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UV-CURABLE PROTON CONDUCTIVE ORGANIC-INORGANIC MEMBRANES BASED ON ACRYLIC MONOMERS AND SOL-GEL DERIVED SILICA

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Abstract

This article describes the synthesis and characterization of the new UV-curable cross-linked hybrid polymer-inorganic materials. The membranes were synthesized *via* UV-initiated copolymerization *in situ* based both on hydrophilic and hydrophobic acrylic monomers with the simultaneous formation of inorganic network in sol-gel reaction of precursors 3-methacryloxypropyl trimethoxysilane (MAPTMS) and tetraethyl orthosilicate (TEOS). The composition of the polymeric counterpart was varied by changing the ratio of hydrophilic and hydrophobic monomers while the content of the inorganic counterpart was kept constant. FTIR, SEM were used to characterize the morphology and chemical structure of the resulting membranes. The proton conductivity, oxidative stability, water and methanol uptake of the synthesized membranes were measured, and strong correlation between the properties of the membranes and the monomer ratio (AMPS : AA) was established, which makes it possible to regulate the membrane characteristics. The obtained new UV-curable cross-linked hybrid polymer-inorganic materials can be used for the development of the proton-conducting membranes for fuel cells.

Keywords: 2-acrylamido-2-methylpropane sulfonic acid; acrylic acid; acrylonitrile; *N,N'*-methylene(bis)acrylamide; sol-gel; proton conductive membrane.

УФ-ЗАТВЕРДЖЕНІ ПРОТОНОПРОВІДНІ ОРГАНО-НЕОРГАНІЧНІ МЕМБРАНИ НА ОСНОВІ АКРИЛОВИХ МОНОМЕРІВ ТА КРЕМНЕЗЕМУ, УТВОРЕНОГО ЗОЛЬ-ГЕЛЬ МЕТОДОМ

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Анотація

У даній статті описано синтез і властивості нових УФ-затверджених зшитих гібридних полімер-неорганічних мембран. Мембрани синтезували методом радикальної фотоініційованої кополімеризації *in situ* – на основі гідрофільних та гідрофобних акрилових мономерів з одночасним проведенням золь-гель процесу прекурсорів: 3-метакрилоксипропілтриметоксисилану (МАПТМС) та тетраетилортоسیлікату (ТЕОС), введених у полімеризаційну композицію допочатку гелеутворення. Склад вихідних композицій для полімерної матриці змінювали, варіюючи співвідношення гідрофільних та гідрофобних мономерів, тоді як вміст неорганічного компонента підтримували постійним. Методи FTIR, СЕМ використовувались для характеристики морфології та хімічної структури отриманих нових гібридних полімер-неорганічних мембран. Були виміряні основні характеристики синтезованих мембран: протонна провідність, окиснювальна стабільність, поглинання води та метанолу. Встановлено значну кореляцію між властивостями мембран та співвідношенням мономерів АМПК : АК, що дозволяє регулювати характеристики мембран. Отримані нові УФ-затверджені зшиті гібридні полімер-неорганічні матеріали можуть бути використані для розробки протонопровідних мембран паливних елементів.

Ключові слова: 2-акриламід-2-метилпропансульфонова кислота; акрилова кислота; акрилонітрil; *N,N'*-метилен(біс)акриламід; золь-гель метод; протонопровідна мембрана.

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УФ-ОТВЕРЖДЕННЫЕ ПРОТОНПРОВОДЯЩИЕ ОРГАНО-НЕОРГАНИЧЕСКИЕ МЕМБРАНЫ НА ОСНОВЕ АКРИЛОВЫХ МОНОМЕРОВ И КРЕМНЕЗЕМА, ПОЛУЧЕННОГО ЗОЛЬ-ГЕЛЬ МЕТОДОМ

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Аннотация

В данной статье описан синтез и свойства новых УФ-отвержденных сшитых гибридных полимер-неорганических мембран. Мембраны синтезировали с помощью радикальной фотоиницированной сополимеризации *in situ* – на основе гидрофильных и гидрофобных акриловых мономеров с одновременным проведением золь-гель процесса прекурсоров: 3-метакрилоксипропилтриметоксисилана (МАПТМС) и тетраэтилортосиликата (ТЕОС), введенных в полимеризационную композицию до начала гелеобразования. Состав исходных композиций для полимерной матрицы изменяли, варьируя соотношение гидрофильных и гидрофобных мономеров, тогда как содержание неорганического компонента поддерживали постоянным. Методы FTIR, СЕМ использовались для характеристики морфологии и химической структуры полученных новых гибридных полимер-неорганических мембран. Были измерены основные характеристики синтезированных мембран: протонная проводимость, окислительная стабильность, поглощение воды и метанола. Установлена значительная корреляция между свойствами мембран и соотношением мономеров АМПК : АК, что позволяет регулировать характеристики мембраны. Полученные новые УФ-отвержденные сшитые гибридные полимер-неорганические материалы могут быть использованы для разработки протонпроводящих мембран для топливных элементов.

Ключевые слова: 2-акриламидо-2-метилпропансульфоновая кислота; акриловая кислота, акрилонитрил; *N,N'*-метилен(бис)акриламид; золь-гель метод; протонопроводящая мембрана.

Introduction

In the industrialized countries the excessive use of fossil fuels has led to negative consequences for the environment and climate. In order to solve this global issue, alternative clean energy resources need to be discovered. Hydrogen is known to be an environmentally friendly fuel, which can serve as an alternative for fossil fuels. Nowadays hydrogen commercialization becomes increasingly popular all over the world. Hydrogen is used as a fuel in polymer electrolyte membrane fuel cells (PEMFC), where its inherent chemical energy is directly converted into electricity with higher efficiency in comparison with the conversion of fossil fuels. On the other hand, hydrogen fueled PEMFCs produce zero pollutants, because the byproducts of the reaction occurring in PEMFCs are only water and heat [1–3].

The most important component of PEMFC is the proton conductive membrane (PEM). Its efficiency determines the performance of the device. Currently, Nafion membranes (sulfonated fluoropolymer) with high proton conductivity and excellent chemical stability are most commonly used.

Recently, direct methanol fuel cells (DMFC) have been considered promising devices due to their highpower density, the ease of handling operating conditions and possible use in fuel cell technology. The use of methanol as a fuel in DMFCs avoids the difficulties associated with hydrogen production and transportation. The commercial Nafion membranes suffer from severe methanol crossover, stimulating the

search for alternative polymers, more resistant to methanol permeability.

Amphiphilic conetworks containing hydrophilic and hydrophobic phases exhibit co-continuous morphology and can be successfully used as membranes for fuel cells. The hydrophilic region facilitates proton transport while the hydrophobic region provides mechanical stability. It is important to achieve the optimal balance between the hydrophilic and hydrophobic regions of the membrane [4].

The water soluble 2-acrylamido-2-methylpropanesulfonic acid (AMPS) drew attention in recent years due to its hydrolytic stability, nontoxicity and low price [5-8]. It contains a hydrophilic sulfonic acid functional group ($-\text{SO}_3\text{H}$) and a nonionic amide group (NH) in its molecular structure. Its homopolymer poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) was found to have a higher proton conductivity than partially hydrated Nafion [9]. The authors [10] confirm that PAMPS is hydrated when associated with ca. 6 molecules per equivalent group, this being much lower than either partially hydrated Nafion or polystyrene sulfonic acid (PSSA) where 15 water molecules per sulfonic acid groups are necessary. Such advantage allows PAMPS to be considered as a new potential component of proton conductive electrolyte membranes in DMFC applications.

However, PAMPS homopolymer is strongly water swollen to the point of dissolution. Copolymerization with a suitable monomer is an effective method to control the swelling level of membranes by regulating the ratio between

hydrophilic and hydrophobic groups [11]. The AMPS monomer is immiscible with most of the monomer oils, thus different approaches are used to solve this problem. Y. Shen and coauthors synthesized AMPS-co-methyl methacrylate (MMA) copolymer *via* free radical polymerization of MMA and AMPS in water [12]. The resulting poly(AMPS-co-MMA) membrane showed high proton conductivity and low methanol permeability.

Another proposed approach is cross-linking, which appears to be an efficient and simple way of enhancing membrane performance. PAMPS homopolymer have often been combined with poly(vinyl alcohol) (PVA) network to form a semi-IPN structure to achieve desirable properties for fuel cell applications [13]. However, PVA/PAMPS based semi-IPNs were found to be stiff and brittle and thus they were difficult to use as membranes. A number of investigations [14–16] was devoted to modify PAMPS-based semi-IPNs with different polymer additives to overcome these shortcomings and provide higher mechanical properties to the resulting membranes without a significant decrease in proton conductivity.

To obtain hybrid organic/inorganic membranes sol-gel process was employed as it seemed to be the most convenient procedure for incorporation of an inorganic phase into an organic matrix under mild reaction conditions [17; 18]. It involves a series of hydrolysis and condensation reactions of alkoxysilane as a precursor to the inorganic domain formation. The properties of the resulting hybrids depend on the distribution of inorganic nanoparticles within the organic matrix. The introduction of TEOS can provide Si–O–Si network into the copolymer structure. The reason for using acrylic silane (MAPTMS) is that the acrylate monomers are able to react with the double bonds of this sol-gel precursor. The authors [19] prepared organic/inorganic materials using acrylate oligomers and MAPTMS and found out that the final hybrids contained chemical bonding between the organic part of MAPTMS and acrylate oligomers. Following the classification of Sanchez et al. [20] the synthesized hybrids may be attributed to the class II of organic/inorganic materials due to exhibiting covalent bonding between organic and inorganic components.

In this article we aim to develop a new hybrid polymer-inorganic membrane with the desired properties for the fuel cell application by combining water soluble monomers (AMPS and AA) with a hydrophobic monomer AN for a

polymer matrix and obtaining the inorganic counterpart *via* sol-gel process.

Experimental

Materials. Acrylonitrile (AN, 99%), 2-acrylamido-2-methylpropane sulfonic acid (AMPS, 99%), acrylic acid (AA, 99%), 2,2-dimethoxy-1,2-diphenylethane-1-on (DMPA, 99%) and *N,N'*-methylene(bis)acrylamide (MBA), 3-methacryloxypropyl trimethoxysilane (MAPTMS, 98%), tetraethyl orthosilicate (TEOS, 99%), phosphoric acid (PhA, 85 %) were purchased from Sigma-Aldrich and used as received.

Synthesis of membranes. The hybrid polymer-inorganic membranes were prepared by polymerizing the mixtures of acrylic monomers simultaneously with the synthesis of the inorganic counterpart *via* sol-gel process.

The aqueous solutions of water soluble compounds (AMPS, MBA and AA) in various compositions were prepared in deionized water (WSC/water = 80/20 wt.%). Then the solution was mixed with the appropriate amount of AN containing DMPA under constant stirring (500 rpm) for 30 min. The sol-gel precursor solution was prepared by mixing of MAPTMS, TEOS, ethanol, water and PhA in respective ratio 0.25 : 0.75 : 4 : 4 : 1.2 mol/mol and stirred continuously at 500 rpm in 50°C water bath for 180-200 min [21]. Then, a sol-gel precursor solution (20 wt.% of the total mass of monomers) was added to the monomer mixture before the gelation point.

The formulations were exposed to UV light (365 nm, 15 J·cm⁻² radiation power) using a multi-lamp BIO-LINK® cross-linker (BLX-365, Witec AG, Switzerland) equipped with five UV lamps (8W, output 0.8W). To prevent the inhibiting effect of oxygen on polymerization process the moulds were covered with glass slides. After UV exposure the obtained membranes were carefully washed, then dried to the constant weight in an oven at 50°C.

The feed compositions for the membrane preparation are presented in Table 1.

Membrane characterization. The chemical structure of the membranes was analyzed by ATR-FTIR spectroscopy. The ATR-FTIR spectra of the hybrid polymer-inorganic membranes were recorded using FTIR microscope Hyperion 2000 (Bruker, Germany) equipped with both MCT detector and ATR objective coupled to FTIR spectrometer Vertex 70 (Bruker, Germany) in 600–4000 cm⁻¹ range with the resolution of 4 cm⁻¹.

Table 1

Sample	Recipes of the hybrid polymer-inorganic membranes							
	SA 1		SA 2		SA 3		SA 4	
	g	mmol	g	mmol	g	mmol	g	mmol
AN	1.20	22.61	1.20	22.61	1.20	22.61	1.20	22.61
AMPS	0.60	2.89	0.50	2.41	0.40	1.93	0.30	1.45
AA	0.20	2.77	0.30	4.16	0.40	5.55	0.50	6.94
MBA	0.06	0.39	0.06	0.39	0.06	0.39	0.06	0.39
DMPA	0.04	0.15	0.04	0.15	0.04	0.15	0.04	0.15

The morphology of the membranes was examined using a scanning electron microscope (SEM) using NEON 40 FIB-SEM workstation (Carl Zeiss AG, Germany). For cross-sectional imaging, dehydrated samples were fractioned upon being immersed in liquid nitrogen. Before imaging, the samples were coated with ca. 3 nm thick carbon layer.

The water uptake (WU) and methanol uptake (MU) of the prepared membranes were determined by measuring the membrane weight difference before and after immersion in water or in methanol solution. Before measuring, the samples were dried at 50°C until the constant weight was obtained. The dried and weighed membranes were placed in deionized water or methanol for 24 h. Subsequently, the samples were taken out from water or methanol, wiped with filter paper to remove droplets of non-adsorbed water and weighed immediately [22].

The oxidative stability was evaluated by immersing the sample in Fenton's reagent (3 % H₂O₂ aqueous solution containing 2 ppm of FeSO₄) at room temperature for 14 days and at 80 °C for 1h. The degradation of the membranes was evaluated by measuring the weight.

The proton conductivity was measured in the longitudinal direction with the standard four-electrode method using a Camry Reference 600 potentiostat in the frequency range from 1 Hz to 100 kHz; the membrane resistance was taken at

the frequency where the phase angle was closest to zero. Before the measurements, the prepared membranes (2 × 4 cm²) were immersed into hydrochloric acid (0.1 N) at room temperature for 2 h. Each sample was equilibrated at the experimental temperature for at least 120 min. Proton conductivity was calculated from the following equation:

$$(\sigma) = L/RdW,$$

where σ , L, d, W, and R represent proton conductivity, distance between two electrodes, thickness of membrane, and width of membrane, respectively.

Proton conductivity, oxidative stability, water and methanol uptake were calculated based on five independent measurements.

Results and discussion

The synthesis strategy of the polymer/inorganic hybrid materials involves two concurrent reactions: 1. Sol-gel hydrolysis and condensation reactions to give silica network (inorganic polymerization); 2. UV-initiated polymerisation of the double bonds of the acrylate monomers to give an organic backbone. These two simultaneous processes play a crucial role in ensuring homogeneity of the resulting materials and in minimizing phase separation. Fig. 1 shows the scheme of the preparation strategy for the polyacrylate/silica membrane.

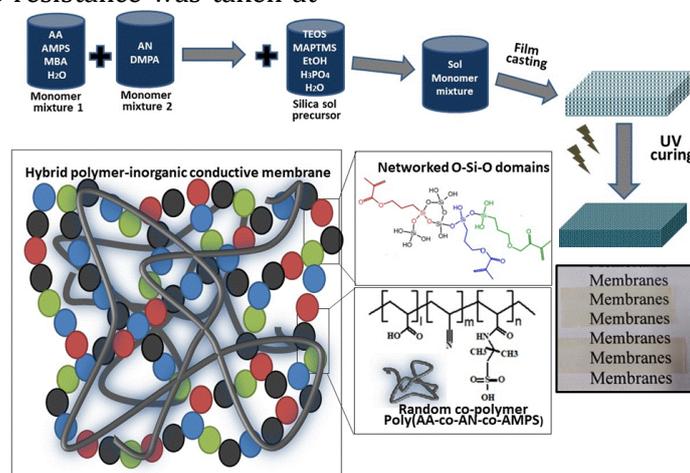


Fig. 1. Scheme illustrating the preparation of hybrid polymer-inorganic cross-linked membranes.

Acrylic monomers can be easily copolymerized using UV-initiated copolymerization process. Compared with other methods, UV-initiated polymerization has many advantages, such as low reaction temperature, short reaction time, simple equipment. This environmentally friendly process can be easily industrialized.

The membranes with four various ratio of AMPS:AA have been prepared, hence they included different number of sulfogroups. All the membranes were visually homogeneous and transparent, their thickness was 100–150 μm .

Fig. 2 shows ATR-FTIR spectra of the prepared membranes in 3600–550 cm^{-1} range, which

determine their chemical composition. The band at 2243 cm^{-1} is designed for tensile wobble $-\text{CN}$ groups of the hybrid polymer/inorganic membrane. The band at 1037 cm^{-1} is ascribed to the symmetric vibration $\text{S}=\text{O}$, and the band at 1207 cm^{-1} represents the asymmetric stretching vibration of the $-\text{SO}_3$ group, that is the characteristic absorption of AMPS [6-8]. Meanwhile, the intensity of $\text{S}=\text{O}$ peak was increased with increasing this proportion. The bands at around 1550 cm^{-1} and 1647 cm^{-1} are due to the stretching vibration of $-\text{NH}$ (amide II) and $\text{C}=\text{O}$ (amide I) of amide groups, respectively [4; 10].

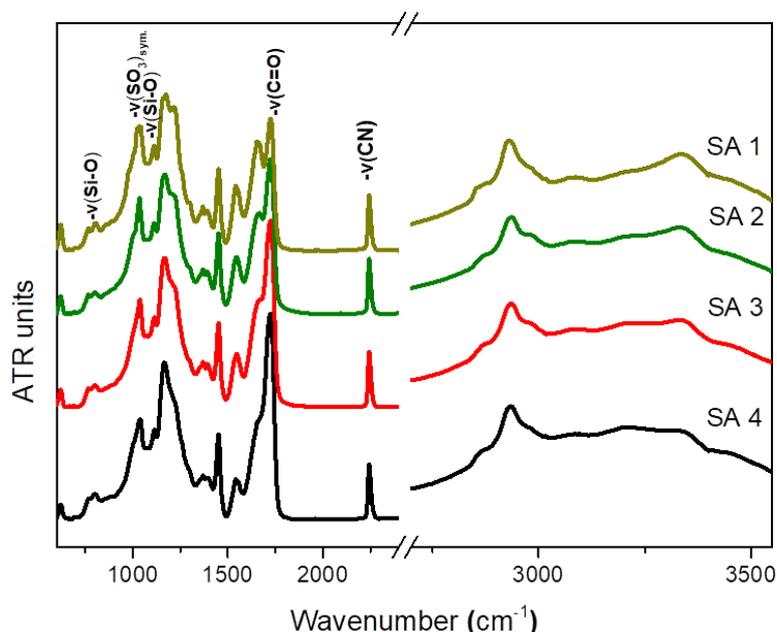


Fig. 2. The FTIR spectra of the hybrid polymer/inorganic membranes

The strong band at 1724 cm^{-1} corresponds to the $\text{C}=\text{O}$ stretching vibration of carboxylic groups. The intensity of the bands at 1724 cm^{-1} increases for the membranes in the following order $\text{SA1} < \text{SA2} < \text{SA3} < \text{SA4}$ due to the increase of the amount of acrylic acid in the feed composition for preparing of the membrane.

The peaks at 1080 cm^{-1} and 800 cm^{-1} correspond to asymmetric and symmetric stretching vibration of $\text{Si}-\text{O}-\text{Si}$, confirming the presence of silica network in all the membrane samples [23; 24]. A broad peak at around 3440 cm^{-1} corresponds to the $-\text{OH}$ stretching vibration owing to the presence of $-\text{SO}_3\text{H}$ groups and absorbed water.

The structure of as-made membranes was evaluated by using SEM, the corresponding images are shown in Fig. 3.

The cross-sectional SEM image of the polymer/inorganic hybrid materials showed featureless dense morphology. The introduction of the inorganic component changes the membrane morphology: the formation of domains and channels can be observed in the structure of the hybrid membranes. Due to the change of hydrophilic/hydrophobic balance at the various AMPS:AA ratio, the laminar structure of the membranes is formed.

The water management problems are of great importance as they are crucial for the improvement of the membrane hydration characteristics. It is well known that water remains in the hydrophilic domains, that facilitates the transport of protons; however, too much water absorption results in the loss of mechanical stability.

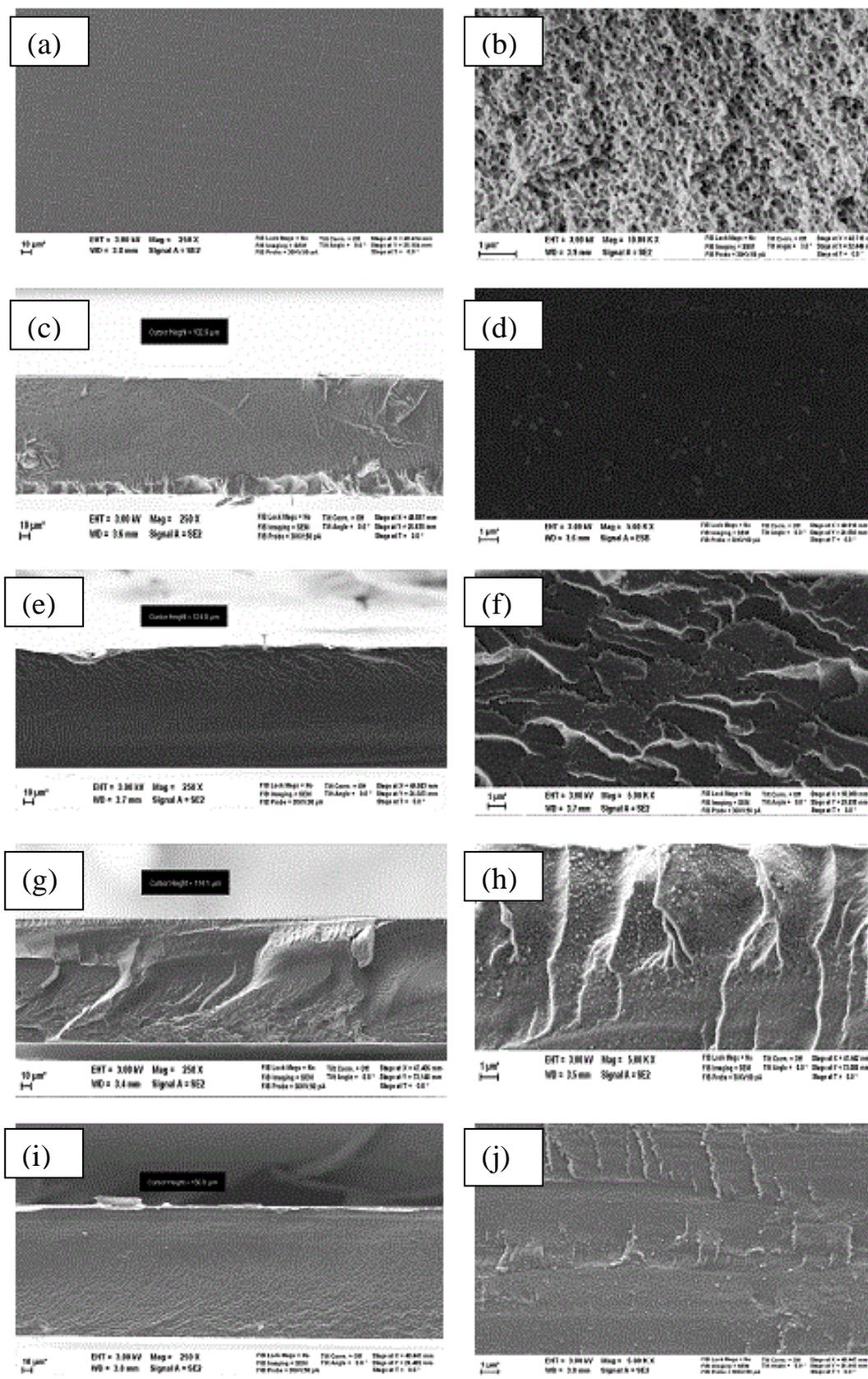


Fig. 3 SEM images at the low (left side) and high (right side) magnification of the membranes with varied monomer compositions: a) the surface of SA1; b) sol-gel; c), d) SA1; e), f) SA2; g), h) SA3; i), j) SA4

The effect of temperature on the water uptake of the cross-linked membranes was investigated.

As Fig. 4b) illustrates, the water uptake had an increasing trend with the increment of

temperature. Taking SA 3, for example, its water uptake increased sharply from 112.9 ± 2.3 wt. % to 144.5 ± 3.1 wt. % as the temperature varied from the room temperature to 80°C . This is because an elevated temperature increases the polymer chain mobility and the free volume for water adsorption, hence, water molecules could penetrate the membrane more easily.

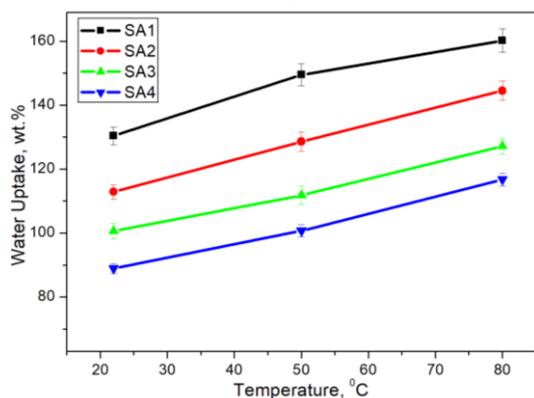
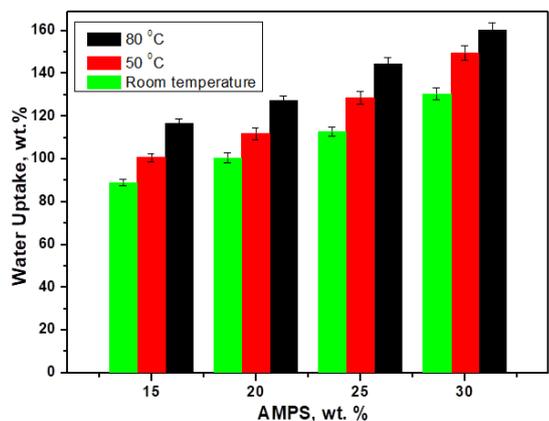


Fig. 4. Water uptake of the membranes: a) vs AMPS content; b) as a function of temperature

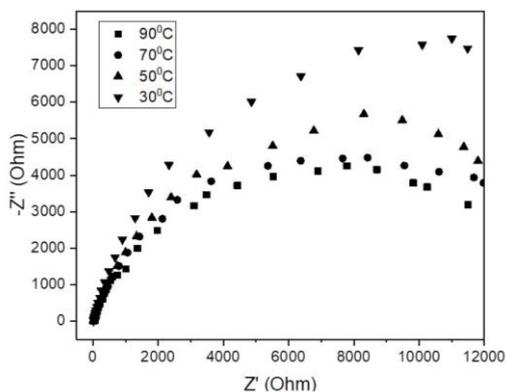
Obviously, the water uptake in the membrane depends mainly on the sulfonic acid content because the groups have a strong solvation property. The results of the water uptake studies for membranes with varied content of

sulfogroups are shown in Fig. 4a). As can be seen, the water uptake of the membranes gradually increased with the increase of AMPS content since the number of $-\text{CONH}$ and $-\text{SO}_3\text{H}$ groups, which are strongly hydrophilic in nature, increased accordingly. Hence, SA 1 membrane possessed the highest water uptake owing to its most sulfonic acid content. In addition, the synergistic effect produced by $-\text{CONH}$ and $-\text{SO}_3\text{H}$ on AMPS and $-\text{COOH}$ on AA took place, leading to the expansion of the three-dimensional network [7-8].

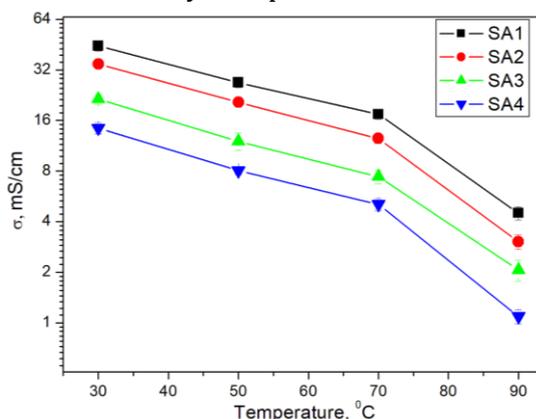
The proton conductivity of the fuel cell membrane is a key property that directly affects operational fuel cell voltage. The proton conductivity measurements of the membranes were run at RH 95% as a function of AMPS content and temperature. The results are shown in Fig. 5. The proton conductivities of the membranes measured at $T = 30^\circ\text{C}$ were in the range of $1.44 \cdot 10^{-2}$ to $4.44 \cdot 10^{-2}$ S/cm, which is comparable with that of Nafion 117 ($\sigma = 4.22 \cdot 10^{-2}$ S/cm).

It was found out that the proton conductivity of the synthesized membranes depended on various factors. First, it can be noted that proton conductivity increased with the increase in the AMPS content. This trend in membrane behavior was the same as that observed for water uptake behavior (Fig. 4). As is known, the increase in water absorption facilitates the proton transfer between ionic clusters consisting of polar groups such as $-\text{SO}_3\text{H}$ [25].

More sulfonic acid groups and water absorption could lead to the formation of more free protons, ionic clusters and larger free volume in the membrane, making the free protons more mobile and allowing them to pass through the ionic clusters more easily in the form of hydronium ion H_3O^+ , therefore the proton conductivity is improved.



a)



b)

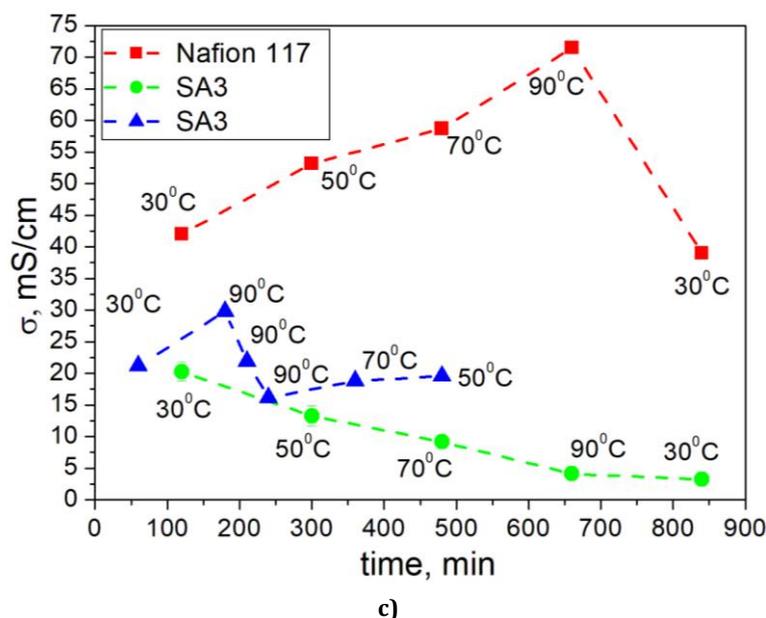


Fig. 5. Proton conductivity characteristics of the membranes: a) Nyquist plots for SA3 membrane at different temperatures; b) the dependence $\sigma - t$; c) the dependence $\sigma - \text{time}$ for Nafion 117 and SA3 membrane

The membrane proton conductivity sufficiently depends on temperature (Fig. 5). It can be seen that all the membranes showed the modest conductivity above the temperature of 50°C. This is due to the loss of water by the membranes. For this reason, these membranes cannot be used in a cell at higher temperature.

The conductivity behavior of the polymer membranes as a function of temperature suggests the presence of two competitive trends: thermal activation and membrane dehydration [26]. At the first moment of the measurement the proton conductivity of the membrane increased with the increasing temperature, but the measurement after two hours showed lower values of proton conductivity (see Fig. 5c).

The data on the membrane swelling in methanol (Fig. 6a) indicate the increase in methanol uptake for the membranes in the order as follows: SA1 > SA2 > SA3 > SA4. These results correlate with the data on water uptake. The value of methanol uptake for our membranes is smaller than that for Nafion 117.

At the same time we observe that all hybrid polymer-inorganic membranes were insoluble in water and methanol even upon heating.

The PEM degrades during fuel cell operation due to the formation of hydroxyl ($\bullet\text{OH}$) and hydroperoxyl ($\bullet\text{OOH}$) radicals at the cathode as these radicals attack the hydrocarbon backbone of the membrane [27]. Therefore, it is necessary to investigate the chemical stability of membrane in oxidative environment.

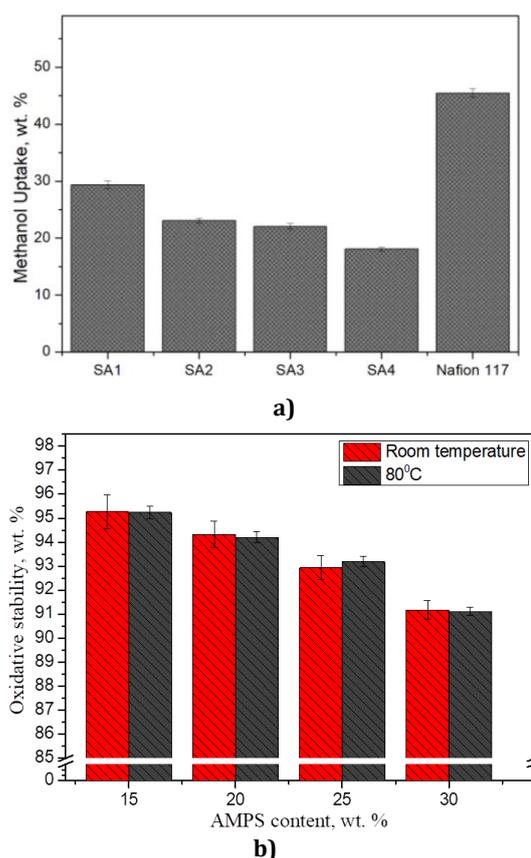


Fig. 6. Methanol uptake and oxidative stability

The prepared membranes showed remarkable oxidative stability in the range of 92 – 95 wt. %. These results reveal that prepared membranes are chemically stable. As it was expected, the most chemically stable was the membrane SA4 with the smallest content of AMPS.

Conclusions

The simple and cost effective process for the preparation of proton conductive copolymers based on an acrylic monomer has been proposed. The cross-linked amphiphilic membranes with different composition were synthesized *via* UV-initiated polymerization and assessed for the applicability as PEMs for fuel cells. The prepared membranes exhibited relatively high proton conductivity depending on the membrane composition, temperature and the time of exposure in fuel cell. Water uptake of the membranes is high, while methanol uptake is relatively low making them suitable for the use in DMFC.

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