

Preparation and Characterization of UV-curable Crosslinked Organic-inorganic Membranes

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Abstract – Organic-inorganic membranes were successfully synthesized by UV-initiated polymerization of acrylic monomers with simultaneous formation of inorganic component via sol-gel process of 3-methacryloxypropyltrimethoxysilane (MSPTMS)-based system. The investigations of membrane characteristics indicate that materials possess high proton conductivity, thermal and chemical stability and are good candidates for fuel cell application.

Keywords – proton conductive membrane, organic-inorganic material, UV curing, sol-gel process, acrylic acid, acrylonitrile, ethyleneglycole diacrylate, sulfopropylacrylate potassium salt, 3-methacryloxypropyltrimethoxysilane

Introduction

Nowadays the widespread use of batteries has created many environmental concerns, such as toxic metal pollution. Battery manufacture consumes resources and often involves hazardous chemicals. Used batteries also contribute to electronic waste. Therefore researchers are challenged to develop new types of efficient environmentally-benign energy devices [1]. Recently direct methanol fuel cells (DMFC) using proton exchange membranes (PEM) are considered as promising energy conversion devices owing to their high energy efficiency, low emission, stable and simple operating conditions at a relatively low temperature, no requirement of fuel reforming process and environmentally friendly nature [2]. To improve the performance of DMFC, especially to reduce methanol crossover, considerable efforts have been devoted to modify Nafion membrane or to develop alternative new nonperfluorinated PEM materials. Organic-inorganic composites also constitute an emerging research field due to their advantages in improving mechanical and thermal properties as well as proton conductivity.

The aim of this work is to propose a new approach to obtain crosslinked organic-inorganic materials on the base of acrylic monomers and silica precursors. The characterization of the synthesized materials was conducted to estimate their potential as proton conductive membranes in fuel cell application.

Experimental

The series of membranes were prepared by UV polymerization of acrylic monomers (at the presence of photoinitiator 2,2-dimethoxy-2-phenylacetophenone, 2.0 wt %) and simultaneous sol-gel transformation of MSPTMS-based sol-gel system. The feed polymerizing composition (Table 1) was placed into the glass mold and UV-irradiated for 10 min, then the resultant membrane was peeled from the glass substrate and immersed in 1.0 M HCl solution. Ethyleneglycole diacrylate (EGDA) was used as a crosslinker.

Proton conductivity of membranes was measured by the method of impedance spectroscopy using AUTOLAB impedance spectrometer (EcoChem, the Netherlands) with FRA software equipped by thermostat.

Feed compositions for membrane preparation

Sample	AN, wt. %	AA, wt. %	SPAK, wt. %	EGDA, wt. %	MAPTMS, wt. %
S1	40	20	25	15	-
S2	40	20	25	15	3
S3	40	20	25	15	5
S4	40	20	25	15	7
S5	40	20	25	15	10

Ion-exchange capacity of the synthesized membranes was determined as a number of mg-equiv. of sulphogroups in 1 g of dry polymer: the membranes first were placed into 0,1 M HCl, washed with distilled water, and then dipped in 10 ml of 2 M NaCl for 24 h to complete a substitution of sulphogroups' protons with sodium ions. After that ion-exchange capacity was determined by carrying out a back titration of solution with 0,1 M NaOH to evaluate the released amount of protons.

Thermogravimetric and differential thermal analysis of samples of polymer and polymer-silica membranes was conducted on Derivatograph Q-1500D (Paulik-Paulik-Erdey) within the temperature range of 20 - 400°C at heating rate 5°C/min. Alumina was used as a standard. The samples weight was 300 mg.

Results and Discussion

A series of polyacrylate silica-containing membranes were synthesized *via in situ* polymerization method as a result of simultaneous formation of organic and inorganic networks. The incorporation of Si(OR)₃ groups of MAPTMS into polymer matrix offers two functions: first, siliconcontaining polymers present high thermal and chemical stability; second, the hydrolysis and condensation reactions of Si(OR)₃ groups lead to a self-crosslinked silica network in membranes [3]. The formation of silica network suppresses the swelling and methanol diffusion and also improves stability, water retention and mechanical strength of PEM.

Proton conductivity is the most essential characteristic determining the efficiency of material use as proton conductive membrane in fuel cell. It was found that proton conductivity of membranes depended on their composition and temperature (Fig 1).

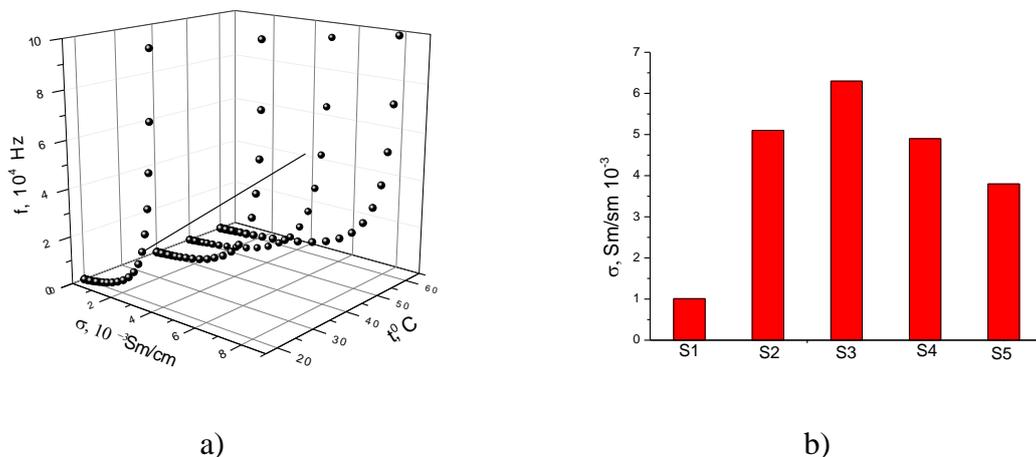


Fig. 1. Dependence of proton conductivity on temperature (S1) and MAPTMS content at 20°C

The positive temperature-conductivity dependency suggested a thermally activated process. Obviously, elevating temperature increased structural reorientation, water uptake and

mobility of water and proton, which facilitated the transport of proton and hence contributed to the improvement of proton conductivity (Fig 1a).

It is known that proton conductivity increased with increasing IEC and water uptake. It is because that protons transferred between ionic clusters consisting of polar groups such as $-\text{SO}_3\text{H}$ and the number of ionic clusters was related to the number of $-\text{SO}_3\text{H}$ groups and water content in the membrane. More inorganic component and, relatively, water absorption made free protons more mobile, proton conductivity of membranes therefore was improved (Fig. 1b) significantly. The values of proton conductivity for the samples were $10^{-3} - 10^{-2}$ Sm/cm and were comparably to those of Nafion, the-state-of-the-art membrane. However, at MAPTMS content above 5 wt % we observed decrease in proton conductivity.

The data of ion-exchange capacity of organic-inorganic nanocomposites are presented in Table 2. The IEC range from 1,12 to 1,68 meq/g and are higher than that of Nafion 117. membrane.

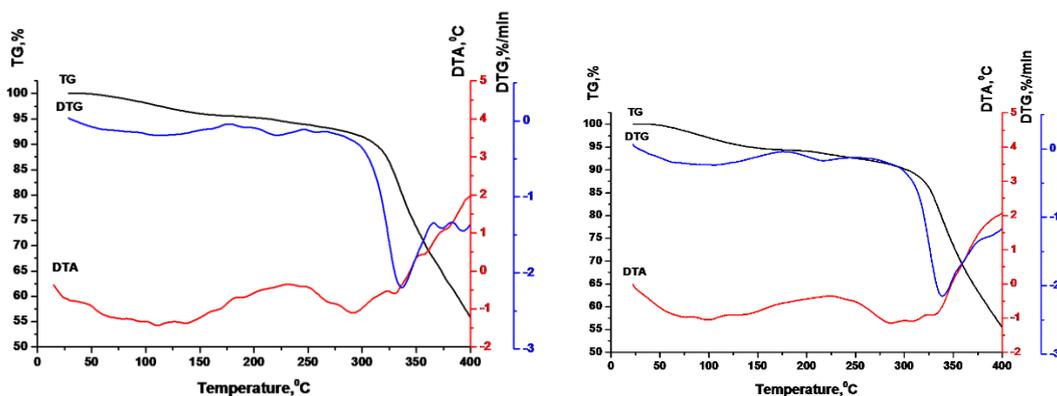
Table 2

The values of ion-exchange capacity of organic-inorganic membranes

Sample	IEC meq/g
S1	1.12±0.05
S2	1.40±0.05
S3	1.68±0.05
S4	1.36±0.05
S5	1.25±0.05

As one can see, the value of IEC gradually increased for the samples S2 and S3 and then decreased for the samples S4 and S5. These results correlate with the data of proton conductivity for these membranes. We suppose it is induced by different morphology of obtained organic-inorganic materials.

To evaluate the thermal stability of polymer and organic-inorganic membranes complex thermogravimetric and differential thermal analysis of samples was conducted. The TGA curves of the membranes are shown in Fig. 2.



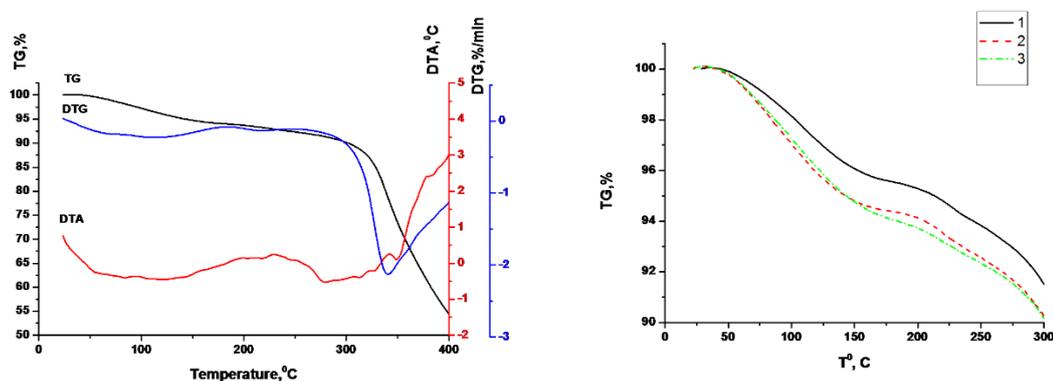


Fig. 2. TGA curves of the samples S1, S2, S5

All the membranes exhibited degradation curve with several steps. The weight losses of the samples, observed in the temperature range of 20 – 150°C, may be attributed to evaporation of physically absorbed and chemically bound water. The weight loss occurring at around 250°C was attributed to the splitting-off of sulfonic acid groups, and the mass losses at this temperature range increased with the rise of IEC. Above 350°C the membranes underwent the degradation step, which corresponded to the decomposition of the main chain and crosslinking bridges.

The inspections of the thermograms suggested that polymer and organic-inorganic membranes had good thermal stability, which could be explained as follows. First, the Si–O bond energy was higher than that of C–C bond. Second, the hydrolysis and condensation reactions of Si(OR)₃ groups in membrane led to the formation of crosslinked silica network structure, which made the membrane more compact and hence improved the thermal stability. So, the temperature of the beginning of sulfogroup decomposition for the polymer membrane S1 was 245°C whereas for S2 and S5 – 252°C; the temperature of the beginning of the membrane matrix thermooxidation increased from 318°C for S1 till 328°C for S2 and S5. The presence of larger content of inorganic counterpart (the sample S5, MAPTMS 10 wt %) leads to an increase in the number of chemically bound water compared to S2, the mass loss at the second step for S2 is 2.77%, and for S5 – 3.35%.

Conclusion

Crosslinked sulfocontaining polyacrylate and silica-polyacrylate membranes were successfully synthesized *via* convenient polymerization *in situ* method. Their suitability as PEMs for DMFC was investigated by impedance spectroscopy, thermogravimetric analysis and determining IEC. The synthesized membranes were found to have good thermal stability, high proton conductivity and IEC. Based on these results, it could be concluded that the membranes had good potential as PEMs for DMFC.

References

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