

## Polycyclotriphosphazene Derivative Grafted and Nanometer $Y_2O_3$ Doped SPEEK Composite Membrane for DMFC

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(Received May 19, 2013; Accepted August 21, 2013)

**ABSTRACT.** A type of polycyclotriphosphazene derivative (PCTPD), hexasulfanic acid polycyclotriphosphazene (HSACP) and HSACP grafting SPEEK, sulfonated poly[2-(petachloropolycyclotriphosphazene-oxy)] etheretherketone (SPPSACPEEK) were synthesized, which were characterized by FTIR and  $^{31}P$  NMR. Then three types of composite membranes such as HSACP grafting SPEEK, HSACP blending SPEEK, and nano  $Y_2O_3$  doping and HSACP grafting SPEEK, respectively, were continuously prepared by solution-casting method. Comparing to SPEEK membranes with different amount of HSACP grafted or blended, grafting 15 wt% HSACP and doping 10 wt% nano  $Y_2O_3$  SPEEK membrane conducted outstanding overall behavior of proton conductivity reaching  $3.18 \times 10^{-2}$  S/cm at 90 °C which was merely junior to SPEEK with 15 wt% HSACP grafted, methanol permeability coefficient getting  $9.46 \times 10^{-8}$  cm $^2$ ·s $^{-1}$ , swelling degree of 20.9% and solid residue of 98.98% which was superior to all specimen.

**Key words:** Polymer membranes, SPEEK, Polycyclotriphosphazene derivative,  $Y_2O_3$

### INTRODUCTION

Nowadays, it is widely thought proton conductivity, methanol permeability coefficient and swelling degree play an important role for proton exchange membranes.<sup>1</sup> Mikhailenko et al.<sup>2,3</sup> have reported that sulfonated polyetheretherketone (SPEEK) with high degree of sulfonation (DS) could reach high proton conductivity and methanol permeability coefficient, which wasn't preferable in terms of its application. As a result, rare earth oxide such as yttrium oxide ( $Y_2O_3$ ), titanium oxide ( $TiO_2$ ) and cerium oxide ( $CeO_2$ ) has been used to improve SPEEK integrative properties because of their broad transparency, excellent physical and chemical stability.<sup>4,5</sup> Tong et al.<sup>6</sup> have prepared the SPEEK/ $Y_2O_3$  composite membranes and concluded that coordination bonds existed between yttrium cation of  $Y_2O_3$  and oxygen anion of sulfonic groups characterized by FTIR and XRD, which showed good effect on methanol resistance while reducing proton conductivity in the long run.

On the other hand, ionic liquid composed of organic cations and organic or inorganic anions at room temperature<sup>7</sup> is considered scientific hotspot, which aimed at upgrading proton conductivity of SPEEK. Chen et al.<sup>8</sup> improved SPEEK integrative properties by doping 1-ethyl-3-methylimidazole tetrafluoroborate (EB) or 1-butyl-3-methylimidazole methanesulfonate (BS) and dispersed  $Y_2O_3$  into system.

Consequently, proton conductivity of SPEEK/EB/ $Y_2O_3$  composite membrane was above  $10^{-2}$  S/cm at 90 °C. However, it is so easy for ionic liquid to run off that modified SPEEK membranes deserved ineffective<sup>9,10</sup> and most ionic liquid is hydrophilic which is beneficial to proton conduction but detrimental to methanol resistance and anti-swelling degree.

Due to the superior flexibility of backbones and diversity of side groups, PCTPD are expected to emerge as novel membrane materials for direct membranes fuel cells (DMFC). Allcock<sup>11</sup> has synthesized poly [(4-bromophenoxy) (3-methyl-phenoxy)] phosphazene and its proton conductivity was approximately  $10^{-2}$  S/cm, methanol permeability coefficient was little lower than Dupont Nafion115 membranes. In this paper, HSACP was used for promoting proton productivity by grafting and blending SPEEK, then doping nano  $Y_2O_3$  to reduce methanol permeability coefficients and swelling degree.

### MATERIALS AND MEMBRANE SPECIMENS

#### Synthesis of SPEEK Grafted by HSACP

Polyetheretherketone (PEEK) was obtained from Chemistry Department of Jilin University (Jilin, China) in the form of particle and SPEEK was prepared as reported earlier.<sup>12,13</sup> After getting SPEEK with DS of 64.10%,  $NaBH_4$  from Sinopharm Chemical Reagent Co. Ltd. (Shanghai,

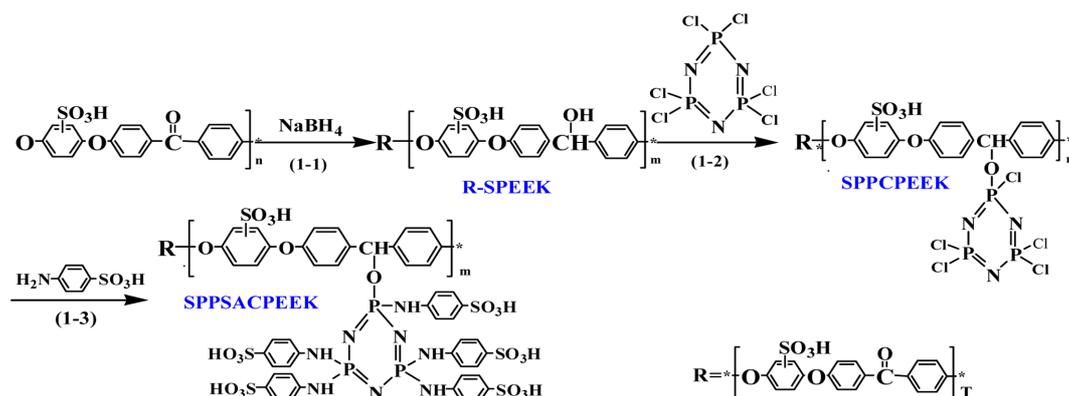


Figure 1. Synthesis of SPSSACPEEK.

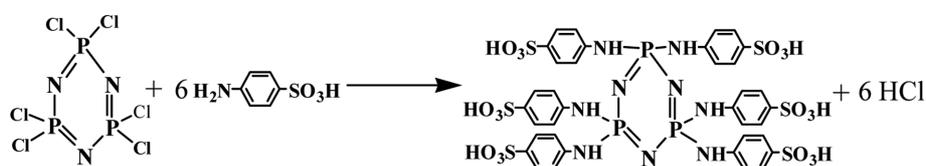


Figure 2. Synthesis of HSACP.

China) was utilized to accomplish carbonyl reduction of SPEEK at 100 °C, 24 h for synthesis of sulfonated poly [2-hydroxy] etheretherketone (R-SPEEK) (Fig. 1, 1-1). Subsequently, sulfonated poly [2-(petachloropolycyclotriphosphazene-oxy)] etheretherketone (SPPCPEEK) was synthesized by adding R-SPEEK solution into hexachlorocyclotriphosphazene (HCCP) (laboratory self-synthesized) dissolving in DMAC at iced-water atmosphere for 20 h with mechanical stirring (Fig. 1, 1-2). After that, certain amount of hexasulfanilic acid (SA) from Aladdin Reagent Co. Ltd. (Japan) was put into SPPCPEEK solution to synthesize sulfonated poly [2-(petasulfanilic acid polycyclotriphosphazene-oxy)] etheretherketone (SPSSACPEEK) (Fig. 1, 1-3) under ultrasonic firstly then at 60 °C for 4 h.

### Preparation of Membranes

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, three kinds of membranes were prepared namely HSACP grafting SPEEK, HSACP blending SPEEK, and

nano Y<sub>2</sub>O<sub>3</sub> doping and HSACP grafting SPEEK. HSACP was synthesized by reacting HCCP with SA shown in Fig. 2 and its experimental condition was identical with reaction (1-3) in Fig. 1.

Different compositions of membranes were described in Table 1, where “GR”, “B” and “Y” represented HSACP grafting SPEEK, HSACP blending SPEEK and Y<sub>2</sub>O<sub>3</sub> doping respectively, and the subsequent values of “GR” in codes GR2, GR5, GR8, GR10, GR15, GR15Y01, GR15Y05 and GR15Y10 indexed grafting degree weight percent of SPEEK (e.g., GR15 represented system with 15 wt% HSACP grafting SPEEK), and that of “Y” indexed weight percent of Y<sub>2</sub>O<sub>3</sub> (e.g., GR15Y10 represented system with 15 wt% HSACP grafting SPEEK and 10 wt% nano Y<sub>2</sub>O<sub>3</sub> doped).

## EXPERIMENTAL

### Analysis Methods of Material Structure and Membrane Surface Morphology

Structural characterization were analyzed by Fourier Transform Infrared (FTIR), <sup>1</sup>H Nuclear Magnetic Reso-

Table 1. Contents of membrane specimens

Code	SPEEK	B05	B10	GR15Y01	GR15Y05	GR15Y10
SPEEK (wt%)	100	95	90	0	0	0
15 wt% HSACP grafting SPEEK (wt%)	0	0	0	99	95	90
HSACP (wt%)	0	5	10	0	0	0
Y <sub>2</sub> O <sub>3</sub> (wt%)	0	0	0	1	5	10

nance ( $^1H$  NMR) and  $^{31}P$  Nuclear Magnetic Resonance ( $^{31}P$  NMR). The FTIR spectra of specimens were recorded with AVATAR370 Infrared Spectrometer (Thermo Nicolet Instrument Co., USA) while  $^1H$  NMR and  $^{31}P$  NMR with AVANCE 500MHz (Bruker, Switzerland). All the specimens were liquid (before preparation of membranes) so we painted them on glass plate directly for FTIR and chose deuterium dimethyl sulfoxide (DMSO- $d_6$ ) as solvent for  $^1H$  NMR and  $^{31}P$  NMR.

The morphology of membrane surface was investigated by scanning electron microscope (SEM) HITACHI S-4800 (Tokyo, Japan). The specimens were pretreated by freezing the dry membranes in liquid nitrogen. The fresh cryogenic fracture of the membrane specimens was sputtered with a thin layer of Au in vacuum prior to SEM measurements.

### Testing Method of Proton Conductivity

Proton conductivity of membrane specimens in the traverse direction was tested in a measurement cell using AC Electrochemical Impedance Spectroscopy (EIS), which was composed of a Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255B 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, and the testing temperature ranged from 30 to 90 °C. The resistance of membranes was measured and the proton conductivity was calculated as described in the reference.<sup>13</sup>

### Testing Method of Methanol Permeability Coefficient

Methanol permeability coefficient of membrane specimen was determined by a home-made diaphragm diffusion cell, which was amply described in reference.<sup>14</sup> 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).

$$P = S \frac{Vl}{AC} \quad (1)$$

### Testing Method of Swelling Degree and Thermal Stability

Swelling degree ( $S_d$ ) was calculated by measuring the

volume difference between the dry and hydrous membrane specimens.<sup>12,13</sup> The dried membranes were measured volume ( $V_{dry}$ ) before being immersed in de-ionized water for 24 h at 30 °C, 50 °C, 70 °C and 90 °C respectively. After that, the membranes were wiped with blotting paper to remove the surface water and measured ( $V_{wet}$ ) again. The  $S_d$  was calculated by the following equation:

$$S_d = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\% \quad (2)$$

Thermal stability of membranes was evaluated by recording thermo-gravimetric (TG) traces in nitrogen atmosphere (Q500, TA Company, USA). Heating rate of 10 °C/min. Temperature ranges from 10 °C to 600 °C and sample weights from 3 to 7 mg in the form of membrane were used for recording TG traces.

## RESULTS AND DISCUSSION

### Structural Analysis

Comparing SPEEK with R-SPEEK spectra in Fig. 3, both of them possessed characteristic peaks at  $1650\text{ cm}^{-1}$  for  $-Ar-C(=O)-Ar-$ ,  $1118\text{ cm}^{-1}$  for  $-Ar-O-$ ,  $1226\text{ cm}^{-1}$  for  $O=S=O$  asymmetric stretching vibration,  $1080\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  for  $O=S=O$  and  $S=O$  symmetric stretching vibration respectively. However, there appeared a wide absorption peak around  $3400\text{ cm}^{-1}$  in R-SPEEK spectra corresponded to  $O-H$  stretching vibration. Because the amount of sulfonic groups remained unchanged after reaction (1-1) in Fig. 1, we cited internal standard method to calculate degree of carbonyl reduction,<sup>15</sup> namely dividing absorption peak areas at  $1650\text{ cm}^{-1}$  ( $-C=O$ ) with  $1080\text{ cm}^{-1}$  ( $-SO_3H$ ) before and after reaction. Therefore, we got degree of SPEEK

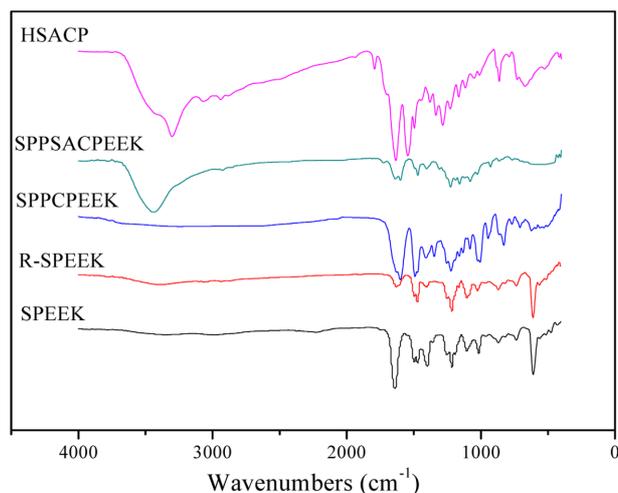
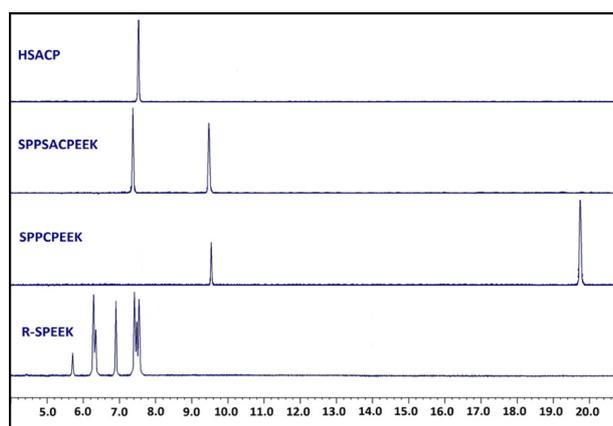


Figure 3. FTIR spectra of HSACP, SPEEK and modified SPEEK.



**Figure 4.**  $^1\text{H}$  NMR spectra of R-SPEEK and  $^{31}\text{P}$  NMR spectra of HSACP and modified SPEEK.

carbonyl reduction as 29.8% according to the following equation (3):

$$\alpha = 1 - \frac{[A_{1650}/A_{1080}]_{\text{After}}}{[A_{1650}/A_{1080}]_{\text{Before}}} \times 100\% \quad (3)$$

While it turned to  $^1\text{H}$  NMR characterization of R-SPEEK in Fig. 4, absorption peaks between 7.0 ppm and 8.0 ppm indexed hydrogen protons of R-SPEEK benzene rings. The weak absorption peak at 5.7 ppm corresponded to hydrogen of tertiary carbon certified structure changing partially from  $-\text{Ar}-\text{C}(=\text{O})-\text{Ar}-$  to  $-\text{Ar}-\text{CH}(\text{-OH})-\text{Ar}-$ .

Moreover, Fig. 3 also included the FTIR spectra of SPPCPEEK. Besides characteristic peaks of SPEEK mentioned above, absorption peaks appeared at  $527\text{ cm}^{-1}$  and  $605\text{ cm}^{-1}$  for different conformation of P-Cl,  $947\text{ cm}^{-1}$  for P-O stretching vibration,  $870\text{ cm}^{-1}$  for P-N absorption and  $1217\text{ cm}^{-1}$  for P=N stretching vibration. Thus, auxiliary to evidence from  $^{31}\text{P}$  NMR spectra of SPPCPEEK, where existed phosphorus atoms of two kind of chemical environments. One chemical shift at 19.8 ppm was for five P-Cl while the other at 9.6 ppm for one P-O within one cyclo-triphosphazene ring. As a result, HCCP proved to be grafted onto SPEEK backbones.

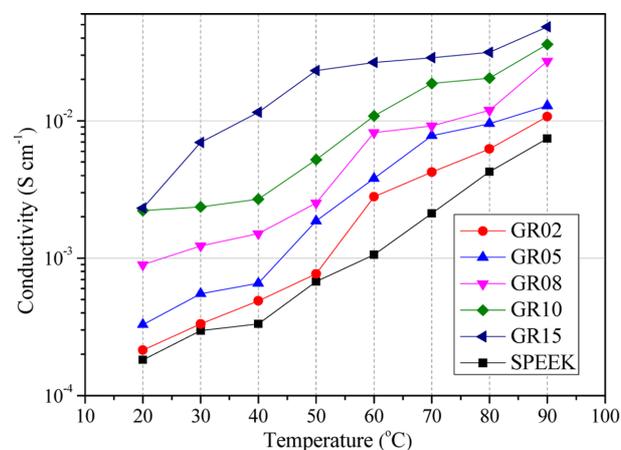
To improve proton conductivity and system stability, SA reacted with SPPCPEEK to increase numbers of sulfonic groups and benzene rings. According to Fig. 3, spectra of SPPSACPEEK still included characteristic peaks of SPPCPEEK except for P-Cl stretching vibration at  $527\text{ cm}^{-1}$  and  $605\text{ cm}^{-1}$  which demonstrated the fact all chlorine atoms were substituted by SA. Absorption peak between  $3400\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$  was for N-H stretching vibration,  $1490\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  were for benzene rings. Fig. 4 showed  $^{31}\text{P}$  NMR spectra of SPPSACPEEK where two kinds of chem-

ical shift were caught. One at 7.4 ppm was for phosphorus atoms connected with SA while the other at 9.6 ppm was with SPEEK backbones. In contrast to  $^{31}\text{P}$  NMR spectra of SPPCPEEK, there was no chemical shift for SPPSACPEEK at 19.8 ppm which proved chlorine atoms were substituted by SA once more.

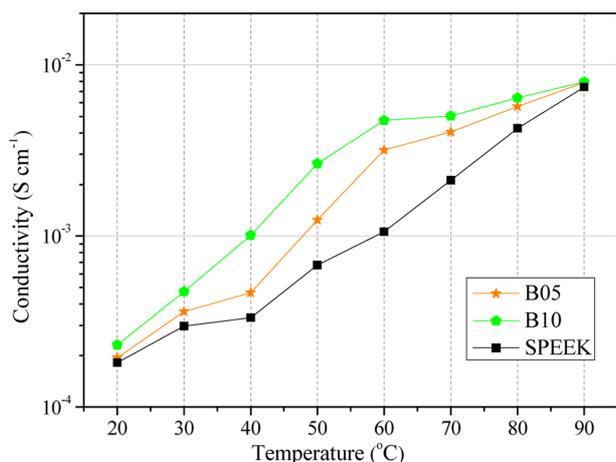
As for synthesis of HSACP, absorption peaks at  $870\text{ cm}^{-1}$  and  $1217\text{ cm}^{-1}$  were for polycyclotriphosphazene rings,  $1490\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  were for  $-\text{NH}-\text{Ar}-$ ,  $710\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$ ,  $1092\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  were for sulfonic groups. Stretching vibration peak at  $3370\text{ cm}^{-1}$  suggested N-H stretching vibration.  $^{31}\text{P}$  NMR characterization proved there only existed one kind chemical atmosphere at 7.62 ppm corresponded to  $-\text{P}-\text{NH}-$ .<sup>16</sup>

### Proton Conductivity of Membranes

Since proton conductivity played an important role in application for DMFC, its value should reach  $10^{-2}\text{ S/cm}$  above. Proton conductivity of SPEEK and SPPSACPEEK membranes were measured from 20 to  $90\text{ }^\circ\text{C}$  shown in Fig. 5. With increasing temperature, proton conductivity of all specimens improved considerably since activity of proton was strengthened to enhance the efficiency of conduction in the membranes. As more HSACP being grafted, proton conductivity advanced more fiercely at the same temperature. Especially for specimen GR15, its productivity was over  $10^{-2}\text{ S/cm}$  at  $40\text{ }^\circ\text{C}$  even reached  $4.81 \times 10^{-2}\text{ S/cm}$  at  $90\text{ }^\circ\text{C}$ . From one way, with more HSACP being grafted, sulfonic groups on SPPSACPEEK 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.<sup>17</sup> From another way,



**Figure 5.** Proton conductivity of SPEEK and SPPSACPEEK membranes.

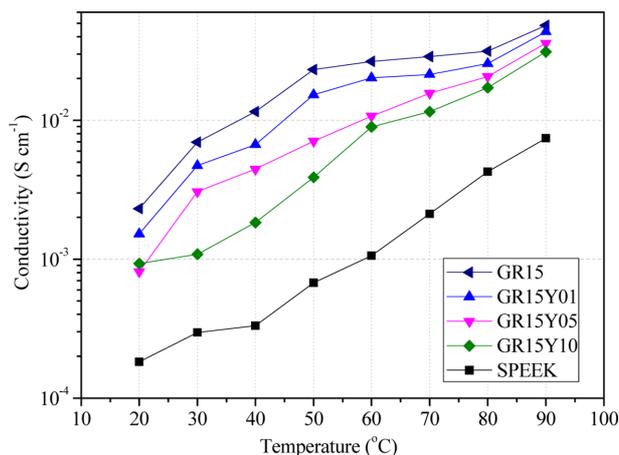


**Figure 6.** Proton conductivity of SPEEK and HSACP blending SPEEK membranes.

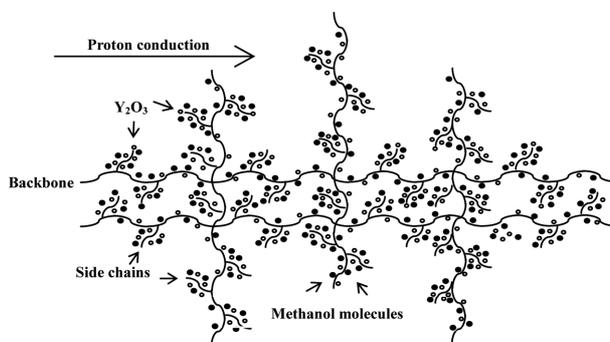
long pair electrons of nitrogen atoms in HSACP contributed to adhesion of water molecules that ensured proton flopping, where HSACP encouraged separation of hydrophilic and hydrophobic phases to reduce difficulty of proton conduction.

In contrast to *Fig. 5*, proton conductivity of B05 and B10 in *Fig. 6* could be divided into two parts although their values were always under  $10^{-2}$  S/cm at whatever temperature. When it rose from 20 to 60 °C, proton conductivity upgraded apparently and the mechanism was likely to the one mentioned in *Fig. 5*. As temperature continuously rose up to 90 °C, both of their conductivity ceased to upgrade directly and reached almost same values with pure SPEEK because bond energy of physical interaction was so weak that thermal energy would destroyed transmission channels generated in blending system and HSACP was doomed to running off.

It was concluded that grafting HSACP was far more effective than doping one on enhancement of proton conductivity. Therefore,  $Y_2O_3$  was doped into SPSSACPEEK system for further research on conductivity promotion. *Fig. 7* displayed the same trend as *Fig. 5* that proton conductivity upgraded from 20 to 90 °C. However, conductivity of specimen GR15Y05 and GR15Y10 was little lower than GR15 from 70 to 90 °C which was near to operating temperature of proton exchange membranes. As was drawn in *Fig. 8*, nano  $Y_2O_3$  mostly dispersed around side chains where were abundant in sulfonic clusters then the sulfonic groups on the backbones took more responsibility for proton conduction because of steric hindrance of side groups that made  $Y_2O_3$  uneasily act on backbones. Moreover, volume effect caused by  $Y_2O_3$  might also be



**Figure 7.** Proton conductivity of SPEEK and  $Y_2O_3$  doping SPP-SACPEEK membranes.

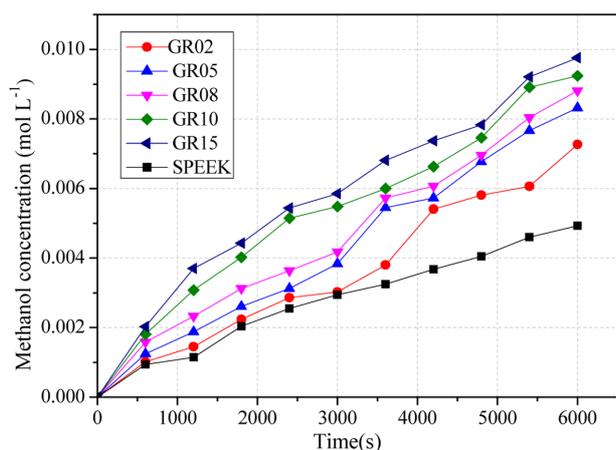


**Figure 8.** Operation principle of  $Y_2O_3$  doping SPSSACPEEK membranes.

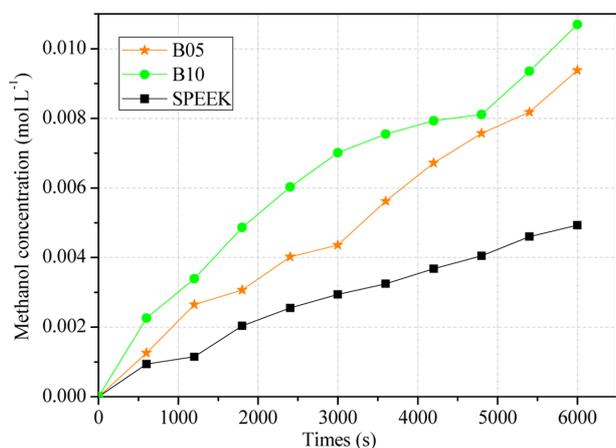
possibly to influence proton conduction a little. Consequently, adding little amount of  $Y_2O_3$  didn't detract from its proton conductivity remarkably from 70 to 90 °C since pure SPEEK with high DS was good at proton conduction.<sup>2,3</sup>

#### Methanol Permeability Coefficients of Membranes

It was known that low methanol concentration was equal to small methanol permeability coefficients. Methanol concentration of SPEEK and SPSSACPEEK membranes was tested shown in *Fig. 9*. With the increase of grafting degree, methanol concentration upgraded simultaneously. At the same time, GR15 reached the highest methanol concentration but its value was only little higher among all specimens. 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. Combined with *Fig. 8*, HSACP as side groups of SPSSACPEEK increased steric hindrance so as to relieve penetration of methanol molecules.



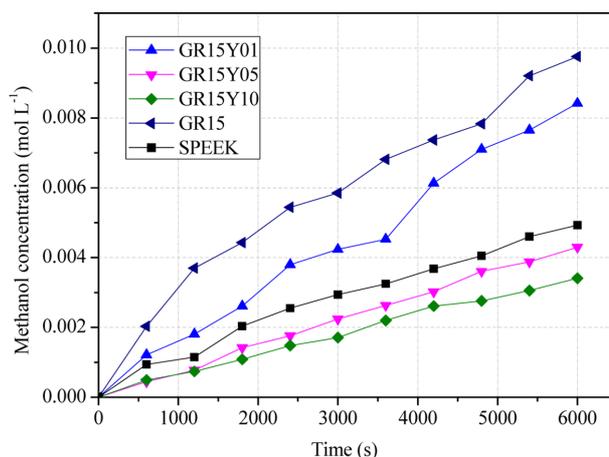
**Figure 9.** Methanol concentration of SPEEK and SPSSACPEEK membranes.



**Figure 10.** Methanol concentration of SPEEK and HSACP blending SPEEK membranes.

Thus, Fig. 10 showed the same trend as Fig. 9 at all. After carefully comparing GR15 with B10 under the same horizon, GR15 had little lower methanol concentration than B10. Maybe this slight difference was caused by the effect of side groups.

As experienced above, grafting modification behaved relatively better than doping one in terms of proton conductivity and methanol permeability coefficients. Since GR15 had the highest proton conductivity from 20 to 90 °C, defined amount of nano  $Y_2O_3$  was doped to enhance its methanol resistance based on the conclusion that small amount of  $Y_2O_3$  shouldn't decrease proton conductivity substantially. In Fig. 11 within the same time, methanol concentration of GR15Y01 was still higher than pure SPEEK but little lower than GR15 which demonstrated the fact that  $Y_2O_3$  was good at methanol resistance but not dominant in system. As for GR15Y05 and GR15Y10,



**Figure 11.** Methanol concentration of SPEEK and  $Y_2O_3$  doping SPSSACPEEK membranes.

their methanol resistance enhanced apparently especially for latter one compared with GR15. It was reported<sup>17,18</sup> that coordination bonds existed between sulfonic groups and  $Y_2O_3$ , which largely destroyed hydrophilic regions around side chains rather than ones near backbones in reference to Fig. 8 and this effect made penetration of methanol molecules through SPSSACPEEK membranes harder. Moreover, as was shown in Fig. 12,  $Y_2O_3$  dispersed evenly in SPSSACPEEK membranes which helped to strengthen density of membranes for preventing the penetration of methanol molecules. Owing to the reasons above, methanol permeability coefficient of specimen GR15Y10 reached  $9.46 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$  calculated by Equation 1.

### Swelling Degree of Membranes

SPEEK proton exchange membranes should also possess good anti-swelling property because cathode of DMFC was mainly filled with water and over-swelling degree would shorten its service life. In Fig. 13, swelling degree was accelerated remarkably especially for specimen GR15 with increasing temperature. Since GR15 membrane was abundant in sulfonic groups, it deserved to absorb plenty of water and thermal energy would push that process happening then led to high swelling degree. As a result, GR15 began to swell at 50 °C and reached swelling degree of 73.8% at 90 °C. Meanwhile, Fig. 14 had the same tendency as Fig. 13 even B10 reached swelling degree of 89.9% at 90 °C because thermal energy ruined physical interaction between SPEEK and HSACP, which resulted in HSACP unevenly dispersed in SPEEK membranes. This consequence would easily cause local over-water absorption and high swelling degree.

When it occurred to Fig. 15, there was no doubt that

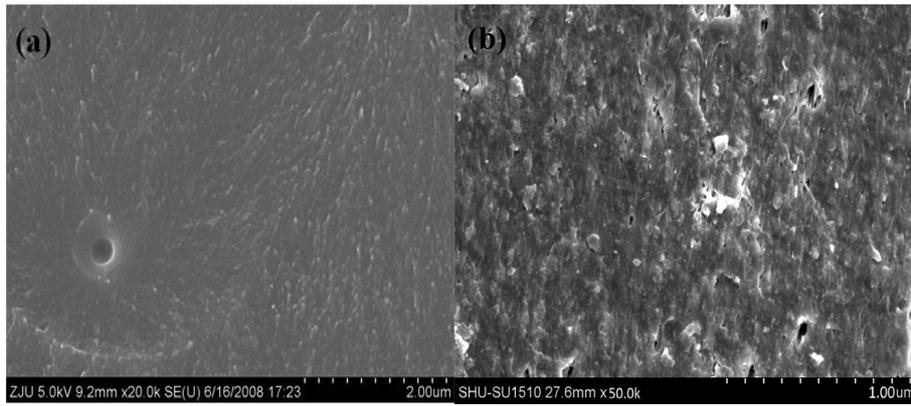


Figure 12. SEM photographs of 10 wt%  $Y_2O_3$  doping SPPSACPEEK membranes.

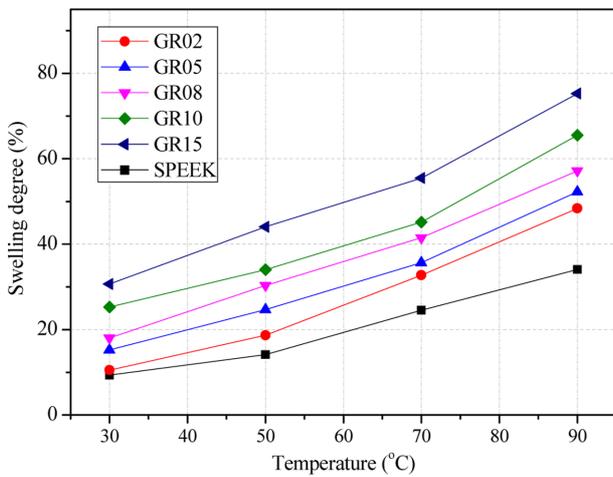


Figure 13. Swelling degree of SPEEK and SPPSACPEEK membranes.

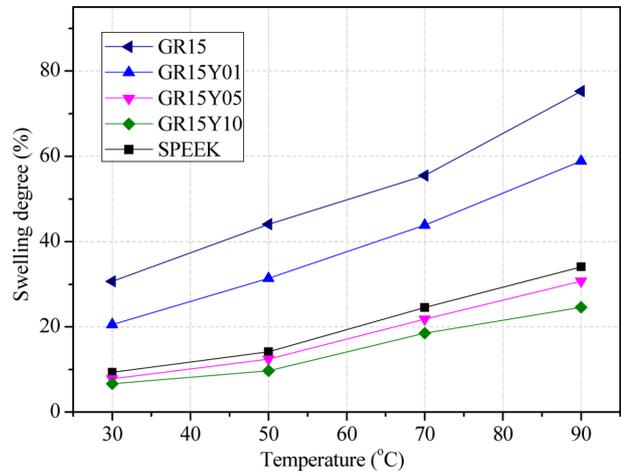


Figure 15. Swelling degree of SPEEK and  $Y_2O_3$  doping SPPSACPEEK membranes.

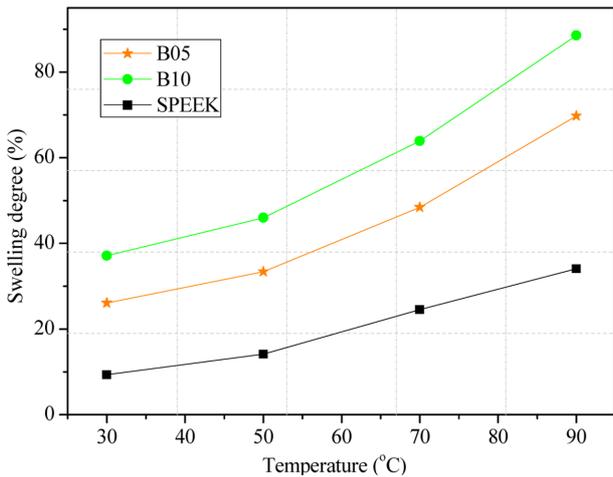


Figure 14. Swelling degree of SPEEK and HSACP blending SPEEK membranes.

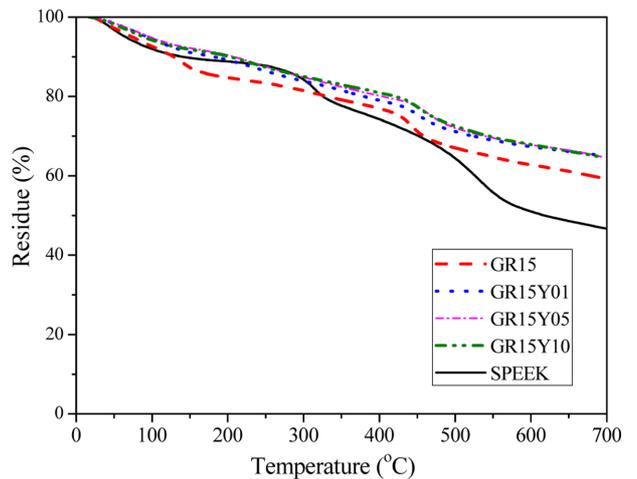


Figure 16. Thermal stability of SPEEK and  $Y_2O_3$  doping SPPSACPEEK membranes.

GR15Y10 displayed the best anti-swelling property, even at 90 °C, its swelling degree was just 20.9% and  $Y_2O_3$  took effect not only to properly decrease number of sulfonic

groups but also to disperse evenly in SPPSACPEEK membranes to avoid mass aggregation of water molecules in membranes.

### Thermal Stability of Membranes

SPEEK proton exchange membranes worked at 90 °C in DMFC normally. As discussed above, doping Y<sub>2</sub>O<sub>3</sub> into grafting system was far more effective than doping it on enhancement of proton productivity, methanol resistance and swelling degree. Therefore, Fig. 16 showed thermal stability of SPEEK and Y<sub>2</sub>O<sub>3</sub> doping SPPSACPEEK membranes. All specimen existed weight loss dividing into three stages. The first one took place around 150 °C largely caused by water and residual solvent evaporation while the second one happened around 400 °C caused by decomposition of sulfonic groups, breakage of P–O and P–N. Eventually, the third stage corresponded to decomposition of SPEEK backbones and ring-opening of phosphazene rings.

### CONCLUSION

A type of polycyclotriphosphazene derivative (PCTPD), hexasulfanilic acid polycyclotriphosphazene (HSACP) and HSACP grafting SPEEK, sulfonated poly [2-(petachloropolycyclotriphosphazene-oxy)]etheretherketone (SPPSACPEEK) were synthesized, which were characterized by FTIR and <sup>31</sup>P NMR. Then three types of composite membranes such as HSACP grafting SPEEK, HSACP blending SPEEK, and nano Y<sub>2</sub>O<sub>3</sub> doping and HSACP grafting SPEEK, respectively, were continuously prepared by solution-casting method. Consequently, grafting 15 wt% HSACP onto SPEEK backbones reached proton conductivity of 4.81×10<sup>-2</sup> S/cm at 90 °C because of great number of sulfonic groups derivative from HSACP, and continuously doping small amount of Y<sub>2</sub>O<sub>3</sub> wouldn't decrease proton conductivity remarkably. After different mass Y<sub>2</sub>O<sub>3</sub> was doped into SPEEK systems with 15 wt% PCTPD grafted, these membranes showed extremely excellent methanol resistance and anti-swelling ability.

To conclude, grafting 15 wt% PCTPD and doping 10 wt% nano Y<sub>2</sub>O<sub>3</sub> to modify SPEEK at 90 °C performed on a quite satisfactory level with proton conductivity reaching 3.18×10<sup>-2</sup> S/cm, methanol permeability coefficient getting 9.46×10<sup>-8</sup> cm<sup>2</sup>·s<sup>-1</sup>, swelling degree of 20.98% and solid residue of 98.98%.

**Acknowledgments.** The authors are grateful to the National Natural Science Foundation of China (No.50975167) and Research Fund for the Doctoral Program of Higher Education of China (Grant No.20113108110015) for the continuing support to this research. And the publication cost of this paper was supported by the Korean Chemical Society.

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