid function and polyvinyl alcohol in an aqueous medium. The initial polyhydroxy sulfonic acid was synthesized via radical polymerization of ethylene glycol vinyl glycidyl ether followed by the modification of epoxide groups with sodium sulfite and treatment with a cation exchanger in the H-form. After doping with orthophosphoric acid, the obtained proton-conducting membranes possess enhanced thermal stability (200–250°C), breaking strength of 1.0–8.9 MPa, elasticity (relative elongation of 1.0–8.2%), chemical resistance, and specific proton conductivity reaching  $10^{-1}$  S/cm [10].

Nonwoven nanofibers made of copolymers of sulfonated styrene with maleic anhydride and polyvinyl alcohol were obtained via electroforming using water as the solvent. Composite ion exchange membranes were obtained by casting a poly(methyl methacrylate) solution in chloroform over the nanofibers. The proton conductivity of the membranes increases with an increase in temperature and reaches the maximum value of  $1.67 \times 10^{-3}$  S/cm at 50°C, which is the best proton conductivity value for the membranes of such a type [11].

Sulfonated copolymers of styrene with epoxy-containing ethers, which are characterized by better mechanical properties when compared to initial polystyrene [12], are promising precursors for ion exchange membranes. In turn, hybrid composite membranes can be obtained via the sol–gel synthesis using the specified copolymers of styrene with organosilicon precursors. Such composites contain mechanically or chemically bound organic and inorganic parts in their composition, which results in the manifestation of the composite effect and substantial improvement of the properties when compared to the initial compounds [13, 14].

The aim of this work was the synthesis, exploration of structure, and investigation of the performance characteristics of new hybrid ion exchange membranes on the basis of the products of the sol–gel synthesis involving sulfonated copolymers of styrene (St) with allyl glycidyl ether (AGE) and tetraethyl orthosilicate (TEOS).

## EXPERIMENTAL

Rectified styrene (St) (99.98%, Angarsk Polymer Plant) and allyl glycidyl ether (AGE) (99.0%, Sigma Aldrich) were used for the synthesis of copolymers. Concentrated sulfuric acid of the OSCh-11-5 special purity grade (GOST 14262-78, Reaktiv) was used for the sulfonation of St–AGE copolymers. Tetraethyl orthosilicate (TEOS) (Reaktiv) was used as the precursor for the preparation of hybrid membranes.

Copolymers of St with AGE were obtained by suspension radical copolymerization according to a procedure described in [15]. To prove the preparation of copolymers, turbidimetric titration of the solutions of the samples in toluene with the copolymer concentration of 0.5 g/100 mL was used; methyl alcohol was used as the coagulator. The absorbance of the solutions was recorded using a PE-5400V photoelectric colorimeter within the wavelength range of 325–1000 nm. The copolymers were sulfonated with concentrated sulfuric acid ( $\rho = 1.825$  g/cm<sup>3</sup>) in a benzene or toluene solution at a temperature from 60 to 90°C for 2 h. The copolymer/sulfuric acid molar ratio was 1 : 8. To determine the composition and structure of the products, turbidimetric titration, elemental (C, H, S) analysis, and <sup>13</sup>C NMR spectroscopy were used.

The formation of ion exchange membranes on the basis of sulfonated copolymers was conducted similar to [14]. To obtain hybrid membranes via the sol–gel method, a mixture of copolymer solutions in ethanol with TEOS was homogenized by agitating with a magnetic stirrer (at a 300 rpm speed) at 50°C for 1 h. After this, the mixture was cooled to room temperature and applied in the form of a thin layer onto a Lavsan surface by casting. The solvent removal and membrane structuring were performed by drying in air followed by thermal treatment in a drying cabinet at temperatures of 60, 80, and 120°C for 30 min.

The structure of the composites was elucidated based on the elemental analysis data (C, H, and Si mass content) and IR spectroscopy. 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 and white oil, as well as on a Bruker IFS-25 spectrometer. <sup>13</sup>C NMR spectra of copolymers were recorded on a Varian VXR-500S spectrometer (operating at 125.5 MHz) with a relaxation delay of 2.5 s and 90° pulses in a DMSO-d<sub>6</sub> solution. Chromium tris(acetylacetonate) (0.02 mol/L) was used as the relaxant.

The specific electric conductivity of ion exchange membranes was determined by impedance spectroscopy within the temperature range of 303–343 K at 75% relative humidity on a Z-3000 instrument (Elins, Russia) in C/membrane/C symmetrical cells. The measurements were conducted within the frequency range of 500–5 kHz. The electric conductivity of the

**Table 1.** The effect of temperature on the sulfonation of styrene copolymers with allyl glycidyl ether

Composition of initial copolymer, mol %		$T, ^\circ\text{C}$	Composition of sulfonated copolymer, mol %			Degree of sulfonation, $\alpha$ , %
St	AGE		St	St <sub>sulf</sub>	AGE	
97.65	2.35	60	86.60	12.00	1.40	12.29
97.65	2.35	80	71.97	26.51	1.51	27.15
97.65	2.35	90	3.69	94.13	2.17	96.40
97.78	2.22	60	81.84	16.80	1.36	17.18
97.78	2.22	80	46.99	51.39	1.61	52.56
97.78	2.22	90	2.03	95.87	2.10	98.05

membranes on the basis of silica-free St–AGE copolymers was determined at 75% humidity and 298 K.

The mechanical properties of the membranes were studied on a Shimadzu AGS-X universal testing machine. Test specimens were prepared in the form of a rectangle of a 25 × 60 mm size. The specimens were tested in the dry state and conditioned prior to testing as described in [16] 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 an automated mode. The modulus of elasticity and elongation at break were determined using the dedicated software. The breaking strength ( $\sigma_r$ , 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<sup>2</sup> (it is determined by the average values of the thickness and width).

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

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

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

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

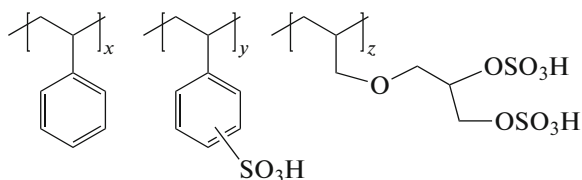
The quantum-chemical study of the mechanism of sulfonation of the St–AGE copolymer using model ethylbenzene and 2-(propoxymethyl)oxirane molecules as an example was performed by means of the Gaussian 09 software suite [17]. The geometry optimization of the structures was performed by the B3LYP method [18] with the 6-311++G(d,p) basis set [19] and taking into account the zero-point vibration energy (ZPVE). The refinement of the total energy was performed at the MP2 level [20] with the same basis set. At all the calculation steps, the nonspecific solvation was taken into account under the IEF-PCM approximation [21]; toluene was used as the solvent. For transition states, intrinsic reaction coordinate (IRC) following [22] was also performed to prove the interrelation of this transition state with the reactants and products. Relative energies presented in the text are provided for the MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) method taking into account the ZPVE calculated under the B3LYP/6-311++G(d,p) method.

## RESULTS AND DISCUSSION

Sulfonated copolymers of St with AGE are cream to dark brown powdery substances highly soluble in benzene and acetone. The degree of sulfonation of the copolymers is determined by the temperature and varies from 12 to 98 mol % (Table 1).

The IR spectra of sulfonated copolymers exhibit absorption bands in the regions of 1260–1150, 1080–1010, and 700–600  $\text{cm}^{-1}$ , which can be assigned to the asymmetric and symmetric stretching vibrations of the sulfo group. The presence of the oxirane cycle is confirmed by the presence of absorption bands at 810 and 950  $\text{cm}^{-1}$  (due to asymmetric stretching vibrations of the epoxide ring), 1250  $\text{cm}^{-1}$  (due to symmetric stretching vibrations of the epoxide ring), and 3040  $\text{cm}^{-1}$  (due to vibrations of the methylene group in the epoxide ring) in the spectrum.

The main active sites for the sulfonation reaction are the reactive oxirane ring of AGE and the aromatic St moiety. The  $^{13}\text{C}$  NMR data give evidence that the process proceeds by both the aromatic ring and the epoxide group to form arenesulfonate, sulfate, and hydroxyl groups in the structure of the copolymers (Scheme 1):



where  $x = 2-72$ ,  $y = 3-43$ , and  $z = 1$

Scheme 1.

The mechanism of sulfonation of the AGE–St copolymer was studied by the example of ethylbenzene and 2-(propoxymethyl)oxirane which mimic the styrene and allyl glycidyl ether moieties in the copolymer. The associate of  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  ( $\text{H}_2\text{S}_2\text{O}_7$ ) was chosen as the electrophilic agent, since it is this species that had been shown [23] to participate in the sulfonation at sulfuric acid concentrations above 80–85%. The performed calculations showed that the formation of products of sulfonation to the *para*-position ( $\text{Et}^p\text{C}_6\text{H}_4\text{SO}_3\text{H}$ ) and the *ortho*-position ( $\text{Et}^o\text{C}_6\text{H}_4\text{SO}_3\text{H}$ ) of ethylbenzene and at the oxirane ring of 2-(propoxymethyl)oxirane is equally probable. The activation barrier of the formation of the aforementioned sulfonation products ( $\Delta E_a$ ) from  $\text{H}_2\text{S}_2\text{O}_7$  and the model molecules is  $\sim 24$  kcal/mol.

The interaction of the epoxide group of 2-(propoxymethyl)oxirane with the sulfonating agent proceeds via the intermediate formation of 1,3,2-dioxathiolane-2,2-dioxide (I). Further opening of the 1,3,2-dioxathiolane ring via the interaction with sulfuric acid, as well as by hydrolysis, can lead to the forma-

tion of several products, namely, 1-(propoxy)propane-2,3-disulfonic acid (II), 3-hydroxy-1-(propoxy)propane-2-sulfonic acid (III), 2-hydroxy-1-(propoxy)propane-3-sulfonic acid (IV), and 1-(propoxy)propane-2,3-diol (V) (Fig. 1).

According to the results of the quantum-chemical calculations, the relative energies of formation of products II–V increase in the order 3-propoxypropane-1,2-disulfonic acid (II) ( $-40.6$  kcal/mol) < 1-hydroxy-3-propoxypropane-2-sulfonic acid (III) ( $-35.3$  kcal/mol)  $\approx$  2-hydroxy-3-propoxypropane-1-sulfonic acid (IV) ( $-33.7$  kcal/mol) < 3-propoxypropane-1,2-diol (V) ( $-18.8$  kcal/mol).

Therefore, the formation of 1-(propoxy)propane-2,3-disulfonic acid (II) is the most energetically favorable; presumably, the driving force of this process is the presence of quite strong intramolecular hydrogen bonds between the sulfo groups in final product II.

It should be noted that the strength of the effect of hydrogen bonding in II–V on their relative energy can be judged on the basis of boiling points of the “simple substances” in a first approximation. It is known that alcohols, e.g., ethanol (analogue of the intramolecular hydrogen bond in compound V) have a quite low boiling point of  $\sim 78^\circ\text{C}$ , while sulfuric acid (analogue of compound II) boils at  $337^\circ\text{C}$ ; in this case, compounds III and IV can be considered as intermediate compounds. Therefore, the formation of relatively weak hydrogen bonds (both intramolecular and intermolecular) should be expected for structure V, stronger hydrogen bonds, for structures III and IV, and, finally, the strongest hydrogen bonds should be in structure II.

As is shown in Fig. 1, product V contains no sulfo groups whatsoever. We suppose that this compound can be formed from I–IV (together with the initial epoxide) under the conditions of long-term operation of the fuel cell, namely, at elevated temperature and in presence of moisture on the polymer surface. It should be noted that the activation energy of formation of sulfonated derivatives for the model molecules is low (24 kcal/mol); thus, the sulfonation process is thermodynamically reversible. In view of the instability of the initial epoxide, the formation of the product of its hydrolysis (compound V) appears to be quite feasible. Moreover, according to the calculation results, the relative energy of compound V is lower by 18.8 kcal/mol than that of the reactant epoxide.

The preliminary estimation of the electric conductivity was performed for the membranes on the basis of silica-free sulfonated St–AGE copolymers. According to the impedance spectroscopy data, the conductivity of such membranes is insufficiently high to be  $5.1 \times 10^{-4}$  S/cm (at 75% humidity and 298 K).

In order to increase the electric conductivity and enhance the ion transport, hybrid composites were prepared on the basis of the copolymers using the sol-gel method involving TEOS.



**Table 2.** The effect of the crosslinking temperature on the mechanical properties of St–AGE–SiO<sub>2</sub> membranes

Crosslinking temperature, °C	Tensile modulus of elasticity $E_t$ , MPa	Ultimate tensile strength, $\sigma_r$ , MPa	Relative elongation at break, $E$ , %
60	17	4	37
80	97	7	12
120	322	4	1

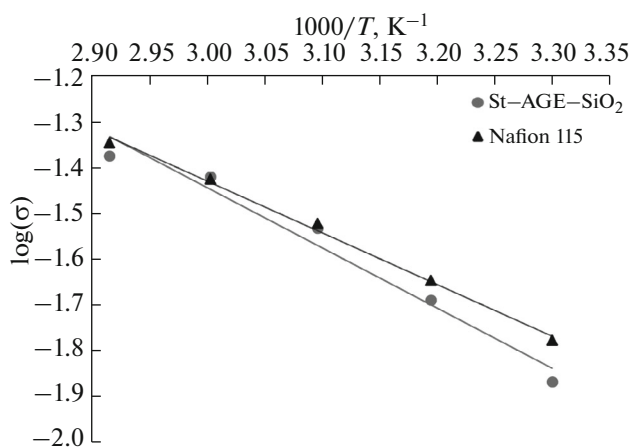
**Scheme 2.**

The subsequent thermal treatment of the composites during the fabrication of the membranes at 60–120°C results in the dehydration of polysilicic acid and the formation of interpenetrating polymer networks consisting of silica, the three-dimensional structure of which contains intercalated macromolecules of the sulfonated St–AGE copolymer.

An indirect proof of the spatially crosslinked structure of the St–AGE–SiO<sub>2</sub> membranes is their insolubility in water and organic solvents and thermal stability to 130°C.

The IR spectrum of the hybrid membranes displays intense absorption bands at 1065, 800–740, and 430 cm<sup>-1</sup> due to asymmetric, symmetric, and rocking vibrations of the siloxane bond (Si–O–Si), respectively, and at 1170–1100 cm<sup>-1</sup> due to stretching vibrations of the Si–O–C bond. This data also confirms the formation of the three-dimensional structure of the silicon framework in the gel formation process. There are also absorption bands at 1420–1300 cm<sup>-1</sup> due to stretching vibrations of the SO<sub>3</sub>H group and in the region of 710–500 cm<sup>-1</sup>, indicating the presence of the C–S bond. The spectra do not contain absorption bands of the epoxide group, confirms the epoxide ring opening during the sulfonation of the copolymers.

The mechanical properties of the synthesized membranes are to a considerable extent determined by

**Fig. 2.** Temperature dependence of the electric conductivity of (▲) Nafion 115 and (●) St–AGE–SiO<sub>2</sub> membranes.

the temperature conditions of crosslinking; thus, the modulus of elasticity of the membranes increases from 17 to 322 MPa with an increase in the crosslinking temperature from 60 to 120°C (Table 2). Note that the elasticity of the materials decreases, as evidenced by the decrease in the relative elongation at break of the samples from 37 to 1%.

In addition to good mechanical characteristics, the membranes prepared at a crosslinking temperature of 80°C turned out to be the most stable in operation in an electrochemical cell. However, the samples prepared at crosslinking temperatures of 60 and 120°C underwent visible deformation and noticeable violation of integrity. In connection with this, reliable results on the proton conductivity of hybrid membranes were obtained only for the samples obtained at the crosslinking temperature of 80°C.

For these membranes based on the St–AGE–SiO<sub>2</sub> composites, the electric conductivity was found to be higher than that of the membranes on the basis of the sulfonated St–AGE copolymers. The values of the conductivity of hybrid membranes are comparable to the corresponding parameters for Nafion 115 and linearly increase from  $1.35 \times 10^{-2}$  to  $4.21 \times 10^{-2}$  S/cm within the temperature range from 303 to 343 K (at 75% relative humidity) (Fig. 2).

The activation energy of proton conductivity in the hybrid membranes ( $E_A$ ) is  $25.2 \pm 2.6$  kJ/mol, which is comparable to the activation energy of the Nafion 115 membrane ( $21.6 \pm 0.8$  kJ/mol). The ion exchange capacity of 3.5 meq/g exceeds that for the Nafion 115 membrane (0.95 meq/g). Such characteristics of the St–AGE–SiO<sub>2</sub> membranes make them promising materials for hydrogen–air fuel cell.

**CONCLUSIONS**

Styrene–allyl glycidyl ether–silica hybrid membranes consisting of a polymer matrix with the particles of hydrated silica distributed inside it have been prepared via the sol–gel synthesis involving tetraethyl orthosilicate and sulfonated copolymers of styrene with allyl glycidyl ether. The synthesized membranes are characterized by the electric conductivity of up to  $4.2 \times 10^{-2}$  S/cm, ion exchange capacity of 3.5 meq/g, and thermal stability up to 130°C. The activation energy of proton transfer in the St–AGE–SiO<sub>2</sub> membranes is  $25.2 \pm 2.6$  kJ/mol. The mechanical proper-

ties of the membranes can be varied by changing the conditions of crosslinking; thus, the elastic modulus of the membranes increases from 17 to 322 MPa, while the elasticity of the materials decreases from 37 to 1% with an increase in the crosslinking temperature from 60 to 120°C. Therefore, the obtained materials can hold promising as membranes for hydrogen–air fuel cell.

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