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Electrochemical Properties of Poly(aminobenzene sulfonic)phosphazene Derivative Grafted SPEEK Proton Exchange Membrane

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A type of poly(aminobenzene sulfonic)phosphazene derivative grafted SPEEK was synthesized which were confirmed by FT-IR and NMR analysis. And a series of grafted SPEEK proton exchange membranes with 65% sulfonation degree were prepared. Comparing to SPEEK membranes, all the properties increased. The proton conductivity reached 4.21×10^{-3} S/cm with 15 % grafting degree and the methanol permeability coefficient increased at 2.72×10^{-7} $cm^2\cdot s^{-1}$ to achieve the using requirements of DMFC proton exchange membrane.

Keywords: graft**,** benzenesulfonic acid, polyphosphazene, SPEEK, properties

1. INTRODUCTION

Sulfonated poly(etheretherketone) (SPEEK) membranes have been paid more attentions to its good properties comparing to Nafion membrane [1-3]. But, it is also has some insufficient should be enhanced at high temperature and low humidity. In the last decade, physical doping modification (SiO_2, Y_2O_3, W_2O_3, Se_2O_3, PES, PPSU, etc. [4-8]) and chemical grafting modification (PWA, ionic liquids, chemical crosslinking, etc. [9-13]) had been researched according to the improving its performance.

In our previous studies, it is found that polycyclotriphosphazene derivatives could slightly increased the proton conductivity by physical doping but does not meet the requirements of PEM methanol permeability and anti-swelling properties [14]. However, the doped particles or macromolecule are easier to outflow to reduce the performance and the service life due to physical blend. Its overall performance is less than pure SPEEK membrane. The performances of SPEEK proton exchange membrane increased, but the proton conductivity has not reached of 10^{-2} S•cm^{-1}. Thereby, choosing polycyclotriphosphazene derivatives grafted SPEEK to improve overall application performance. 64.5% sulfonation degree of the SPEEK resin was selected in order to ensure the behaviors of methanol permeability and water swelling, and then grafted cyclotriphosphazene groups by a chemical substitution reaction to SPEEK to be formed novel polymer as SPEEK backbone with cyclic phosphazene large molecule pendant. The residual chlorine atoms were nucleophilic replaced by sulfanilic acid in the suspension means to improve the proton conductivity, while ensuring resistance alcohol and anti-swelling properties of the membrane. Comparing to linear phosphazene, conjugated ring structure is more stable and can improve the thermal chemical stability of the membrane. This technique differs from the doping modified. Through chemical grafting can solve the stability and working life of the membrane, and also can control the number of sulfonated functional groups on the side groups, greatly improve the proton conductivity. All over cannot be achieved by any other doping, blending technologies.

In this paper, the composite membranes based on SPEEK would be prepared by grafting with a novel poly(aminobenzene sulfonic)phosphazene derivative and their properties were investigated, like proton conductivity, methanol resistance and thermal stability.

2. EXPERIMENTAL SECTION

2.1 The materials

Hexachlorocyclotriphosphazene (HCCP) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp=112.5-113 °C). Phenol, tetrahydrofuran (THF), dimethylacetamide, sulfanilic acid, $NaBH_4$ were obtained from Sinopharm Chemical reagent Co., Ltd (Shanghai China). All chemicals and solvents were provided commercially by Sinopharm Chemical Regents Co. Ltd (China) and used without further purification unless otherwise noted. All glassware was dried in an oven under vacuum before use.

Poly (etheretherketone) (PEEK) was obtained from Chemistry Department of Jilin University (Jilin, China), in the form of particle, and SPEEK was prepared as reported in the literature 4. After SPEEK with DS of 65% was triturated, it was dissolved in dimethylacetamide to make 10wt% solution.

2.2 The preparation of Membranes

According to the synthetic route shown in figure 1, SPEEK was prepared as reported earlier [14]. After getting SPEEK with DS of 64.10%, NaBH4 was utilized to accomplish carbonyl reduction of SPEEK at 100 ^{o}C, 24 h for synthesis of sulfonated poly[2-hydroxy]etheretherketone (SP30, reduction degree is 30%.). Subsequently,sulfonated poly[2-(petachloropolycyclotriphosphazene-oxy)]etheretherketone (SPCEK) was synthesized by adding SP30 solution into hexachlorocyclotriphosphazene (HCCP) (laboratory self-synthesized) dissolving in DMAC at iced-water atmosphere for 20 h with mechanical stirring. After that, certain amount of hexasulfanilic acid (SA) from Aladdin Reagent Co. Ltd. (Japan) was put into SPCEK solution to synthesize sulfonated poly[2-(petasulfanilicacidpolycyclotriphosphazene-oxy)]etheretherketone (SPSCEK) under ultrasonic firstly then at 60 ^{o}C for 4 h.

Composite membranes were obtained by casting their viscous solution onto a glass plate and thickness of the dried composite membranes was about 100 μm. Accordingly, a series of cyclotriphosphazene grafting SPEEK membranes were prepared and described as GR02, GR05, GR08, GR10, GR15, where 'GR' represented grafting, and the subsequent values of 'GR' indexed grafting degree weight percent of SPEEK.

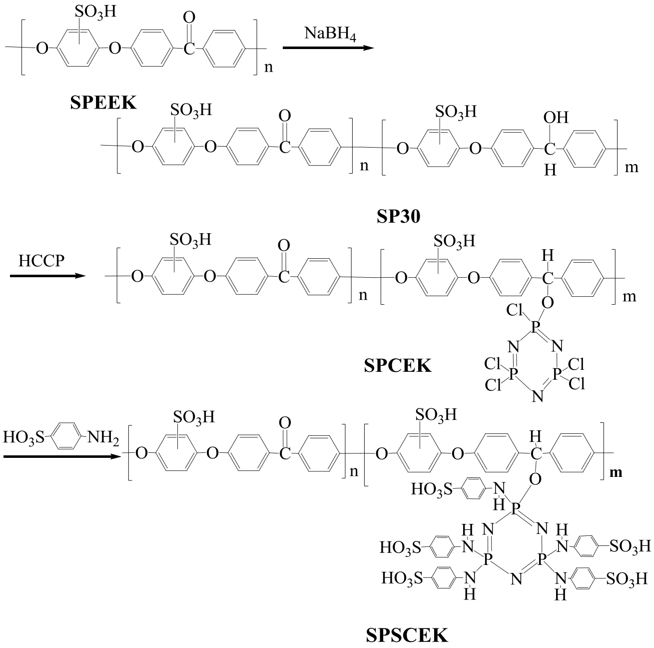

Figure 1. Synthesis of grafted SPSCEK

2.3 The characterization and testing

Fourier Transform Infrared (FT-IR) spectra of the membrane specimens were recorded with an AVATAR370 infrared spectrometer (ThermoNicolet Instrument Co., USA). The NMR spectra were recorded on a Varian DRX 400 NMR spectrometer with the operating frequency at 400 MHz using $CDCl_3$ or DMSO as a solvent, using TMS as inner reference and H_3PO_4 (85%) as external reference. The thermal stability of membranes was evaluated by recording thermo-gravimetric (TG) traces in nitrogen atmosphere (Q500, TA Company, USA). Heating rate was $10°C \cdot min^{-1}$, temperature ranged from 50 °C to 400 °C and specimen weight of 5±2 mg in the membrane form was used for recording TG traces.

The proton conductivity of membrane specimens in the traverse direction was measured in a measurement cell using AC Electrochemical Impedance Spectroscopy (EIS), which was composed of a

Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255 B frequency response analyzer (Farnborough, UK), both of which were interfaced via GPIB to a computer. The EIS recorded over a frequency range of 1-10^6 Hz. The amplitude of the sinusoidal modulation voltage was 10 mV. The temperature ranged from 30ºC to 90ºC and the RH was 50% and 100%, respectively. Before the test, all membrane specimens were soaked in 1 mol·L^{-1} hydrochloric acid solution for 4h, and then rinsed for several times with deionized water. The resistance of the membranes was measured and the proton conductivity was calculated as described in detail in reference [15].

Methanol permeability coefficient of membrane specimen was determined by a home-made diaphragm diffusion cell, which was amply described in reference 6. The membranes were immersed in de-ionized water at room temperature for 24 h before testing, and both thickness and area of wet membrane specimens were measured. Thereafter, membrane specimens were placed in diffusion cell for the measurement of methanol permeability. 70 ml 5 mol/L methanol solution was placed in one side of the diffusion cell and de-ionized water of the same volume was placed in the other side. The methanol permeability coefficient was calculated by the second of law of Fick's diffusion as showed below (Equation 1) [16].

$$S_d = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\% \qquad (1)$$

3. RESULTS AND DISCUSSION

The chemical structure of SPCEK was confirmed by FT-IR as shown in figure 2. From the curve, we can see that a characteristic absorption peak due to the N=P group at 1256 cm^{-1}, P-N stretching vibration appeared at 870 cm^{-1}, P-O stretching vibration appeared at 947 cm^{-1}, which are proved the existence of phosphazene cycle. The characteristic absorption peak due to the P-Cl groups at 550 and 650 cm^{-1} [17]. All over prove that the chemical structure of SPCEK.

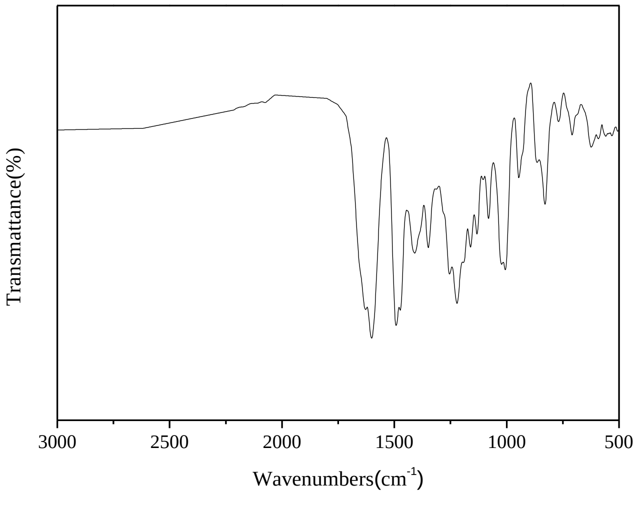

Figure 2. FT-IR spectrum of SPCEK

The chemical structure of SPSCEKwas confirmed by FT-IR as shown in figure 3. From the curve, we can see that a characteristic absorption peak due to the N=P group at 3400-3450 cm^{-1}. The characteristic absorption peak due to the P-Cl groups at 550 and 650 cm^{-1} disappears which indicated that Cl has been completely replaced by aminobenzene sulfonic. The sulfonic acid groups were corresponding to characteristic absorption peaks as 1250, 1092, 1020 and 710 cm^{-1}.

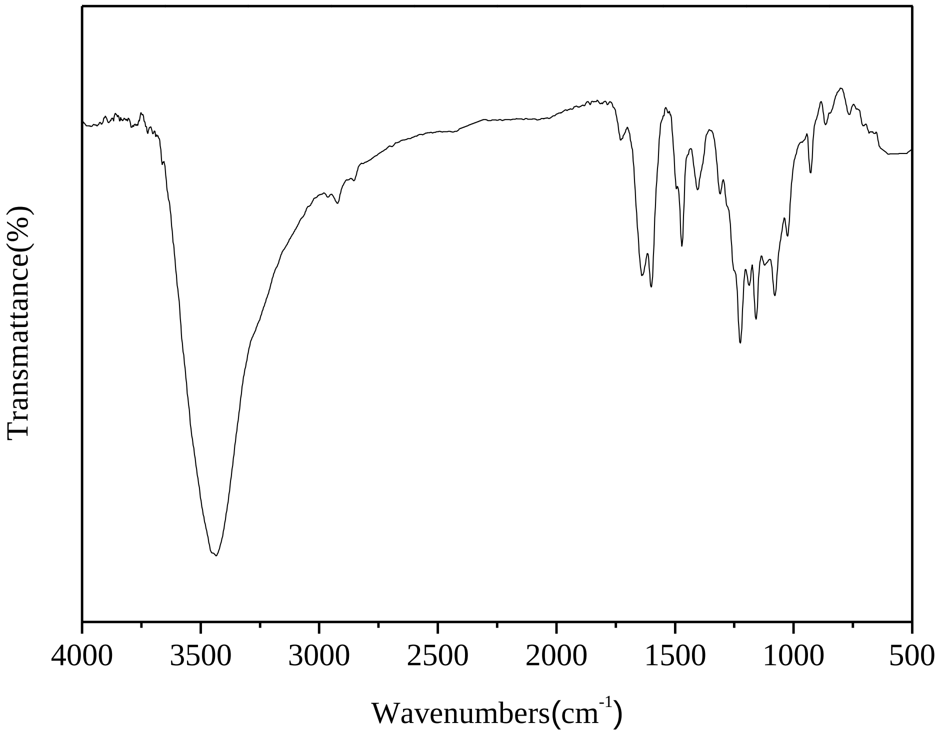

Figure 3. FT-IR spectrum of SPCEK

The P^{31} NMR spectra of SPCEK and SPSCEK are shown in figure 4 and 5. Figure 4 showed NMR spectra of SPCEK where two kinds of chemical shift were caught. One at 19.8 ppm was for phosphorus atoms connected with Cl while the other at 9.6 ppm was with SPCEK backbones. In contrast to spectra of SPSCEK, there was no chemical shift for SPCEK at 19.8 ppm which proved chlorine atoms were substituted by aminobenzene sulfonic once more [18].

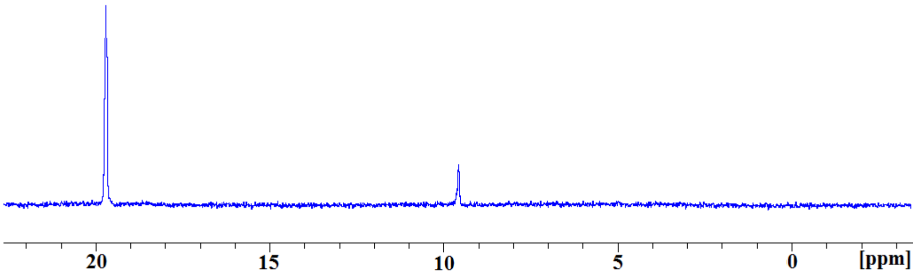

Figure 4. ^{31}P NMR spectrum of SPCEK

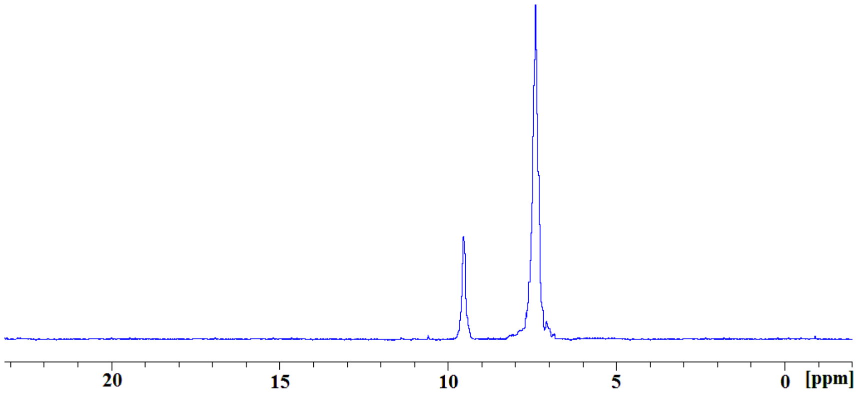

Figure 5. ^{31}P NMR spectrum of SPSCEK

Table 1 was the proton conductivity of SPEEK membrane and polycyclotriphosphazene derivative grafted SPEEK membranes at 90 °C. Proton conductivity increased than pure SPEEK by polycyclotriphosphazene derivatives grafted, and an order of magnitude higher than pure SPEEK membrane which reached 10^{-2} S • cm^{-1}.

Table 1. Proton conductivity of SPEEK and grafted membranes at 90 °C

CODE	Thickness (cm)	Area (cm^2)	Impedance (Ω)	Proton conductivity ($S\cdot cm^{-1}$)
SPEEK	0.0101	0.145	9.38	7.42×10^{-3}
GR02	0.0102	0.145	6.56	1.07×10^{-2}
GR05	0.0102	0.145	5.49	1.28×10^{-2}
GR08	0.0111	0.145	2.82	2.71×10^{-2}
GR10	0.0110	0.145	2.11	3.59×10^{-2}
GR15	0.0111	0.145	1.59	4.81×10^{-2}

The proton conductivity of the membranes is shown in figure 6. As the temperature rising, the proton conductivity of the pure SPEEK membrane increased. The active participation of the proton transfer has been strengthened to improve the efficiency of their transitions in the membrane, resulting in proton conductivity increases. The proton conductivity of 64.5% DS pure SPEEK membrane was 1.82×10^{-4} S•cm^{-1} at 20 °C. But after grafted, all the proton conductivity increased to an order of magnitude than pure SPEEK membrane. But did not reach 10^{-2} S•cm^{-1} at 20 °C. Combined table 1, it reached a maximum 7.42×10^{-3} S•cm^{-1} at 90 °C. G15 is up to 4.81×10^{-3} S•cm^{-1} at 90 °C. The proton conductivity of all the graft membranes reached above 10^{-2} S•cm^{-1} at 90 °C.

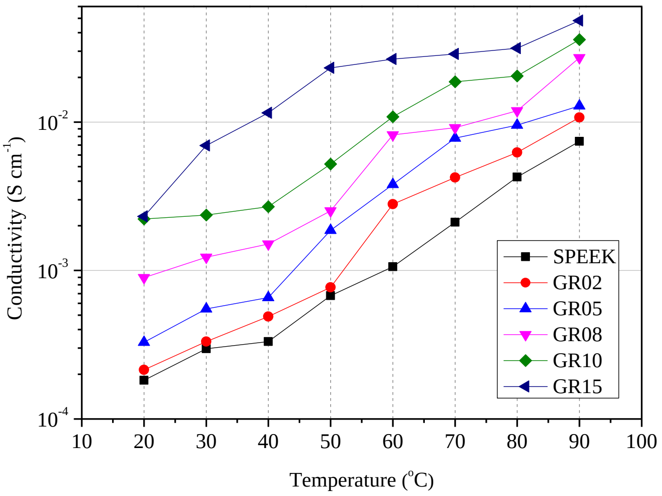

Figure 6. Proton conductivity of SPEEK and grafted membranes vs temperature

From the curves, it is indicated that the proton conductivity increased with the temperature increasing, wherein the proton conductivity of GR02 membrane was rather with pure SPEEK membrane. The proton conductivity increases with the degree of grafting increasing. The proton conductivity of GR15 membrane was the best, reached 10^{-2} S•cm^{-1} 40 ^{o}C, remained stable at between 50-90 ^{o}C, and arrived the highest 4.81×10^{-2} S•cm^{-1} at 90 ^{o}C. An order of magnitude higher than pure SPEEK and significantly promoted the proton conductivity performance.

With the increase of the grafting degree, polycyclotriphosphazene derivatives on SPEEK side chains were increased and the sulfonic acid groups in the membrane corresponding increased. Also the hydrophilic area increases and proton conduct easier. Alternating nitrogen and phosphorus formed a conjugated ring in the side chain, the introduction of large number of -SO_3H groups, 65Å peculiar cluster of polycyclotriphosphazene derivatives and the electronic effect of N atoms in the N-P ring increasing the adhesion of water molecules, which have to ensure effective proton transition and the proton conductivity increases [19]. From one way, with more polyphosphazene pendant groups being grafted, sulfonic groups on SPSCEK side chains might generate wide range of transmission channels with ones on backbones which facilitated speed and efficiency of proton conduction and hydrogen bonds interaction bridged between sulfonic and amino groups. From another way, long pair electrons of nitrogen atoms in pendant groups contributed to adhesion of water molecules that ensured proton flopping, where pendant groups encouraged separation of hydrophilic and hydrophobic phases to reduce difficulty of proton conduction. The proton conductivity of each group membrane increases with the temperature increasing which may be due to the increase of the number of protons can be activated to lead proton transitions easier, so the proton conductivity increase with the temperature increasing.

Table 2 was the methanol permeability coefficient of SPEEK membrane and polycyclotriphosphazene derivative grafted SPEEK membranes. According to table 2, the methanol permeation coefficient of DS 64.5% pure SPEEK is 1.30×10^{-7}cm^2•s^{-1}. After grafted by polycyclotriphosphazene derivatives, methanol permeability coefficient increases with the grafting degree increasing. But the overall increases changes not, within $10^{-7}cm^2•s^{-1}$, to meet the use requirements of the proton exchange membrane.

Table 2. Methanol permeability coefficient of SPEEK and grafted membranes

CODE	Thickness (cm)	Area (cm^2)	Straight Slope ($\times10^{-6}mol\cdot L^{-1}\cdot s^{-1}$)	Methanol permeability coefficient ($\times10^{-7}cm^2\cdot s^{-1}$)
SPEEK	0.0101	0.345	0.746	1.30
GR02	0.0102	0.345	1.16	2.04
GR05	0.0102	0.345	1.42	2.52
GR05	0.0111	0.345	1.43	2.77
GR10	0.0110	0.345	1.47	2.81
GR15	0.0111	0.345	1.49	2.86

From figure 7, it is indicated that the concentration of methanol diffusion of membrane samples increases with time and increasing. The slope of methanol permeable concentration curves of grafted membranes was higher than pure SPEEK. The changes in methanol osmotic concentration of pure SPEEK membrane was stabilizing trend. For GR15 film, pre-osmotic concentration trend change than pure methanol SPEEK membrane increases, the slope of the curve is large, but the late slope of the curve is similar to pure SPEEK membrane.

In the grafted SPEEK membrane, the methanol permeability coefficient increased with the degree of grafting increasing. The probably reasons are: On the one hand, the introduction of polycyclotriphosphazene derivatives formed ring structure side groups on SPEEK main chain. Increasing the steric hindrance and compactness of the membrane, obstructing methanol molecules permeate. On the other hand, a large number of sulfonic acid groups in the phosphazene ring formed hydrophilic region in membrane which is conducive to methanol molecule penetration. And the higher the degree of grafting, the greater number of hydrophilic regions, leading to the increase of methanol permeation coefficient. Combined the effect of these two aspects, the methanol permeability coefficient of grafted membranes was increased compared to pure SPEEK membrane, but increased marginally, to meet the use requirements of DMFC proton exchange membrane. Both sulfonic groups on side chains and ones on backbones would generate hydrophilic regions in membranes and this effect was in favor of methanol molecules running through membranes [20]. The water absorption rate increases in favor of improving the proton conductivity. But when the excessive water absorption and swelling, it will cause swelling and poor dimensional stability to be cannot even use.

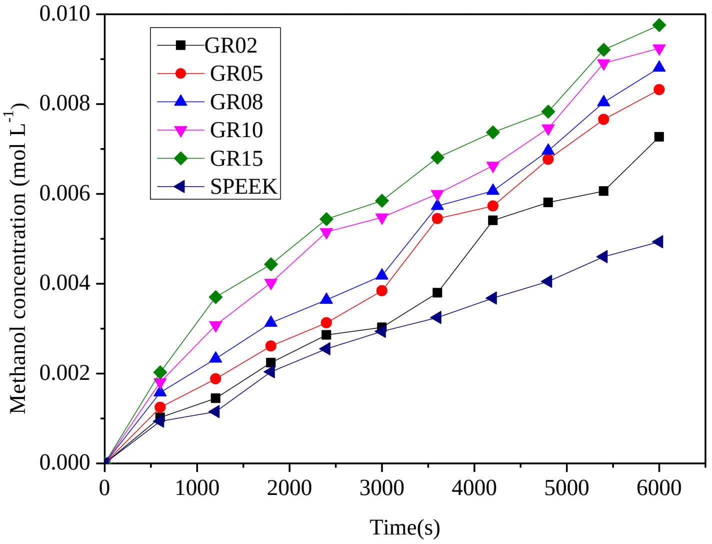

Figure 7. Methanol concentration of SPEEK and grafted membranes vs time

The thermal properties of the membranes were analyzed by thermal gravimetric analysis and TG curves are shown in figure 8. From the curves, its shows that all the grafted membranes have significant weight loss processes. The first process of a thermal weight loss occurs at room temperature to 150 °C which due to a small amount of water evaporation or volatile solvent remaining in the molding process. The weight loss of this process increased with the grafting degree increasing, which may be due to the bound water removal with the increase of introduced of sulfonic acid groups. The second hermogravimetric process took place at 250-400 °C which due to the thermal decomposition of the sulfonic acid groups. The third thermogravimetric process was 450-550 °C corresponding to the heat degradation of the polymer main chain [21].

The thermal stability of grafted membrane was higher than pure membrane. But it was showing the first rise after falling trend with increase of grafting degree. GR08 has the best thermal stability. However, the residual rate rises of grafted membranes are all more than pure SPEEK. The main reason could be the chemical grafting method and sulfonic acid groups and ternary phosphazene ring structures effectively improve the heat resistance of the membranes, reducing the thermal decomposition rate especially high temperature thermal decomposition rate. It can be readily attributed to the inherent thermal-stability properties of the cyclotriphosphazene cores and masses of sulfonic acid groups. The cyclotriphosphazene moieties produce phosphoric acid, metaphosphoric acid or orthophosphorous acid during pyrolysis. With the presence of cyclotriphosphazene, cross-linking and gelation occurs in the thermal decomposition. As the network structure and gelatin can inhibit the production of small molecules, the higher char yield is an effect of achieving synergy between the individual units. Polyphosphazene rings took placed ring-opening reaction in the thermal generation process to from a P-O-P crosslinked structure [18, 22-23]. The appearance of P-O-P group is considered as crosslinking to different species, resulting in the formation of complex phosphorus structures. All the above cases due to the decomposition rate slowed upon 400 °C and significantly higher rate of solid residual.

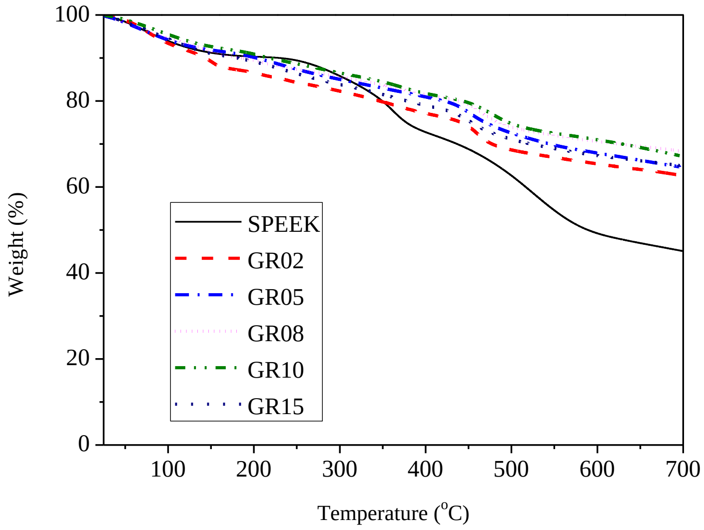

Figure 8. TG curve of polycyclotriphosphazene derivative grafted SPEEK membranes

4. CONCLUSIONS

Poly(sulfonic acid)cyclotriphosphazene derivative can improve the performance of proton conductivity by grafting SPEEK. The proton conductivity of grafted membranes were higher than pure SPEEK at 20 °C. The proton conductivity exhibits a tendency to increase over temperature and grafting degree. The proton conductivity reached above 10^{-2} S·cm^{-1}. The improved effect is obvious. GR15 has a max proton conductivity of 4.81×10^{-2} S·cm^{-1}.

The methanol permeability of grafted SPEEK membrane is slightly lower than pure SPEEK, but kept within the 10^{-7} cm^{2}•s^{-1}. With the increase of the grafting degree, the methanol permeability coefficient of grafted membrane was increased up to 2.86×10^{-7} cm^{2}•s^{-1}, an order of magnitude lower than the Nafion membrane but reach the use requirement of DMFC proton exchange membrane.

Grafted polycyclotriphosphazene derivatives improve the thermal stability properties of the membranes. With the increase of the grafting degree, the thermal stability of grafted membrane was slightly lower, wherein GR02 membrane has the highest thermal stability. The grafting membrane samples had excellent thermal stability and achieved the use requirements of proton exchange membrane.

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References

1. L. Du, X.M. Yan, G.H. He, X.M. Wu, Z.W. Hu and Y.D. Wang, *Int. J. Hydrogen Energ.* 37 (2012) 11853.

2. V.S. Silva, B. Ruffmann, S. Vetter, M. Boaventura, A.M. Mendes, L.M. Madeira and S.P. Niunes, *Electrochim. Acta*, 51 (2006) 3699.
3. M. Gil, X.L. Ji, X.F. Li, H. Na, J.E. Hampsey and Y.F. Lu, *J. Membrane Sci.*, 234 (2004) 75.
4. S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver and S. Kaliaguine, *J. Membrane Sci.*, 173 (*2000*) 17.
5. J.Y. Tong, Q. Guo and X.X. Wang, *Express Polym. Lett.*, 3 (2009) 821.
6. M.M. Radhi, W.T. Tan, M.Z. Rahman, and A.B. Kassim, *Int. J. Electrochem. Sci.*, 5 (2010) 254.
7. S.P. Nunes, B. Ruffmann, E. Rikowsky, S. Vetter and K. Richau, *J. Membrane Sci.*, 203 (2002) 215.
8. Z.Y. Dou, S.L. Zhong, C.J. Zhao, X.F. Li, T.Z. Fu and H. Na, *J. Appl. Polym. Sci.*, 109 (2008) 1057.
9. O. Nakamura and I. Ogino, *Mater. Res. Bull.*, 17 (1982) 231.
10. R. Gosalawit, S. Chirachanchai and S. Shishatskiy, *J. Membrane Sci.*, 323 (2008) 337.
11. X.F. Li, C.P. Liu, D. Xu, C.J. Zhao, Z. Wang, G. Zhang, H. Ha and W. Xing, *J. Power Sources*, 162 (2006) 8.
12. V.S. Silva, B. Ruffmann, S. Vetter, M. Boaventura, A.M. Mendes, L.M. Madeira and S.P. Niunes, *Electrochim. Acta*, 51 (2006) 3699.
13. R. N. Bonifácio, A. O. Neto and M. Linardi, *Int. J. Electrochem. Sci*., 8 (2013) 159.
14. J.W. Wang, Z.R. Yue and J. Economy, *J. Membrane Sci.*, 291 (2007) 210.
15. Z.P. Zhao, Z.P. Zhou and M.Q. Zhong, *Int. J. Electrochem. Sci*., 9 (2014) 8120.
16. J. Kerres and A. Ulrich, *Sep. Purif. Technol.*, 22 (2001) 1.
17. S. Jankowsky, M.M. Hiller, O. Fromm, M. Winter and H.D. Wiemhofer, *Electrochim. Act*a, 155 (2015) 364.
18. Z.P. Zhao, Q. Guo, W.K. Zhai and Z.J Nie, *J. Appl. Polym. Sci.*, 128 (2012) 4368.
19. X.Y. Zhang, J. Weston and H.R. Allcock, *Electrochim. Acta*, 48 (2012) 2173.
20. J. Kerres, A. Ulrich, M. Hein, V. Gogel, K.A. Friederich and L. Jörissen, *Fuel Cells*, 4 (2004) 105.
21. A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla and J.E. Mcgrath, *Chem. Rev.*, 104 (2004) 4587.
22. O. Weichold, B. Tigges, W. Voigt, A. Adams and H. Thomas, *Adv. Eng. Mater.*, 5 (2009) 417.
23. E. Morales and J.L. Acosta, *Solid State Ionics*, 96 (1997) 99.