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PROTON CONDUCTIVE POLYMER AND HYBRID POLYMER-INORGANIC MEMBRANES

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The aim of the work is to synthesize polymer and hybrid polymer-inorganic proton conductive membranes on the base of water soluble acrylic monomers and sol-gel precursor, and characterize their properties.

Materials, used for membrane preparation - acrylonitrile (AN), acrylic acid (AA), 3-sulfopropyl acrylate potassium salt (SPAK), tetraethoxysilane (TEOS), 3-methacryloxypropyltrimethoxysilane (MAPTMS), ethyleneglycol dimethacrylate (EGDMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA) and phosphoric acid (85 wt. %).

Methods of investigation – impedance spectroscopy, water and methanol uptake measurement, laser interferometry, SEM.

Proton conductive polymer and organic-inorganic membranes were synthesized based on acrylic monomers and silica inorganic component, derived as a result of sol-gel transformation of precursors – tetraethoxysilane (TEOS) and 3-methacryloxypropyl trimethoxysilane (MAPTMS). AA, AN and SPAK were cross-linked by irradiation with UV light at the presence of photoinitiator DMPA and cross-linker EGDMA and simultaneous hydrolytic polycondensation of sol-gel precursors. Kinetics of polymerization in situ was investigated by laser interferometry. Membranes characterization includes morphology, methanol uptake and proton conductivity at different temperatures. Morphology of the membranes investigated using SEM evidences that the material structure is homogeneous without cracks and phase separation. The membranes obtained exhibit low methanol uptake and high values of proton conductivities ($3.6 \cdot 10^{-3}$ -9.6 \cdot 10^{-3} Sm/cm) making them attractive for fuel cell application. Contact angle measurements allow to evaluate free surface energy of the membranes.

The proposed method of UV-initiated polymerization in situ allows one to obtain cross-linked sulfo group containing polymer and hybrid polymer-inorganic materials, which possesse a complex of necessary properties for their use in methanol fuel cells.

Keywords: organic-inorganic membrane, sol-gel method, proton conductivity, UV-curing, acrylate, 3-methacryloxypropyltrimethoxysilane

INTRODUCTION

In recent years the global demand for energy increased significantly as a result of industrial development and population growth. The environmental demands associated with energy production are increasing with every passing year. So, production of efficient and clean energy became a desired goal for modern industrial societies. The fuel cell technology has received a great researchers' attention due to their advantages over other types of energy production [1].

The main challenge in this scientific area is the development of a low cost membrane for fuel cell. Proton conductive membrane is the most important part of fuel cell as it is responsible for proton transport from the anode to the cathode and thus the entire fuel cell performance. Polymer electrolyte membranes (PEM) must meet the following requirements: high protonic conductivity, low electronic conductivity, impermeability to fuel gas or liquid, good mechanical toughness in both dry and hydrated states, and high oxidative and hydrolytic stability in the actual fuel cell environment [2]. Currently, the most commercially available membranes for fuel cells are based on perfluorosulfonic acid polymer membranes (e.g., Nafion, Flemion and Aciplex) [2]. These membranes have many advantages including high proton conductivity, good mechanical and chemical stability. However, they have several drawbacks which have limited their wide application: high cost and high methanol permeability. To overcome these obstacles researchers develop novel low-cost materials as alternative PEMs.

Nowadays there are several alternative novel materials that show promising properties for direct methanol fuel cell (DMFC) applications. In

the last years "heavyweight players" such as Sony, Toshiba, Nokia, Siemens, Motorola and Samsung, among others, are investing serious amounts of money in the development and commercialization of DMFC for portable applications [3].

Different methods are being explored to obtain the materials with desired properties: copolymerization, grafting, polymer blending or cross-linking. Regardless of the fabrication method, the selection of the polymers for PEMs is a very important consideration because membrane properties are significantly dependent on the polymers used.

Water soluble polymers (WSPs) have recently become increasingly interesting to both industry and academia, as they can be used in different applications such as biomaterials, drug delivery, dispersants, flocculants, membrane materials [4]. The advantage of WSPs is that they confer additional water retention capability to the membrane (particularly at high temperatures and low RHs) [5]. The investigations of the suitability of the application in fuel cells for WSPs, such as chitosan, poly(ethylene glycol), poly(vinyl alcohol), poly(vinylpyrrolidone), poly(2acrylamido-2,1-propane sulfonic acid). poly(styrene sulfonic acid) are described in numerous articles [6-8]. However, such copolymers have an excessive water absorption and, therefore, are fragile, what makes it impossible to use them for producing proton conductive membranes for fuel cells.

One of the approaches to develop PEM with higher chemical and mechanical stability is to use water soluble monomers and modify them with inorganic component, for example, combining the process of organic polymerization and sol-gel transformation of sol-gel system. For example, the authors [9] proposed the method of synthesis of a cross-linked proton conductive membrane for fuel cell based on poly(2-acrylamide-2methylpropane sulfonic acid) (PAMPS). The first sol-gel precursor is prepared on the basis of tetraethoxysilane (TEOS) and 3-methacryloxypropyl trimethoxysilane (MAPTMS). Nanocomposite organic-inorganic membranes are synthesized by free-radical copolymerization of monomers – N-vinyl-2-pyrrolidone, acrylic acid and 2-acrylamide-2-methylpropane sulfonic acid - in the presence of poly(ethylene glycol dimethacrylate) (PEGMA) and ethylene glycol dimethacrylate (EGDMA). The resulting membranes were dried in a vacuum oven at 35 °C for several days until constant weight. The nanocomposite membranes obtained have significant proton conductivity compared to that of Nafion-117. In general, the incorporation of SiO₂ improves the water retention of the hybrid membranes at high temperature.

In the present work we prepared novel polymer membranes based on water soluble acrylic monomers and polymer hybrid organicinorganic membranes based on the same monomers and sol-gel precursors MAPTMS and TEOS. Hybrid membranes synthesized using solgel method are nanocomposites, since all the products of sol-gel technique are considered to be nanomaterials [10]. Proton conductivity and water uptake measurements have been used for characterization of the obtained membranes.

EXPERIMENTAL

All reagents for membrane preparation: acrylonitrile (AN), acrylic acid (AA), potassium 3-sulfopropyl acrylate (SPAK), tetraethoxysilane (TEOS), 3-methacryloxypropyltrimethoxysilane (MAPTMS), ethyleneglycol dimetacrylate (EGDMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA) and phosphoric acid (85 wt. %) were purchased from Sigma-Aldrich and used as received.

Two types of membranes were prepared: polymer membrane based on acrylic monomers and hybrid polymer-inorganic membrane based on acrylic monomers and inorganic component formed as a result of sol-gel reaction of precursors MAPTMS and TEOS.

Synthesis of polymer membranes was carried out by the method of photoinitiated radical polymerization of acrylic monomers - acrylic acid, acrylonitrile and 3-sulfopropyl acrylate potassium salt. EGDMA was used as a crosslinker to form the cross-linked structure of copolymer. The following synthetic procedure was used for membrane preparation: the appropriate amount of SPAK was dissolved in distilled water; after the monomer was dissolved, an appropriate amount of AA and EGDMA was added to the solution and the mixture was continuously stirred at 500 rpm for 10 min. Separately the solution of a photoinitiator in a less hydrophilic monomer - AN was prepared by stirring at 500 rpm for 10 min. To initiate the process of photopolymerization, DMPA (2 wt. %) was used as a photoinitiator. Two solutions were

merged together and stirred at 500 rpm for 10 min. For polymerization, a portion of the photocomposition was cast into a glass mold $(50 \times 20 \times 0.15 \text{ mm})$ and irradiated with UV light (365 nm) for 30 min at room temperature. To prevent an access of oxygen (an inhibitor of polymerization) to a photocomposition, the mold was covered with a thin glass slide and the process was conducted in an inert atmosphere (Ar).

The organic-inorganic membranes were prepared by the similar way, additionally involving the adding of MAPTMS solution. The

SPAK, EGDMA, MAPTMS, AN, AA, SGS. Composition wt. % wt. % wt. % wt. % wt. % wt. % **S**1 45 25 15 15 _ _ 25 10 S2 45 15 15 _ S3 45 15 25 15 10 _

 Table 1. Feed compositions for membrane preparing

The method of laser interferometry was used to investigate the kinetics of photoinitiated polymerization of the prepared photocompositions. The changes in intensity of the interference pattern during contraction of polymerizing compositions were recorded as an interferogram. Conversion P (the relative degree of integrated transformation) was calculated as the ratio of contraction at a given moment to the maximal attainable one. The latter was determined as the number of peaks on the interferogram. The results of the experiment were presented as the integral kinetic curves "conversion P – time t" and their differential anamorphoses. The statistical analysis of experimental kinetic curves was performed using the ORIGIN program. In order to provide the assurance of the experimental data (due to the high fluctuation sensitivity of the polymerization process), 5 kinetic curves were obtained for each experimental condition, which were then averaged.

After UV irradiation the obtained membranes were some times washed with a large excess of acetone and water to remove unreacted compounds and dried in an oven at 50 °C until constant weight.

The morphology of the membranes was determined by scanning electron microscopy (SEM) using a NEON 40 FIB-SEM workstation (Carl Zeiss AG, Germany). For cross-sectional imaging dehydrated samples were fractioned sol-gel precursor solution was prepared by mixing of TEOS:MAPTMS (1:3 wt. p.), ethanol, water and phosphoric acid with respective ratio 1:4:2:1.8 mol/mol and stirred for 180 min at 500 rpm in 50 °C water bath. Then, sol-gel precursor solution in appropriate amount was added to the monomer mixture before gelation point and the whole formulation was stirring for 30 min. The feed monomer compositions for the preparing of polymer and hybrid organic-inorgnic membranes are summarized in Table 1.

upon being immersed in liquid nitrogen. Before imaging, samples were coated with 3 nm of Pt layer.

Water uptake of the membranes was determined by measuring of the difference of membrane mass before and after hydration. Dried at 50 °C until constant weight and weighed membranes were placed in distilled water for 24 h. Then the samples were wiped with filter paper to remove water droplets and immediately weighed. Water uptake was calculated based on 5 independent measurements using following equation:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$
where m_{dry} and m_{rry} are masses of dry and

where m_{dry} and m_{wet} are masses of dry and hydrated membrane, respectively.

The resistance of polymeric and organicinorganic membranes was measured at different temperatures by the method of impedance spectroscopy using an AUTOLAB impedance spectrometer (EcoChem, the Netherlands) with FRA software equipped by a thermostat. The films were sandwiched between Pt electrodes. Prior to the measurement the membranes were converted to acid form by immersing them in 0.1M HCl. Nyquist curves for all the samples were plot over the frequency range $10-10^5$ Hz. Specific proton conductivity was calculated using the following formula: $\sigma = 1/RS$,

where *R* is a sample resistance, Ohm; l is a sample thickness, cm; *S* is an electrode-electrolyte contact area, cm^2 .

RESULTS AND DISCUSSION

In order to prepare proton conductive membrane from commercially available monomers we choose suitable acrylic monomers - AA, AN and SPAK. Acrylic monomers are often used for preparation of hydrogel copolymers which have significant swelling and exhibit poor mechanical properties so they cannot be used as membranes. This obstacle can be overcome to a certain degree by introducing into their structure polyacrylonitrile (PAN), which creates an additional network due to the strong dipole-dipole interaction between nitrile groups of different polymer chains [11]. However, it has been found that the simple addition of presynthesized PAN to a hydrogel copolymer does not lead to increased strength. To solve this problem, acrylonitrile should be introduced into the copolymer structure at the synthesis stage.

SPAK was chosen as sulfo groupcontaining monomer. It is known that in a hydrated state immobile sulfonic acid groups of sulfonated polymers dissociate and hydronium ions $(H_3O^+, H_5O_2^+, H_9O_4^+)$ are formed *via* hydrogen bonding around sulfonic groups [12]. Hence, a choice of SPAK is based on its high proton conductivity for preparing of membranes with sufficient performance.

AA, AN and SPAK were cross-linked by irradiation with UV light (the photoinitiator DMPA (2 wt. %) was added to the photocomposition) in the presence of the crosslinker EGDMA. The scheme of the reaction of copolymer poly(AA-co-SPAK-co-AN) is synthesis presented in Fig. 1.



Fig. 1. Scheme of the synthesis of poly(AA-co-SPAK-co-AN)

As it is not easy to have a balance of proton conductivity and mechanical stability of membrane in hydrated state, the researchers test different kinds of modified materials, involving hybrid organic-inorganic systems, which can be tailored via the proper combination of monomer and inorganic components. In the present study we prepare proton conductive polymer hybrid membranes using a combination of sol-gel technique and organic polymerization. The monomers used were the same as for the synthesis of polymer membrane, additionally sol-gel TEOS-based system was used. MAPTMS was used as a monomer and simultaneously as a solgel precursor (Fig. 2).

As a result of the reactions of hydrolytic polycondensation of methoxy groups of MAPTMS and binding of the silanol groups due to hydrogen bonding, the organic-inorganic network is formed providing the channels for proton transport (Fig. 3).

By means of laser interferometry kinetic dependences of free radical cross-linking photoinitiated copolymerization of abovementioned polymerizing systems were revealed. The integral and differential curves of photoinitiated polymerization of different polymerizing systems are given in Fig. 4.

All integral kinetic curves have a typical S-shape and consist of three sections: the first

short section corresponding to the stage of polymerization initiation, the second sharp section corresponding the stage to of autoacceleration and the third section corresponding to the stage of braking of polymerization process. Kinetic parameters, presented in Table 2, indicate that adding of the sol-gel system to photocomposition significantly decreases polymerization rate, the time of the

reaching of the maximal rate, relatively, significantly increases. The maximal rate of polymerization reaction in the presence of the solgel system based on TEOS+MAPTMS (composition S2) is higher than that in the presence of MAPTMS only (composition S3). It can be attributed to the steric hindrances due to the large size of MAPTMS molecules.



Fig. 2. Scheme of the synthesis of poly(AA-co-SPAK-co-AN-co-MAPTMS)



Fig. 3. The scheme of the formation of organic-inorganic structure of hybrid membranes



Fig. 4. Integral (a) and differential (b) kinetic curves of photoinitiated polymerization 1 - S1, 2 - S2, 3 - S3

Composition	Time of w_{max} , τ_{max} , s	Conversion P at w _{max}	Max rate, w _{max} , s ⁻¹
S1	4.6	0.36	0.28
S2	21.2	0.29	0.06
S3	61.9	0.63	0.03

Table 2. Kinetic parameters of the process of photoinitiated polymerization

The determination of gel-fraction of obtained products confirms the completeness of photoinitiated polymerization and formation of the insoluble in organic solvents (acetone, methanol) cross-linked structure (Table 3).

Table 3. Gel-fraction of membranes

Sample	S1	S2	S3	
Gel-fraction, wt. %	99.88	99.64	99.74	

The synthesized membranes were homogeneous, transparent, crack-free. Their thicknesses are included in the range between 150 and 200 mµ. Morphology of the membranes were investigated using SEM. SEM image of the crosssection of membrane with a smaller and greater approximation evidences that the material structure is homogeneous without visible phase separation (Fig. 5).

Free surface energy of the composite membranes was evaluated by contact angle measurements using two liquids. Substituting the values of the measured angles of the membrane surface wetting by two fluids into the Owens-Wendt equation and solving the system of two equations, we obtain the values of the dispersive λ_s^d and hydrogen λ_s^h components of the surface energy and the total surface energy λ_s (Table 4).

As it can be seen from Table 4, the dispersive component of the membrane S2 is larger as compared to that of the membrane S3 (37.6 mN/m–31.3 mN/m), while hydrogen component of the membrane S2 is much smaller (11.2 mN/m–19.2 mN/m). The total free surface energy of the membrane S2 is also smaller as compared to that of the membrane S3, it testifies the change in hydrophilic-hydrophobic balance of the membrane surface at introducing of the sol-gel system.



Fig. 5. SEM photograph of a cross-section of the membrane S1

Sorption capability is one of the most important criteria that affects the proton conductivity and mechanical properties of the material: water medium enhances proton transport through the material, at the same time too high water uptake worsens dimensional stability of membranes. The results obtained are presented in Fig. 6.

The values of the experimentally determined water uptake of the synthesized membranes are relatively high, what is caused by the large amount of sulfo groups in the material. Unfortunately, they are also higher than the analogous value for Nafion 115 membrane. At the same time, the absorption of methanol by the membrane S1 is substantially less than the absorption of water (Fig. 6 *b*). The absorption of methanol determines the possibility of using membranes in DMFC. Taking into account the fact that the proposed membranes exhibit significantly less methanol absorption than Nafion 115, they are promising candidates for this type of fuel cells.

Proton conductivity of synthesized polymer and polymer hybrid organic-inorganic membranes was estimated from Nyquist plots (Fig. 7).

 Table 4.
 Values of contact angles and free surface energy for hybrid membranes

Sample	θ, <i>degree</i> C3H8O3	θ, <i>degree</i> CH2I2	λs ^d , mN/m	λs ^h , mN/m	λ _s , mN/m
S2	37.6	33.2	37.6	11.2	48.7
S3	34.3	35.8	31.3	19.8	51.1



Fig. 6. Sorption characteristics: a – water uptake (50 °C) of the membranes S1, S2, S3; b – water and methanol uptake of the membrane S1



Fig. 7. Nyquist diagrams for the samples S1 (a), S2 (b), S3 (c) at room temperature

The investigated membranes exhibit high values of proton conductivities: $S1 - 3.6 \cdot 10^{-3}$ Sm/cm, $S2 - 6.5 \cdot 10^{-3}$ Sm/cm, $S3 - 9.6 \cdot 10^{-3}$ Sm/cm. Proton conductivity of polymer membrane S1 was measured also at different temperatures. Fig. 8

presents a plot of conductivity values as a function of temperature. As it was expected, proton conductivity was strongly dependent on the temperature as proton transport through membrane is a thermally stimulated process [13].



Fig. 8. Ln σ of the membrane S1 as a function of temperature

CONCLUSIONS

Polymer and polymer hybrid organicinorganic membranes have been synthesized by UV polymerization of acrylic monomers and simultaneous hydrolysis-polycondensation of alkoxyradicals of sol-gel precursors TEOS and MAPTMS. The proposed method of UV polymerization in situ allows to obtain crosslinked sulfo group containing polymer and hybrid polymer-inorganic materials, which possess a complex of necessary properties for their use in methanol fuel cells. The investigated membranes exhibit sufficient water uptake and high values of proton conductivities: $S1 - 3.6 \cdot 10^{-3}$ Sm/cm, S2 - $6.5 \cdot 10^{-3}$ Sm/cm, S3 – 9.6 $\cdot 10^{-3}$ Sm/cm. The water retention property provided by formed SiO₂ clusters leads to higher proton conductivities for membranes S2 and S3 as compared to that for membrane S1 due to the connected paths for proton transport.

Протонопровідні полімерні та органо-неорганічні мембрани

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Мета роботи – синтезувати полімерні та органо-неорганічні протонопровідні мембрани на основі водорозчинних акрилових мономерів та золь-гель прекурсорів і охарактеризувати їхні властивості. Матеріали, використані для дослідження: акрилонітрил (AN), акрилова кислота (AA), 3-сульфопропілакрилат калію (SPAK), тетраетоксисилан (TEOS), 3-метакрилоксипропілтриметоксисилан (MAPTMS). етиленглікольдиметакрилат (EGDMA), 2,2-диметокси-2-фенілацетофенон (DMPA)ортофосфорна кислота (85 мас. %). Методи дослідження — імпедансна спектроскопія, вимірювання поглинання води та метанолу, лазерна інтерферометрія, SEM.

Протонопровідні полімерні та органо-неорганічні мембрани були синтезовані на основі акрилових мономерів та неорганічного компонента кремнезему, отриманого внаслідок золь-гель перетворення прекурсорів – тетраетоксисилану (TEOS) і 3-метакрилоксипропілтриметоксисилану (MAPTMS). AA, AN і SPAK були зишті з допомогою УФ випромінювання у присутності фотоініціатора DMPA і зишваючого агента EGDMA та одночасної гідролітичної поліконденсації золь-гель прекурсорів. Досліджено кінетику полімеризації іп situ методом лазерної інтерферометрії. Характеристика мембран включає морфологію, поглинання метанолу та протонну провідність при різних температурах. Морфологія мембран, досліджена методом SEM, свідчить, що структура матеріалу є однорідною, без тріщин та видимого фазового розділення. Отримані мембрани демонструють низьке поглинання метанолу та високі значення протонної провідності (3.6·10⁻³–9.6·10⁻³ См/см), що робить їх перспективними для застосування у паливних елементах. Вимірювання кутів змочування дозволило оцінити вільну поверхневу енергію мембран.

Запропонований метод УФ-ініційованої полімеризації іп situ дозволяє одержати зишті сульфовмісні полімерні і гібридні полімер-неорганічні матеріали, які мають комплекс властивостей, що забезпечують потенційне застосування їх у метанольних паливних елементах.

Ключові слова: органічно-неорганічна мембрана, золь-гель метод, протонна провідність, УФ-затвердження, акрилат, 3-метакрилоксипропілтриметоксисилан

Протонпроводящие полимерные и органо-неорганические мембраны

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Цель работы — синтезировать полимерные и органо-неорганические протонопроводящие мембраны на основе водорастворимых акриловых мономеров и золь-гель прекурсоров и охарактеризовать их свойства.

Материалы, использованные для приготовления мембран: акрилонитрил (AN), акриловая кислота (AA), 3-сульфопропилакрилат калия (SPAK), тетраэтокисисилан (TEOS), 3-мета-крилоксипропилтриметоксисилан (MAPTMS), этиленгликольдиметакрилат (EGDMA), 2,2-диметокси-2-фенилацетофенон (DMPA) и ортофосфорная кислота (85 масс. %).

Методы исследования - импедансная спектроскопия, измерение поглощения воды и метанола, лазерная интерферометрия, SEM.

Протонопроводящие полимерные и органо-неорганические мембраны были синтезированы на основе акриловых мономеров и неорганического компонента кремнезема, полученного в результате золь-гель преобразования прекурсоров - тетраэтоксисилана (TEOS) и 3-метакрилоксипропилтриметоксисилана (MAPTMS). АА, AN и SPAK получены сишванием с помощью УФ излучения в присутствии фотоинициатора DMPA и сишвающего агента EGDMA и одновременной гидролитической поликонденсации золь-гель прекурсоров. Исследована кинетика полимеризации in situ методом лазерной интерферометрии. Характеристика мембран включает морфологию, водопоглощение и протонную проводимость при различных температурах. Морфология мембран, установленная методом SEM, подтверждает формирование однородной структуры материала, без трещин и видимого фазового разделения. Полученные мембраны демонстрируют низкое поглощение метанола и высокие значения протонной проводимости (3.6·10⁻³ – 9.6·10⁻³ См/см), что делает их перспективными для применения в топливных элементах. Измерение углов смачивания позволило оценить свободную поверхностную энергию мембран.

Предложенный метод УФ-инициированной полимеризации in situ позволяет получать сиштые содержащие сульфогруппы полимерные и гибридные полимер-неорганические материалы, обладающие комплексом свойств, обеспечивающих потенциальное их применение в метанольных топливных элементах.

Ключевые слова: органо-неорганическая мембрана, золь-гель метод, протонная проводимость, УФ-затвердевание, акрилат, 3-метакрилоксипропилтриметоксисилан

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