

M.M. Zhyhailo¹, I.Yu. Yevchuk¹, O.I. Demchyna¹, V.V. Kochubei², O.I. Makota²

Cross-linked composite proton conductive membranes

¹Department of Physical Chemistry of Fossil Fuels L.M. Lytvynenko Institute of Physico-organic Chemistry and Coal Chemistry
NAS of Ukraine, 3a Naukova Str., 79053 Lviv, Ukraine, zhyhailo.mariia@gmail.com

²Lviv National Polytechnic University

Using UV-curing technique the proton conductive polymer materials based on acrylic monomers: 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA) and acrylonitrile (AN), cross-linked by varying amounts of *N,N'*-methylene(bis)acrylamide (MBA), and the hybrid polymer/inorganic membrane of the same content with addition of sol-gel system (SGS) based on 3-methacryloxypropyl trimethoxysilane (MAPTMS) and tetraethoxysilane (TEOS) were synthesized. The obtained materials were characterized by analysis of thermal, mechanical and morphological properties. Proton conductivity and water uptake were found to depend on the level of cross-linking of the materials. The value of proton conductivity of the hybrid membrane was sufficiently high reaching $3.46 \times 10^{-2} \text{ S cm}^{-1}$.

Keywords: 2-acrylamido-2-methylpropane sulfonic acid, UV-curing, sol-gel system, proton conductive membrane, fuel cell.

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Introduction

Nowadays one can observe the trend for searching new methods for energy generation because of the reduced availability of the traditional non-renewable energy resources. Alternatives seem to be fuel cells – electrochemical energy devices, using the energy from chemical reactions between a fuel and an oxidant [1-3]. The main components of a fuel cell are anode, cathode and electrolyte.

Among different types of fuel cell the polymer exchange membrane fuel cells (PEMFC) have many advantages: relatively low operating temperature, long service life, low cost and possibility for fast startups. The core component of PEMFC is a polymer electrolyte membrane (PEM) sandwiched between the electrodes. High-performance membrane material is a challenge for researchers as the effective PEMFC operation is related to PEM effectiveness. The PEMs have to meet the requirements of high proton conductivity, electrical isolation, impermeability to fuel and oxidant alongside with thermal and chemical stabilities.

Proton conductive membranes are polymers

containing fixed ionic groups, most often sulfo groups. At the contact with water the dissociation of ionic groups occurs, resulting in protons that in the form of hydronium ions H_3O^+ move from the anode to the cathode.

Recently hybrid organic/inorganic membranes have been intensively developed as the alternative for proton conductive polymer membranes since they provide unique combination of organic and inorganic component properties meeting necessary objectives. As a rule composite membranes have reduced methanol crossover making them suitable for the use in direct methanol fuel cells (DMFCs). The most popular organic/inorganic proton conductive membranes are those based on Nafion filled by inorganic nanoparticles. In the same time a lot of alternative types of proton conductive materials have been prepared and characterized [4-7]. Most of organic/inorganic hybrid materials reported in literature are thermally cured, alternatively, hybrid materials can be prepared by UV-irradiation curing.

The main goal of this work is the development of novel UV-curable organic/inorganic hybrid membranes based on acrylic monomers (2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA),

acrylonitrile (AN)) and silica nanoparticles formed in simultaneous sol-gel process. In the hybrid system, AMPS and AA units act as a proton conducting moiety while silica formed from the added sol-gel system provides structural stability and rigidity that should in turn reduce methanol permeability. AMPS was chosen as it is known as a hydrophilic monomer that contains a hydrophilic sulfonic acid functional group and a nonionic amide group [8]. AMPS homopolymer could only form gels, therefore copolymerization or extensive cross-linking is required to transform it into a solid phase. AMPS can be copolymerized easily with acrylonitrile (AN), a hydrophobic functional monomer. Acrylic acid was also used due to the ability of this hydrophilic monomer to combine with AMPS. The system was cross-linked with N,N'-methylene(bis)acrylamide. For silica nanoparticle formation the sol-gel process was used. It is the most commonly used method for the preparation of organic/inorganic hybrid materials that involves a series of hydrolysis and condensation reactions of alkoxy silane precursors.

Photopolymerization was used for curing the system as it is a high-speed, environmentally friendly technique. The substrate does not need to be heated as in traditional thermal curing; hence it saves energy [9].

I. Materials and methods

The reagents acrylonitrile (AN), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA), N,N'-methylene(bis)acrylamide (MBA), 3-methacryloxypropyl trimethoxysilane (MAPTMS), tetraethyl orthosilicate (TEOS) and photoinitiator 2,2-dimethoxy-1,2-diphenylethane-1-one (PhI) were purchased from Sigma-Aldrich. Milli-Q® water and absolute ethanol were used as solvents and phosphoric acid (85 %) as a catalyst of sol-gel reaction. All chemicals were used as received.

The preparing of the polymerizing mixtures and sol-gel systems based on TEOS and MAPTMS was carried out according to the procedures described in [10]. The feed compositions for polymerization are given in Table 1.

UV-curing were conducted by means of a multi-lamp BIO-LINK® cross-linker (BLX-365, Witec AG, Switzerland) equipped with 5 UV lamps (8W, output 0.8W). The formulations were placed into the glass moulds and exposed to UV light (365 nm) for 85 min. The resulting membranes were washed with water to remove unreacted compounds. Finally, the samples were dried in an oven at 50°C to a constant weight.

Scanning electron microscopy (SEM) images of the membranes were obtained using NEON 40 FIB-SEM

scanning electron microscope (Carl Zeiss Microscopy GmbH, Germany) using a secondary electron detector. For cross-sectional imaging, the membranes were fractured upon immersing them in liquid nitrogen. Before imaging, all the membranes were coated with ≈20 nm thick carbon layer to reduce charging in the electron beam.

The water uptake (WU) of the membranes were determined by gravimetric method. The prepared samples were dried at 50°C until constant weight was reached. Then they were weighed and placed into water solution for 24 h. When taken out from water, the samples were wiped with filter paper to remove water droplets and weighed immediately. Water uptake was calculated based on 5 independent measurements using the equation:

$$WU(\%) = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$

where m_{dry} and m_{wet} are the masses of dry and wet samples, respectively.

Mechanical properties of the membranes were analyzed by a standard tensile stress – strain test using Zwick Tensile Tester with optical strain measurement by an extensometer of Messphysik. The Young's modulus (E_t), the stress (δ_B), as well as elongation at break (ϵ_B) were determined with a crosshead speed of 1 mm min⁻¹. The membranes were punched in form of dog-bone shaped specimens for mechanical testing. The membrane specimens had a gauge length of 0.12 mm, and a cross section of 0.13 ± 0.02 mm × 1.67 ± 0.12 mm. The membranes were conditioned at room temperature and relative humidity (RH) of 50 % for 24 h before testing.

Thermogravimetric analysis was performed using Derivatograph Q-1500D (Paulik-Paulik-Erdey) within the temperature range of 20 – 800°C with a heating rate of 5°C/min under an air atmosphere.

Proton conductivity of the membranes was measured in a temperature- and humidity-controlled chamber using a four-point probe (FuMaTech GmbH, Germany). The in-plane membrane conductivity was calculated from cell geometry and membrane resistance:

$$\sigma = \frac{l}{w \times d \times R}$$

where l is the distance between electrodes (1 cm), w is the width (1.5 cm), d is the thickness of the sample, and R is the measured resistance. Membrane resistance was determined at frequency that produced the minimum imaginary response (phase angle close to zero). A Gamry Reference 600 potentiostat, operated over a frequency

Table 1

Feed formulations for membrane synthesis.

Sample	AN (wt. %)	AMPS (wt. %)	AA (wt. %)	MBA (wt. %)	PhI (wt. %)	SGS (wt. %)
PA-1	60	25	15	1	2	–
PA-2	60	25	15	2	2	–
PA-3	60	25	15	3	2	–
PA-3/SGS	60	25	15	3	2	20

range from 1 Hz to 100 kHz, was used for the conductivity measurements. The relative humidity (RH) in the sample compartment was calculated from the saturated water vapor pressure in the water compartment and in the sample compartment, at the adjusted temperatures and ambient pressure (1013 HPa), respectively:

$$RH = \frac{SWVP_{T_s}}{SWVP_{T_w}} \times 100\%$$

where $SWVP_{T_s}$ is the saturated water vapor pressure in the sample compartment at sample temperature and $SWVP_{T_w}$ is the saturated water vapor pressure in the water reservoir at water temperature. All samples were soaked in 0.1M HCl aqueous solution for 2 h at room temperature prior measurements.

II. Results and discussion

The series of the polymeric membranes was synthesized with the varied content of a cross-linker (1-3 wt. %) (Table 1). The synthesis of the polymeric membranes was carried out by photoinitiated radical polymerization of acrylic monomers AN, AMPS and AA under UV irradiation in the presence of PhI. As a result the statistic copolymer poly(AN-co-AMPS-co-AA) was formed. N,N'-methylene(bis)acrylamide (MBA) acting as a cross-linker provides 3D structure of the membrane.

This reaction is schematically expressed in Fig. 1.

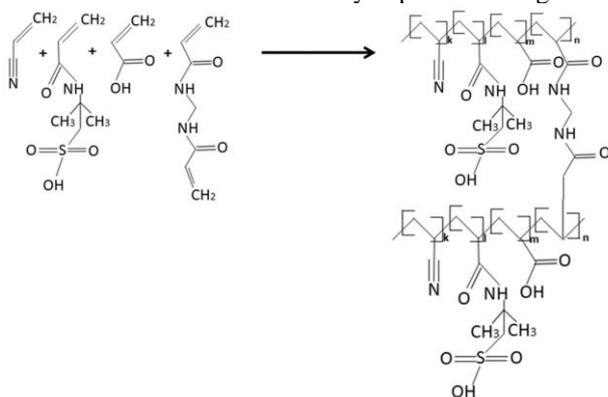


Fig. 1. Scheme of the membrane synthesis.

In the case of the hybrid polymer/inorganic membrane solutions of the sol-gel precursors – TEOS and MAPTMS – were added to the monomer mixture before the polymerization process. Simultaneously with the monomer polymerization the alkoxy groups of TEOS and MAPTMS under go in the presence of water sol-gel hydrolysis and condensation reactions giving the cross-linked silica network in the membrane. In the same time, the acrylic moiety of the organofunctional silane MAPTMS chemically bonds to a growing polymer chain to afford a homogeneous intermixing of the two networks [11, 12]. The attachment of MAPTMS from its alkoxy side with the hydrolyzed TEOS joins MAPTMS to that precursor [13]. As a result, the homogeneous material is formed consisting of the entangled interpenetrated networks containing chemically bonded inorganic and organic parts. Apart from this, in hybrid material hydrogen bonds and physical interaction are

present, therefore, well-dispersed nanostructured phases result [14-16]. Hence, the use of sol-gel method provides incorporation of an inorganic phase into an organic matrix with strong interaction (covalent bonds) in order to compatibilize two phases.

The surface morphology of materials is of a great importance as it greatly affects the thermal, mechanical and proton conductive properties of the membranes. All the synthesized membranes were thin (150 μm), transparent and exhibited sufficient flexibility. SEM images of the different parts of the poly(AN-co-AMPS-co-AA) membrane cross-section (Fig. 2a)-2d) indicate a homogeneous and compact morphology without any phase separation or voids. The cross-section of the hybrid membrane (Fig. 2e), 2f) confirms that silica is distributed uniformly in the polymer matrix. A good compatibility between the inorganic and organic components can be observed.

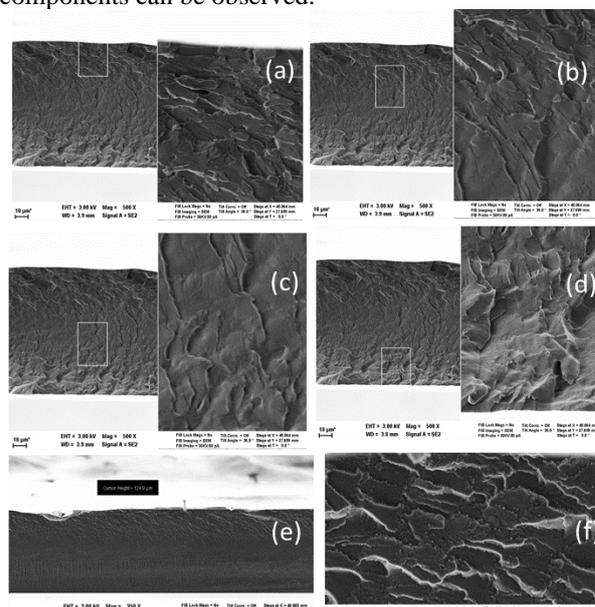


Fig. 2. SEM images of the membranes: PA-3 - a), b), c), d) and PA-3/SGS – e), f).

Water uptake is another important characteristic of the membranes as the existence of water molecules in polyelectrolyte membranes significantly affects the hydrated structures formed around the negatively charged fixed ions and the transport of protons [17]. In this study, water uptake of the membranes are plotted as a function of the amount of the added cross-linker at three different temperatures and shown in Fig 3. As one can see, the water uptake of the membranes gradually decreases with the increase of MBA content. For example, at the room temperature for the membrane PA-1 the value of WU is 270 wt. %, while for the membrane PA-3 the value of WU is 100 wt. %. This tendency takes place at all three temperatures.

At increasing temperature water uptake increases sufficiently: by 1.3, 1.25 and 1.2 times for the membranes PA-1, PA-2 and PA-3, relatively. Hence, temperature much less influences water uptake as compared with the cross-linker content in the tested range. However, water uptake of prepared membranes is too large.

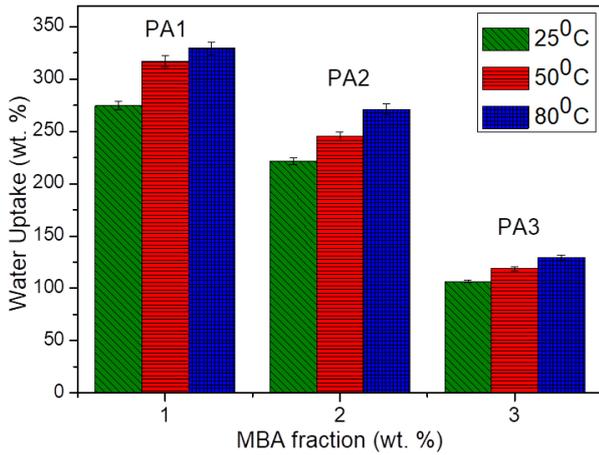


Fig. 3. Sorption properties of the membranes.

From the point of application, the proton conductivity is the major parameter used to estimate the membrane efficiency. Proton conductivity of the synthesized membranes run at the temperature 30°C, RH 95% was found to depend on the content of cross-linker component (Fig. 4): the increase in the cross-linker content leads to more dense structure resulting in the decrease of the value of proton conductivity. This trend in the membrane behavior was the same as that observed for the water uptake behavior (Fig. 3). The measured proton conductivities of the membranes were in the range $>10^{-2}$ S/cm (Fig. 4), what is comparable with the commercial membranes Nafion.

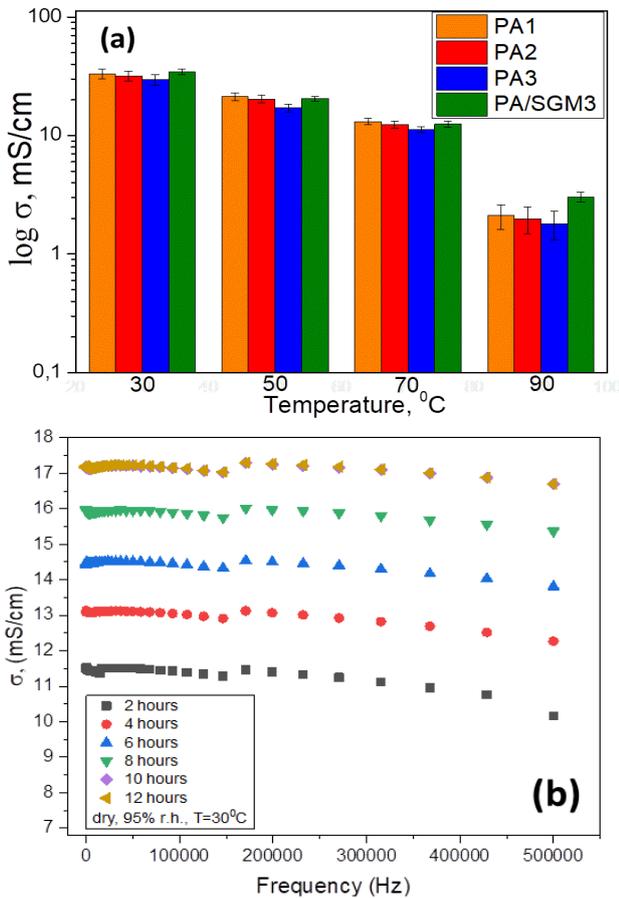


Fig. 4. Proton conductivity characteristics of the membranes: a) the dependence $\sigma - t$; b) σ for dry membrane PA-3 (equilibrium time 2 h)

The conductivity behavior of composites membranes as a function of temperature suggests the presence of two competing trends: thermal activation and membrane dehydration. Membrane degradation is well-known problem for membranes Nafion, operation limit of these membranes is 80 - 90°C. At the same time further increase of efficiency of polymer-electrolyte membrane fuel cells is associated with their possibility to function in the range of intermediate temperatures (100-120°C). For our membranes the values of proton conductivity are maximal (20-30 mS/cm) at temperatures of about 30-50°C.

The sol-gel derived silica in the membrane has an effect on improving the formation of pathways for proton transport due to molecular water absorption. The groups $\equiv\text{SiOH}$, which can bond hydrogen, have strong bonding with H_2O molecules. The dissociated proton from sulfo group moves to a water molecule bound with the SiOH bond, forming the activated $\text{H}_2\text{O} : \text{H}^+$ state ($\text{SiOH} + \text{H}_2\text{O} \rightarrow \text{SiO}^- + \text{H}^+ : \text{H}_2\text{O}$). The proton from the activated $\text{H}_2\text{O} : \text{H}^+$ state dissociates to form a new activated state with a neighboring H_2O [18]. Therefore, the proton conductivity increases due to the synergistic effect between the hydrated sulfonic group and the hydrated silica particle absorbed water molecules.

The hybrid polymer-inorganic membrane (the sample PA-3/SGS) demonstrates higher values of proton conductivity as compared with the polymeric membranes, especially at the temperature of 90°C (Fig. 4).

To determine thermal stability of the membranes we conducted thermogravimetric analysis for the samples PA1 and PA2. TGA curves (Fig. 5) show that the first weight loss at temperature range 20 - 200°C is corresponded to the loss of adsorbed and bound water. The next weight loss between 200°C and 450°C is related to the sulfo groups destruction [19]. At this stage destruction of cross-links, followed by destruction of functional groups occurs. Further heating to 800°C leads to total destruction of the membranes.

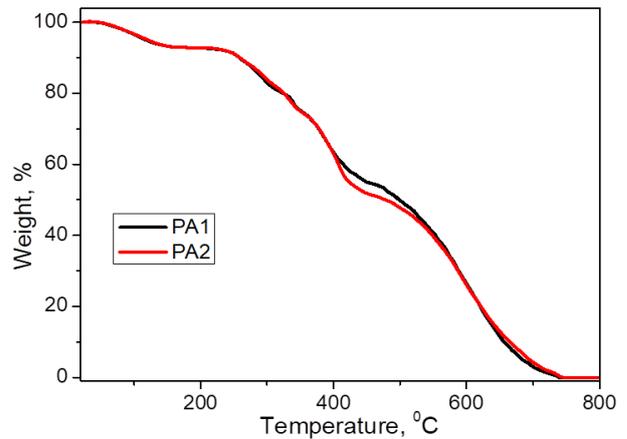


Fig. 5. Thermograms for PS1 and PS2

The measured values of mechanical properties (the Young's modulus (E_t), stress (δ_B) and elongation at break (ϵ_B)) of two sets of membranes synthesized with and without addition of the sol-gel component, are summarized in Table 2.

Table 2

Mechanical properties of the membranes.			
Membranes	Young's modulus, E_t [GPa]	Stress at break, δ_B [MPa]	Elongation at break, ϵ_B [%]
PA-3	3.34 ± 0.15	28.39 ± 0.94	8.72 ± 0.84
PA-3/SGS	2.71 ± 0.11	17.11 ± 0.86	9.96 ± 0.96

With the incorporation of the silica network, we observed a slight decrease of Young's modulus and stress at break values, while the values of ϵ_B increased slightly. An increase in the ϵ_B points toward an increased contribution of plastic deformation during membrane stretching, which may be the effect of the differences in nature and degree of cross-linking of polymeric and hybrid membranes.

Conclusions

Using UV curing method, the proton conductive polymer and hybrid polymer/silica membranes with good proton transport, mechanical properties and thermal stability were synthesized. The results obtained in this work revealed the sufficient influence of the amount of the cross-linker N,N'-methylene(bis)acrylamide in the

polyacrylate membranes. Prepared membranes reach conductivities up to $3.46 \times 10^{-2} \text{ S cm}^{-1}$, which makes them good candidates as proton exchange membranes in fuel cells.

Zhyhailo M.M. – Senior Engineer;
Yevchuk I.Yu. - Candidate of Chemical Sciences, Senior Researcher;
Demchyna O.I. – Candidate of Chemical Sciences, Research fellow;
Kochubei V.V. - Candidate of Chemical Sciences, Associate Professor of the Department of Physical, Analytical and General Chemistry;
Makota O.I. - Doctor of Sciences, Professor of the Department of Physical, Analytical and General Chemistry.

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М.М. Жигайло¹, І.Ю. Євчук¹, О.І. Демчина¹, В.В. Кочубей², О.І. Макота²

Зшиті композитні протонопровідні мембрани

¹ Відділення фізико-хімії горючих копалин Інституту фізико-органічної хімії і вуглехімії ім. Л.М. Литвиненка НАН України, вул. Наукова 3а, 79053 Львів, Україна, zhyhailo.maria@gmail.com

² Національний університет «Львівська політехніка»

Із використанням методу УФ-твердження шляхом вільно-радикальної фотоініційованої кополімеризації суміші мономерів було проведено синтез протонопровідних полімерних матеріалів на основі акрилових мономерів: 2-акриламід-2-метилпропансульфокислоти (AMPS), акрилової кислоти (AA) та акрилонітрилу (AN), які були зшиті різною кількістю зшивача *N,N'*-метилен(біс)акриламід (MBA), та гібридної неорганічно/полімерної мембрани такого ж складу з додаванням золь-гель системи (SGS) на основі 3-метакрилоксипропілтриметоксисилану (MAPTMS) та тетраетоксисилану (TEOS). Досліджено морфологічні, механічні та термічні властивості, протонну провідність та водопоглинання отриманих матеріалів. Встановлено, що протонна провідність і водопоглинання залежать від ступеня зшивання синтезованих матеріалів. Значення протонної провідності гібридної мембрани було достатньо високим, досягаючи $3,46 \times 10^{-2} \text{ См} \cdot \text{см}^{-1}$.

Ключові слова: 2-акриламід-2-метилпропансульфонова кислота, УФ-твердження, золь-гель система, протонопровідна мембрана, паливний елемент.