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SULFONATED POLY(ETHER–ETHER–KETONE) POLYMER MEMBRANES FOR FUEL CELLS

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In the work, sulfonated poly(ether–ether–ketone) (SPEEK) ionomers were synthesized using an original (submitted for patent) and simple method. The resulting membranes were tested to determine parameters that are important for the use of this material in fuel cells (water absorption, sulfonation degree, conductivity, etc.). The thermo-gravimetric analysis has shown a good thermal stability in the range from RT to 200–220 °C, and two characteristic regions of weight loss – 7.4% at ~140 ^{o}C (reversible water loss) and 10.3% at 200–220 °C (due to polymer degradation when cross-linked polymer chains permanently break down and their SO_3H-groups are lost). The conductivity values obtained by the through-plane measurements of SPEEK membranes were 12 mS/cm at RT and 23 mS/cm at 80 °C.

Key words: *proton conductor, polymer membrane, SPEEK, differential thermal analysis.*

1. INTRODUCTION

The sulfonated poly(ether–ether–ketone) (SPEEK) ionomer has been reported in the literature as a low-cost alternative membrane for hydrogen-powered polymer electrolyte membrane (PEM) fuel cells (PEMFC) and methanol-powered direct methanol (DM) fuel cells (DMFC) [1–3]. The PEM fuel cells have been widely researched in the last two decades as they can be applied in transportation, stationary and portable power devices (mobile phones, notebooks, etc). The best way of using hydrogen as fuel is chemical burning in fuel cells whose theoretical efficiency reaches 83% (for hydrogen's higher heating value), which is by far better than that of today's engines [4]. Nevertheless, there remain problems that need to be overcome for wide commercialization of fuel cells – those of cost and performance. While the cost of a fuel cell is mostly determined by three main components: the carbon cloth, catalyst and membrane, its performance depends on the membrane and catalyst properties. To find an alternative membrane and catalyst materials that are less expensive but exhibit performance equivalent or superior to the state of the art (Nafion® (Dupont), Flemion® (Asahi Glass company), Aciplex® (Asahi chemical Industry), Neosepta-F® (Tokuyama) and Gore-Select® (W.L. Gore and Associates) and Pt and Pt–Ru) wide research has been carried out [5].

Development of sulfonated perfluorinated and partially fluorinated ionomers is reported in [6]. However, the costs of these polymers are also high due to the complex process of production. In the last decades, numerous types of arylene main chain polymers have been developed. A huge number of these polymers were subject to sulfonation in order to provide the proton conductivity by substituting the sulfonic groups in the main chain of polymers. However, the mechanical properties of a post-sulfonated polymer tend to deteriorate progressively with the degree of sulfonation. The polymers begin to swell too vigorously so that they lose their mechanical stability. Furthermore, the polymers can even be hydrolyzed in water. Over the last decade, membranes based on polyetheretherketone (PEEK) have shown considerable promises. These membranes were found to possess good thermal stability, appropriate mechanical strength, and high proton conductivity, which depends on their degree of sulfonation. However, the mechanical properties of PEEK deteriorate progressively with sulfonation [7], which makes the long-term stability of a highly sulfonated polymer questionable. The mechanical weakness of non-crosslinked sulfonated polymers initiated several attempts to prepare more stable and mechanically stronger cross-linked proton exchange membranes (PEMs). The cross-linking is thought to be an effective approach to reduce the water swelling and methanol crossover [8–10].

According to our method, a cross-linked chlorosulfonated and sufonated PEEK (CCSPEEK) membrane is simply prepared in only one step [11]. Here we are reporting first results of the research into the properties of new SPEEK membranes, including such an important parameter as the proton conductivity.

2. EXPERIMENTAL

2.1. Materials

SPEEK membrane was prepared from poly(ether-ether-ketone (PEEK) supplied by Aldrich. After a reducing reaction, cross-linked sulfonated and sufinated PEEK (CSSPEEK) was produced as the basic polymer; then double cross-linked proton-conducting membrane was prepared using post-crosslinking by alkylation of the sulfinate groups (with mono- di- or oligo-functional electrophiles). To prepare membranes from SPEEK a casting from solution was used.

2.2. Methods

The procedure for investigation of the key properties of SPEEK membranes was as follows.

The water uptake was determined classically – by weighting a dried sample and that after placing it in water for 24 h. The uptake values in w% were calculated by the formula:

$$\text{Water Uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \cdot 100\% .$$

The DTA analysis was chosen to test the thermal stability of the membranes, since in fuel cells they often reach temperatures up to 100 °C and higher, so a good stability in this interval is required. Also, this method allows determination of the sulfonation degree (as described by Zaidi *et al*. [1]). For the measurements, which were taken at temperatures not exceeding 350 ^{o}C in Al crucibles, Shimadzu DTG equipment was used.

The proton conductivity was measured to determine whether it is possible to use this type of membranes in fuel cells. For the proton conductivity measurements a typical scheme was employed, but without a catalyst and a carbon cloth layer (Fig. 1). A closed chamber was chosen to provide conductivity measurements at constant moisture. A membrane was taken as wet as possible to provide the highest achievable humidity in the chamber during measurements. The steel electrodes used in the tests prevented water evaporation from the membrane surface at different temperatures, so that the humidity could be considered invariant at different temperatures. The proton conductivity of the membrane was calculated from the impedance measured with the help of a Hioki 3560 AC multi-ohmmeter.

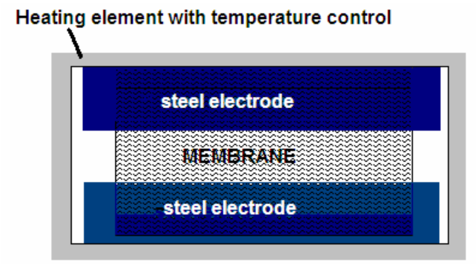

Fig. 1. Scheme for measuring the proton conductivity.

3. RESULTS AND DISCUSSION

Thermogravimetric analysis of different new SPEEK membranes has shown a good thermal stability in the range from RT to 200–220 °C (Fig. 2). The weight loss around 7.4% from RT to 140 ^{o}C is connected with dehydration (water loss). As determined from the water uptake measurements, the overall water uptake of the prepared SPEEK membranes was 30 w% at room temperature.

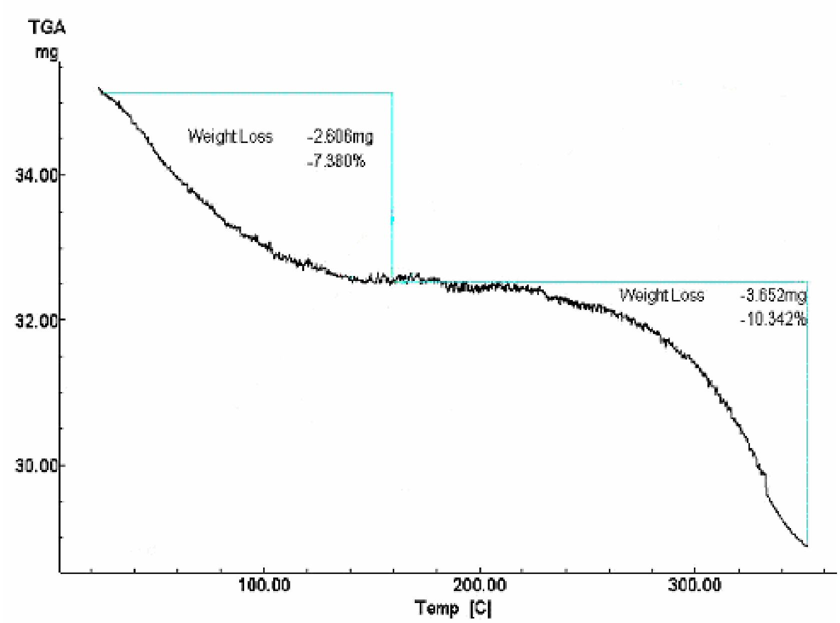

Fig. 2. Results of DTA analysis for SPEEK membranes (with mass and energy changes shown).

The difference can be explained with the fact that during the classical uptake measurements the membrane is placed directly in water, while for TG measurements dry membranes are used, which means that the absorbed water amount is much smaller. All measurements were performed under laboratory conditions, with humidity RH = 40%.

The next in importance mass losses observed for SPEEK membranes starting from 200–220 °C indicate the polymer degradation when cross-linked polymer chains permanently break down due to the loss of SO_3H-groups. This interesting result shows that our SPEEK membranes can be used in PEM and DM fuel cells at considerably higher temperatures than other commercial polymers (e.g. for Nafion® (Dupont) this temperature is ~110 °C [4]). The irreversible weight losses from ~200 °C for SPEEK membranes (seen in Fig. 2) reflect a very high degree of sulfonation – more than 100% [1] (100% sulfonation means that only one SO_3H-group is connected to each repetitive segment of the polymer chain as shown in Fig. 3). Such a high sulfonation degree often leads to a polymer's dissolution in water, however our method of synthesising SPEEK membranes allows achieving the sought-for result without any negative effect.

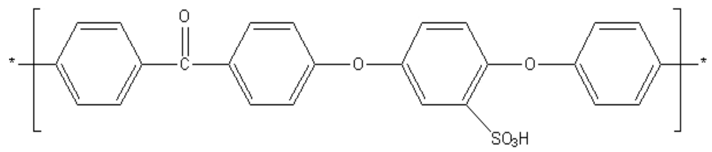

Fig. 3. SPEEK structural form at 100% sulfonation degree.

The proton conductivity is an important factor which determines if the membrane is good enough to use it in fuel cells. At measuring the through-plane conductivity the values of ~ 12 mS/cm at RT and 23 mS/cm at 80 °C were obtained for typical SPEEK membrane samples (Fig. 4).

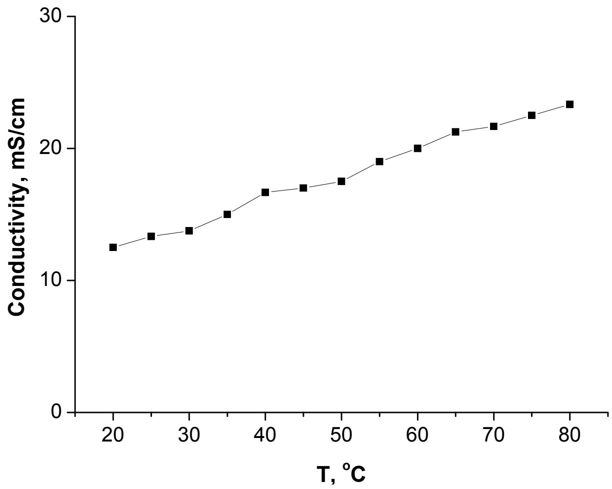

Fig. 4. The temperature dependence of proton conductivity for a SPEEK membrane obtained by cross-linking the sulfonated and sufinated PEEK.

In both cases the proton conductivity values were compared with those for a Nafion® membrane and some other typical membranes whose proton conductivities reach 10–100 mS/cm [4]. Typically, in polymer electrolytes based on hydrocarbon polymers the water molecules are completely dispersed, while in perfluorinated membranes they have a spontaneous hydrophilic/hydrophobic separation [12]. This structural drawback makes previously known SPEEK membranes a poor choice as polymer electrolytes for fuel cells, which also possess lower thermal decomposition temperatures [5]. In the case when SPEEK membranes are obtained by cross-linking of sulfonated and sufinated PEEK [11], all measured parameters indicate that these membranes are promising for application in fuel cells.

4. CONCLUSIONS

The results of our work allow the following conclusions to be drawn.

1. According to the TG analysis, the SPEEK membranes obtained by cross-linking of sulfonated and sufinated PEEK possess a good thermal stability in the range from RT to 200–220 °C.
2. Two characteristic regions of weight loss observed in the TG measurements are: around 140 °C and at 200–220 °C, corresponding to the 7.4% water loss and the 10.3% mass loss due to polymer degradation when cross-linked polymer chains permanently break down and SO_3H-groups are lost.
3. Through-plane conductivity measurements performed for the SPEEK membranes give the values 12 mS/cm at room temperature and 23 mS/cm at 80 °C, which means that they can be competitive with commercial Nafion® (Dupont) membranes when applied for hydrogen-powered PEM fuel cells and methanol-powered direct methanol fuel cells.

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REFERENCES

1. Zaidi, S.M.J., Mikhailenko, S.D., Robertson, G.P., Guiver, M.D., & Kaliaguine, S. (2000). *J. Membr. Sci.* **173**, 17–34.
2. Yang, B., & Manthiram, A. (2003). *Electrochem. Solid-State Lett.* **6** (11), pp. A229–A231.
3. Li, L., Zhang, J., & Wang, Y. (2003). *J. Membr. Sci.* 226, pp. 159–167.
4. Barbir, F. (2005). PEM Fuel Cells. Theory and Practice, Elsevier Academic Press. P.421.
5. Rikukawa, M. & Sanui, K. (2000). *Prog. Polym. Sci.* **25** , pp. 1463–1502.
6. Lufrano, F., Gatto, I., Staiti, P. (2001). V. *Solid State Ionics,* **145**, pp. 47-51.
7. Jin, X., Bishop, M. T., Ellis, T. S., & Karasz, F. E. (1985). *British Polym. J.*, **17**, 4.
8. Zhong, S., Fu, T., Dou, Z., Zhao, C., & Na, H. (2006). *J. Power Sources* 162, pp. 51–57.

9. Jinhua Chen, Yasunari Maekawa, Masaharu Asano, Masaru Yoshida, (2007). *Polymer.* **48**, (20), pp. 6002-6009.
10. Di Vona, M. L., Marani, D., *et al*. (2006). *Chemistry of materials*, **18**, (1), pp. 69-75.
11. Luo, H., Vaivars, G., & Kleperis, J. (2007). A novel double cross-linked proton conducting membrane and the methods. *Latvian Patent Application* P-07-145.
12. Kreuer, K.D. (2001). *J. Membr. Sci.* **185**, pp. 29–39.

KURINĀMĀ ELEMENTIEM PIEMĒROTAS SULFONĒTA POLI(ĒTER–ĒTER–KETONA) POLIMĒRA MEMBRĀNAS

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K o p s a v i l k u m s

Pēc oriģinālas un vienkāršas metodes sintezēts sulfonēts poli(ēter–ēter–ketona) (SPEEK) jonomērs (SPEEK). Iegūtām membrānām testētas dažādas īpašības, ko nepieciešams zināt, ja membrānu izmantos kurināmā elementos - absorbētā ūdens daudzums, sulfonēšanas pakāpe un protonu vadītspēja. Termogravimetriskie mērījumi liecina, ka jaunās membrānas ir stabilas pat līdz 200–220 ^{o}C, un pirmais novērojamais 7.4% svara zudums temperatūru apgabalā no istabas līdz 140 ^{o}C saistāms ar atgriezenisku ūdens zaudēšanu, bet otrs 10.3% svara zudums, kas sākas virs 220 ^{o}C, saistāms ar neatgriezeniskām izmaiņām sakrustoto polimēru ķēdēs, neatgriezeniski zaudējot SO_3H-posmus. Mērot vadītspēju caur membrānas plakni, iegūtas sekojošas vērtības: 12 mS/cm pie istabas temperatūras un 23 mS/cm pie 80 °C.

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