

PAPER • OPEN ACCESS

Sulfonated polymer-polyorganosiloxane proton exchange membrane for alternative energy applications and environmental problem solving

To cite this article: E A Malakhova *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **320** 012044

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the [collection](#) - download the first chapter of every title for free.

Sulfonated polymer-polyorganosiloxane proton exchange membrane for alternative energy applications and environmental problem solving

E A Malakhova¹, T V Raskulova¹, O V Lebedeva² and Yu N Pozhidaev²

¹ Angarsk State Technical University, Angarsk, 665835, Russia

² Irkutsk National Research Technical University, Irkutsk, 664074, Russia

E-mail: raskulova@list.ru

Abstract. By the sol-gel synthesis involving copolymers of ethylene glycol vinyl glycidyl ether and vinyl chloride (VGE–VC) and carbofunctional organosilicon precursor 2-([triethoxysilylpropyl]amino)pyridine (TEAP), hybrid organic–inorganic membranes possessing proton conductivity after doping with orthophosphoric acid have been fabricated. The proton conductivity of the membranes VC/TEAP/H₃PO₄ in the temperature range of 30–80 °C is characterized by the values of 1.19–2.89 mS cm^{−1}.

1. Introduction

Fuel cells are a promising technology for use as a source of heat and electricity because hydrogen can be produced in an environmentally friendly manner. The main component of the fuel cell is the proton exchange membrane.

Research on the synthesis of hybrid membranes and investigation of their properties is one of the most intensively developing areas in the field of science and technology of ion-exchange materials [1]. This is determined by the broad possibilities for modifying transport properties, selectivity, mechanical and chemical stability of membranes by varying the components comprising their structure.

Heteropoly acids, oxides, transition metal salts, carbon and graphene nanoparticles, etc. showed good results as the inorganic part of hybrid membranes [2–11]. Membranes of this kind are characterized by improved ionic conductivity, mechanical properties, pore and channel structures, and water retention capacity and by significantly enhanced selectivity of transport properties in comparison with organic polymer membranes.

A vast group of organic-inorganic ion-exchange membranes includes materials doped with silica [12–20]. Nanosized silica particles can be incorporated into membranes in the form of a finished product [12–16] or obtained in the process of synthesis of a membrane via hydrolysis of tetraethoxysilane [17–20].

Due to the surface hydroxyl groups, silica can be easily modified by functional compounds to impart the required properties to it in the membrane composition [21]. For example, mesoporous silica modified with orthophosphoric acid improves the water uptake of a SiO₂/Nafion composite membrane in addition to increasing the proton conductivity [15]. Silicon dioxide functionalized with



2-(methoxy[polyethyleneoxy]propyl) trimethoxysilane is better dispersed in a polymer matrix than untreated SiO_2 [16].

Trialkoxysilanes bearing carbofunctional groups on the silicon, the hydrolysis of which leads to crosslinked silsesquioxane polymers, often serve as precursors of the silica modifier of ion-exchange membranes [10, 22–28]. Composite membranes containing polyhedral oligomeric silsesquioxanes can be used for proton transport at high temperatures and low humidity [29, 30].

Along with an increase in electrical conductivity, mechanical strength and heat resistance, a notable positive effect of the incorporation of silica or functionalized fillers on its basis into the membrane composition is the stabilization of the interphase interaction between the electrolyte and electrodes, an increase in the volume of channels providing ion transport, a decrease in the leaching of functional dopants, an increase in flexibility of composite membranes, etc. [17–21, 24]. The presented data show good prospects for research on the development of ion-exchange membranes with silicone fillers.

To obtain new proton-exchange membranes for hydrogen-air fuel cells, we use nitrogen containing organosilicon monomer – 2-([triethoxysilylpropyl]amino)pyridine, as organosilicon precursor.

Copolymers of ethylene glycol vinyl glycidyl ether (VGE) and vinyl chloride (VC) served as the polymer matrix of the membranes. The choice of these copolymers is determined by the fact that epoxy compounds are a conventional component for the production of composite materials and possess good film-forming capacity. They are also actively used for the formation and modification of hybrid nanocomposites involving nanotubes [31], montmorillonite [32], and kaolin [33]. The presence of epoxy groups in their composition makes it possible to achieve strong binding of the organic part with the organosilicon block of the membrane in the process of sol-gel synthesis and promotes the improvement of the mechanical characteristics of the membrane [34]. Earlier, we studied membranes based on sulfonated styrene–allyl glycidyl ether copolymers and silica, which provide proton conductivity of $1.35\text{--}4.21 \times 10^{-2} \text{ S cm}^{-1}$ at a relative humidity of 75% and ultimate tensile strength of 4–7 MPa [35, 36].

The aim of this work was the synthesis and investigation of the physicochemical characteristics of hybrid proton-conducting membranes on based copolymer of VGE and VC/2-([triethoxysilylpropyl]amino)pyridine/ H_3PO_4 .

2. Models and Methods

The chemicals used for the preparation of membranes were ethylene glycol vinyl glycidyl ether (VGE), vinyl chloride (VC), 2-([triethoxysilylpropyl]amino)pyridine (TEAP), orthophosphoric acid, and polyvinyl butyral (PVB). The organosilicon monomer TEAP were obtained via condensation of equimolar amounts of 3-(triethoxysilyl)propylamine with 2-aminopyridine in the presence of catalytic amounts of ammonium sulfate according to procedures described in [37]. Vinyl chloride, PVB, and reagent-grade orthophosphoric acid were commercial products.

The binary radical copolymerization of VGE with VC was carried out in a medium of organic solvents (benzene and toluene). In the course of the experiments, the concentration of the monomers in the initial mixture was varied from 5 to 90 wt % at 70 °C for 2 h at a tenfold excess of the solvent. Azobisisobutyronitrile in the amount of 1% of the total weight of the monomers was used as the initiator. The VGE–VC copolymers were precipitated with methanol and purified via reprecipitation from acetone to methanol. After reprecipitation, the copolymers were dried in a vacuum drying oven to a constant weight.

The composition of the VGE–VC copolymers was determined by elemental analysis (mass concentration of chlorine, carbon, and hydrogen), functional analysis (concentration of epoxy groups), IR and ^{13}C NMR spectroscopies.

The concentration of epoxy groups in the composition of the copolymers was determined via back titration with hydrochloric acid. A copolymer with a chlorine content of 43.86–43.42 wt % and a concentration of epoxy groups of 6.81–7.05 wt % was used for further synthesis of the composites. The molar composition of the copolymer was as follows: 88.4 mol % VC and 11.6 mol % VGE. At a higher concentration of epoxy groups, the molecular weight, strength, and elasticity of the copolymers substantially decrease.

The hybrid membrane VGE-VC/TEAP/H₃PO₄ were obtained using the sol-gel technique [15, 24, 33]. An aqueous alcohol solution of an TEAP and a solution of the VGE-VC copolymer in dimethylformamide with a weight ratio of TEAP : VGE-VC = 1 : 4 were placed into a round-bottom flask equipped with a reflux condenser and a stirrer. The flask was placed into a thermostat, and the monomer mixture was stirred at a speed of 300 rpm at 50 °C for 1 h. After completion of the reaction, the mixture was cooled to room temperature, the film forming agent PVB (10 % of the weight of the main components) was added and the mixture was homogenized and applied as a thin layer by casting onto a lavesan surface. To remove the excess of the solvents and crosslink the organosilicon component, the films were dried in air for 12 h and then in a drying oven at 80 °C for 30 min.

The obtained membranes were doped with a 9 M solution of orthophosphoric acid for 24 h and repeatedly dried in air. The phosphorus content in the VGE-VC/TEAP/H₃PO₄ membrane was 3.1 wt %.

The ¹³C NMR spectra of the copolymers were recorded on a Varian VXR-500S spectrometer (a working frequency of 125.5 MHz) with a relaxation delay of 2.5 s and a 90° pulse in a DMSO-d₆ solution.

The elemental analysis of the membranes was performed on a Thermo Finnigan gas analyzer.

The IR spectra of the copolymers and membranes on their basis were recorded on a Varian 3100 FT-IR spectrophotometer.

The investigation of the obtained composites by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) was performed on a NETZSCHDSC 204F1 Phoenix 240-12-0093-L instrument.

The ion-exchange capacity was determined via back titration, for which the membrane samples were preliminarily held in 0.05 M NaOH solution for 24 h and then titrated with 0.05 M HCl. The endpoint was determined using phenolphthalein as an indicator.

The specific electrical conductivity of the ion-exchange membranes was determined using impedance spectroscopy in the temperatures range of 30–80 °C at a relative humidity of 75% on a Z-3000 instrument (OOO Elins) in symmetrical C/membrane/C cells. The measurements were performed in the frequency range of 500–5 kHz.

The mechanical properties of the membranes were investigated on a Shimadzu AGS-X universal testing machine. Samples in the form of a rectangle with a size of 25 × 60 mm were prepared for the test. The samples were tested in a dry state and were conditioned for 24 h at 23 °C prior to testing. The tests were performed at a crosshead speed of 1 mm min⁻¹. The continuous measurement of the load and elongation of the samples was performed in the automatic mode. The Young's modulus and elongation at break were determined using the dedicated software of the instrument. The ultimate tensile 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 breaking point, N, and A_0 is the initial cross-section of the sample, mm² (determined from the average values of the thickness and width).

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

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

where l_0 is the initial calculated length of the sample, mm, and Δl_{or} is the change in the calculated length of the sample at the breaking point, mm.

Membranes samples were held in a drying oven for 24 h at 50 ± 3 °C. The dried membranes were cooled in a desiccator with a desiccant and weighed on an analytical balance with an accuracy of 0.001 g. Distilled water and the membrane samples were placed into a round-bottom flask equipped with a reflux condenser in such a way that they were fully covered with water and touched neither one another nor the flask walls.

The flask was placed in a thermostat and kept at 30, 40, 50, 60, 70, and 80°C for 24 h. After this, the membrane samples were taken out from the water, dried with filter paper, and weighed on an analytical balance with an accuracy of 0.001 g. The time lapsed from the moment of taking out to the moment of weighing should not exceed 1 min. The water uptake was calculated in percent to the weight of the dried sample according to the formula:

$$B = m_1 - m / m \cdot 100,$$

where m and m_1 are the weights of the dried sample and the sample after contact with water, respectively, g ($m = 0.199$ g and $m_1 = 0.209$ g).

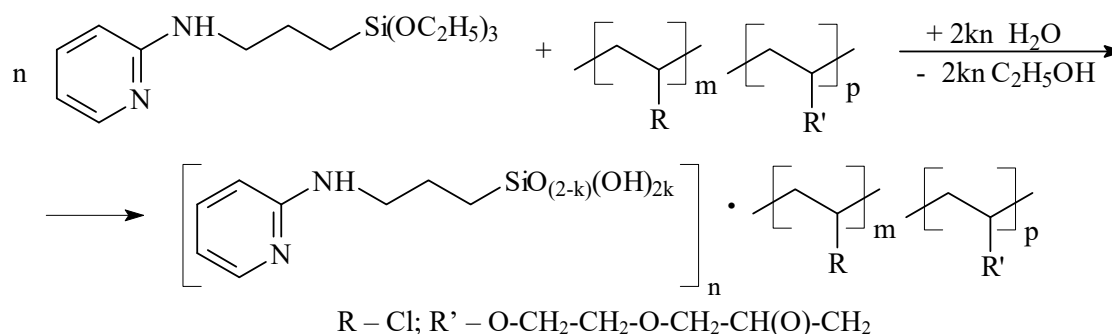
The arithmetic mean value of three experiments was taken as the result and rounded to 0.1 %.

3. Results and Discussion

The ion-exchange membranes VGE-VC/TEAP/H₃PO₄ were prepared using the hydrolytic polycondensation 2-([triethoxysilylpropyl]amino)pyridine in the presence of copolymers of ethylene glycol vinyl glycidyl ether and vinyl chloride followed by doping with orthophosphoric acid. It is known [37] that the result of the full hydrolysis of trialkoxysilanes is insoluble network polymers, so that the fabrication of elastic membranes on their basis is impossible.

Therefore, in the sol-gel synthesis of the membranes under consideration, the hydrolytic polycondensation of the reactant TEAP needs to be inhibited in order to obtain soluble products at the first stage of the synthesis and introduce a base polymer with a high film-forming capacity into the system. In this connection, the composites were formed in two steps. At the first step, a mixture of aqueous alcohol solutions of TEAP and solutions of VGE-VC copolymers in DMF was hydrolyzed in the absence of a catalyst at a ratio of TEAP : copolymer = 1 : 4. The organosilicon products of such a process are a soluble mixture of mainly linear polyorganosiloxanes with a large amount of terminal silanol groups. To increase the elasticity of the membranes, polyvinyl butyral was added to the obtained mixture as the film-forming agent.

The formation of the hybrid membranes by the sol-gel method involving TEAP in the presence of VGE-VC copolymers (in DMF solution) can be depicted by scheme:



Upon further preparation of the membranes, the film-forming agent polyvinyl butyral was added to the obtained mixture to increase the elasticity of the membranes. At the second step, the hydrolytic condensation product was subjected to thermal treatment, which leads to the additional crosslinking of polyorganosiloxanes by the terminal silanol groups and preparation of insoluble membranes with high chemical and mechanical stability and heat resistance.

The composition of the membranes based on the hybrid composites was confirmed by IR spectroscopy and elemental analysis data. The IR spectra of the VGE-VC/TEAP membranes exhibit Si-O-C and Si-O-Si stretching vibration bands and bands due to stretching and bending vibrations of the epoxide ring and aminopyridine moieties (Table 1).

Table 1. Data of the IR spectroscopy and elemental analysis of the membranes.

Characteristic bands, cm^{-1}	Concentration, wt %			n : m ^a
	N	Si	Cl	
3450, 1550 (N–H), 1660–1580 (C=N), 1370–1330 (C _{arom} –N), ~1040, 790–740, 450 (Si–O), 1120–1000 (Si–O–C), 700–600 (C–Cl), 3000–2900, 1250, 950–815, 880–750, 450 (epoxy group)	5.19	9.79	23.40	3 : 1

^aThe ratio of the organosilicon and organic polymers in the composition of the membrane.

The thermo-oxidative stability of the VGE–VC base copolymer and hybrid undoped membrane upon heating in air was studied via TG and DSC. The thermogram of VGE–VC has several characteristic segments that correspond to different copolymer degradation steps. Physically adsorbed water escapes in the range of 40–100 °C (weight loss of up to 8.0 %) without the degradation of the sample, giving the endothermic peak in the DSC curve. At 100–240 °C, the copolymer degradation processes associated primarily with the dehydrochlorination of VC units occur. The weight loss of the sample in this range was up to 30 %. Further degradation of the copolymer in the range of 240–340 °C is associated with the decomposition of the main macromolecular chain and is accompanied by the weight loss of up to 70 % of the initial weight of the sample. The decomposition of the copolymer in the temperature range of 340–550 °C leads to the full burnout of the carbon skeleton with the formation of low-molecular-weight products.

The undoped membrane possess heat resistance up to 228 °C. The character of their thermal decomposition differs from the degradation of the initial VGE–VC copolymer. The weight loss of the sample at 300 °C is up to 40 % and is associated with the decomposition of the organic copolymer and side fragments of the organosilicon part in the first place. At temperatures above 420 °C, full burnout of the organic base of the composite occurs, and the residue is silica. Therefore, the higher thermo-oxidative stability of the synthesized membranes is associated with the presence of silsesquioxane units in their composition.

The obtained membranes were subjected to doping with a 9 M solution of orthophosphoric acid for 24 h.

The doping of the membranes with orthophosphoric acid leads to the appearance of a wide IR band at 2000–2500 cm^{-1} characteristic of O–H...N hydrogen bond, which can serve as the confirmation of the formation of acid–base complexes between the nitrogen atoms of the VGE–VC/TEAP membrane and H₃PO₄. The fixation of phosphate groups by the pyridine nitrogen atoms of the organosilicon modifier determines the ion-exchange activity of the membranes.

Table 2. Physicochemical and electrical properties of the hybrid membranes.

T, °C	Water uptake, %	Ion-exchange capacity, meq g ⁻¹	Specific electrical conductivity, mS cm ⁻¹	Activation energy E _A , kJ mol ⁻¹
30	6.8	1.6	1.19	15.1
40	16.0		1.56	
50	43.5		1.73	
60	49.5		2.04	
70	54.4		2.52	
80	60.8		2.89	

The mechanical characteristics of the membranes are doped with orthophosphoric acid are represented by values: Young's modulus – 92 MPa, tensile stress at break – 7 MPa, elongation at break – 12 %.

The analysis of the impedance hodographs of the membranes under study showed that an increase in temperature from 30 to 80 °C was accompanied by a growth in the specific electrical conductivity. The activation energy of proton transport is 15.11 kJ mol⁻¹ and the ion-exchange capacity is 1.6 meq g⁻¹ (Table 2).

The low values of the water uptake of the hybrid membranes – from 6.8 to 60.8 % are determined by the presence of a crosslinked organosilicon polymer in their composition. However, this parameter substantially increases with temperature (Table 2).

4. Conclusion

Membranes that acquire proton conductivity after doping with orthophosphoric acid have been obtained via sol-gel synthesis involving ethylene glycol vinyl glycidyl ether-vinyl chloride copolymers and 2-([triethoxysilylpropyl]amino)pyridine. The proton conductivity of the orthophosphoric acid-doped membrane in the temperature range of 30–80°C is characterized by specific electrical conductivity values of 1.19–2.89 mS cm⁻¹. The activation energy of proton transport is 15.11 kJ mol⁻¹, the ion-exchange capacity is 2.5 meq g⁻¹, and the water uptake is from 6.8 to 60.8 %.

Acknowledgments

This work was supported by Russian Foundation for Basic Research, projects nos. 18-08-00718 and 18-58-45011.

References

- [1] Yaroslavl'tsev A B 2009 *Russ. Chem. Rev.* **11** 1013-29
- [2] Safronova E Yu, Parshina A V, Yankina K Yu, Ryzhkova E A, Lysova A A, Bobreshova O V and Yaroslavl'tsev A B 2017 *Pet. Chem.* **4** 327-33
- [3] Helen M, Viswanathan B, Srinivasa S 2017 *J. Membr. Sci.* **292** 98-105
- [4] Makulova S A, Karavanova Yu A, Ponomarev I I, Stenina I A and Volkova Yu A 2018 *Pet. Chem.* **4** 304-8
- [5] Prikhno I A, Safronova E Yu and Yaroslavl'tsev A B 2016 *Int. J. Hydrog. Energy* **41** 15585–92
- [6] Tasaki K, De Sousa R, Wang H B, Gasa J, Venkatesan A, Pugazhendhi P and Loutfy R O 2016 *J. Membr. Sci.* **1-2** 570-80
- [7] Ramani V, Kunz H R and Fenton J M 2004 *J. Membr. Sci.* **1-2** 31-44
- [8] Yaroshenko F A and Burmistrov V A 2018 *Pet. Chem.* **9** 770-3
- [9] Shalimov A S, Perepelkina A I, Stenina I A, Rebrov A I and Yaroslavl'tsev A B 2009 *Russ. J. Inorg. Chem.* **3** 356-60
- [10] Salarizadeh P, Javanbakht M and Pourmahdian S 2017 *RSC Adv.* **7** 8303-13
- [11] Ahmad A L, Farooqui U R and Hamid N A 2018 *RSC Adv.* **8** 25725-33
- [12] Sakamoto M, Nohara S, Miyatake K, Uchida M, Watanabe M and Uchida H 2015 *Electrochemistry* **3** 150-4
- [13] Lee J-W, Kim K, Khan S B, Han P, Seo J, Jang W and Han H 2015 *Journal of Nanomaterials* 460232
- [14] Lee J, Yi C-W and Kim K 2012 *Bull. Korean Chem. Soc.* **5** 1788-90
- [15] Lee J, Yi C-W and Kim K. 2012 *Bull. Korean Chem. Soc.* **4** 1397-400
- [16] Liu Y, Lee J Y and Hong L J 2002 *Power Sources* **2** 507-14
- [17] Qu S, Li M, Zhang C, Sun Y, Duan J, Wang W, Li J and Li X 2018 *Polymers* **1** 7
- [18] Farrukh A, Ashraf F, Kaltbeitzel A, Ling X, Wagner M, Duran H, Ghaffar A, Ur Rehman H, Parekh S H, Domke K F et al. 2015 *Polymer Chemistry* **31** 5782-9
- [19] Lebedeva O V, Sipkina E I and Pozhidaev Yu N 2016 *Pet. Chem.* **5** 401-5
- [20] Lebedeva O V, Chesnokova A N, Badlueva T V, Sipkina E I, Rzhchitskii A E and Pozhidaev Yu N 2015 *Pet. Chem.* **5** 333-8
- [21] Jung S, Kim D W, Lee S D, Cheong M, Nguyen D Q, Cho B W and Kim H S 2009 *Bull. Korean Chem. Soc.* **10** 2355-61

- [22] Huang S-L, Yu H-F and Lin Y-S 2017 *Journal of Chemistry* 4590952
- [23] Mosa J, Durán A and Aparicio M 2015 *Journal of Power Sources* **297** 208-16
- [24] Yao Z, Cui M, Zhang Z, Wu L and Xu T 2017 *Polymers* **12** 631
- [25] Vélez J F, Aparicio M and Mosa J 2016 *Electrochimica Acta* **213** 831-41
- [26] Lee J-H, Choi H, Song J-M, Sohn J-Y and Shin J 2012 *Polymer (Korea)* **6** 816-21
- [27] Lee J-H, Sohn J-Y, Shin D-W, Song J-M, Lee Y-M, Nho Y-C and Shin J 2012 *Polymer (Korea)* **4** 525-30
- [28] Lee J, Yi C-W and Kim K 2011 *Bull. Korean Chem. Soc.* **6** 1902-6
- [29] Karuppasamy K, Prasanna K, Vikraman D, Kim H-S, Kathalingam A, Mitu L and Rhee H W 2017 *Polymers* **6** 192
- [30] Kim S-K 2016 *Journal of Nanomaterials* 2954147
- [31] Irzhak V I 2011 *Russ. Chem. Rev.* **8** 787-806
- [32] Chang-fen L, Zheng-fa Zh, Hua Sh, Seng Ya, Wei-bing X and Shao-ming Y 2007 *Polym. Mater. Sci. Eng.* **2** 211-13
- [33] Noravyan O A, Karamyan R A, Eritsyanyan M L 2003 *Khim. Zh. Arm.* **3** 106-10
- [34] Raskulova T V, Volkova L I, Salaurov V N, Raskulov R M and Khaliullin A K 1998 *Russ. J. Appl. Chem.* **7** 1184-89
- [35] Lebedeva O V, Malahova E A, Sipkina E I, Chesnokova A N, Kuzmin A V, Maksimenko S D, Pozhidaev Yu N, Rzhetskiy A E, Raskulova T V and Ivanov N A 2017 *Pet. Chem.* **9** 763-9
- [36] Malahova E A, Chernigovskaya M A and Raskulova T V 2015 *Procedia Engineering* **113** 441-5
- [37] Belousova L I, Vlasova N N, Pozhidaev Yu N and Voronkov M G 2001 *Russ. J. Gen. Chem.* **12** 1879-82