

# Modified Sulfonated Poly(phthalazinone ether ketone) Membranes with Inorganic Particles for Potential Applications in PEMFCs

Zhang Hongwei, Zhu Baoku, Xu Youyi

*Institute of Polymer Science, Zhejiang University, Hangzhou 310027, People's Republic of China*

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**ABSTRACT:** Composite membranes of sulfonated poly(phthalazinone ether ketone)s (SPPEK)s and Zirconium hydrogen phosphate (ZrP) or 12-phosphotungstic acid (PWA) were prepared by direct blending method. The physicochemical properties of these composite membranes were studied through Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy, field-emission scanning electron microscope (FSEM), X-ray diffraction (XRD) and

thermogravimetry analysis (TGA). The SPPEK/PWA composite membranes showed better properties, whose highest proton conductivity could reach 0.17 S/cm at 80°C under 100% relative humidity (R.H.). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3972–3977, 2006

**Key words:** polyelectrolytes; thermogravimetric analysis; mechanical properties; poly(phthalazinone ether ketone)

## INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) uses a solid polymer membrane as its electrolyte. This membrane is an electronic insulator, but an excellent conductor of protons (hydrogen cations).<sup>1</sup> The proton exchange membrane used to date is perfluorosulfonic acid (PFSA) polymer such as Nafion resin manufactured by Du Pont, which consists of a fluorocarbon polymer backbone, similar to Teflon, to which are attached sulfonic acid groups.<sup>1,2</sup> The high electro-osmotic water flows and high costs of PFSA, however, are undesirable for fuel cell applications and have promoted research into alternate proton exchange membrane (PEM) materials.<sup>3</sup> In the past years, two different strategies have been adopted to develop new and improved membranes. One is to identify new or improved polymers that could replace the PFSA membrane, including polyketones,<sup>4–6</sup> polyimides,<sup>7–9</sup> polysulfones,<sup>10–12</sup> and poly(phthalazinone)s<sup>13–16</sup> with diverse mechanical and electrical properties, long-term stability, high efficiency, and low cost. The other concentrates on improving the performances of the existing polymer membranes to make them even more interesting, including organic–inorganic composite or hybrid materials<sup>17–24</sup> with nanosize interfaces between organic and inorganic domains.

The poly(phthalazinone ether ketone)s (PPEK)s have a very high glass transition temperature ( $T_g$ ) more

than 200°C, excellent high-temperature stability, and many other good properties.<sup>15</sup> The sulfonated poly(phthalazinone ether ketone)s (SPPEKs) show proton conductivity above  $10^{-2}$  S/cm at elevated temperature, which is in the range needed for high performance PEMFC.<sup>14</sup>

Zirconium hydrogen phosphate hydrate (ZrP,  $Zr(HPO_4)_2 \cdot nH_2O$ ,  $n = 1$  for  $\alpha$ -form and  $n = 2$  for  $\gamma$ -form) and 12-phosphotungstic acid (PWA) are representative inorganic materials which can transport protons. Their particles have been doped into various polymer matrices and excellent performances were obtained.<sup>19,25</sup> Yu Seung Kim et al. have reported partially disulfonated poly(arylene ether sulfone)s doped PWA having a conductivity of 0.08 S/cm at room temperature.<sup>19</sup> G. Alberti and his group have reported zirconium phosphates containing organic function groups used as inorganic–organic proton conducting membranes, whose conductivity reaches 0.05 S/cm at 100°C (100% R.H.).<sup>26,27</sup> And a kind of zirconium phosphate with acidic properties was reported in Ref. 28 too.

In this study, the  $\alpha$ -ZrP and PWA particles are incorporated into SPPEK membranes (Scheme 1). The primary objectives of this study are to prepare flexible, organic–inorganic, composite membranes. And preliminary conductivity at temperatures between 40 and 80°C under ambient pressure will be presented.

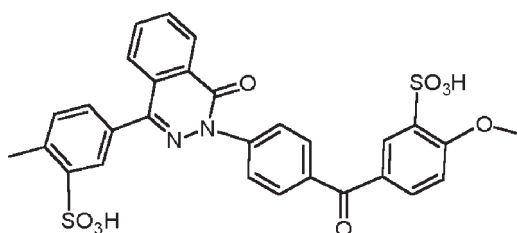
## EXPERIMENTAL

### Materials

PPEK was purchased from Dalian Polymer New Material Co., Ltd., China. It was dried at 105°C for 4 h

Correspondence to: Y.-Y. Xu (opl-yyxu@zju.edu.cn).

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Scheme 1 The chemical formula of SPPEK.<sup>13</sup>

before use. *N,N*-Dimethyl acetamide (DMAc) (Shanghai Chemicals, China) was distilled under reduced pressure and stored with 4Å molecular sieves. Chlorosulfonic acid (Shanghai Tingxin Chemical Plant, China), concentrated sulfuric acid (Shanghai Sanying Chemical Plant, China), Zirconyl chloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , Sinopharm Chemical Reagent Co., China), Phosphoric acid ( $\text{H}_3\text{PO}_4$ , Linping Chemical Plant, Zhejiang Province, China), PWA (Sinopharm Chemical Reagent Co., China) were all analytical reagents and were used as received. ZrP was synthesized by reacting a solution of  $\text{ZrOCl}_2$  with  $\text{H}_3\text{PO}_4$  at room temperature. The ZrP precipitate was filtered from the solution and washed with distilled water, then dried at 80°C for 12 h. The ZrP powder was measured by X-ray diffraction (XRD).

### Sulfonation of PPEK

In a typical experiment, 5 g PPEK powder was dissolved in 50 mL concentrated sulfuric acid of 98% under an argon atmosphere and the mixture was heated to 90°C. 10 mL of chlorosulfonic acid (0.15 mol) dissolved in 30 mL of 98% concentrated sulfuric acid was added in dropwise at the same temperature and the reaction mixture was vigorously stirred for 3 h. The reaction mixture was poured onto crushed ice, and the resulting precipitate was collected by filtration, washed with deionized water until pH 6–7, and then dried at 80°C for 15 h.

### Preparation of membranes

The composite membranes were prepared by direct blending method. The inorganic particles (ZrP or PWA) were blended with SPPEK powder in dimethylacetamide (DMAc) (20% w/v) and the solution of the mixture was stirred for 16 h at 50°C. After treated 1 h in ultrasonic, the solution was spread on a glass plate with a glass knife. The film was dried under ambient conditions for 3 days, and then under vacuum at 80°C for 24 h and 120°C for 24 h. The weight ratio of inorganic particles to SPPEK was 1:9. The SPPEK/PWA composite membranes were transparent, while the SPPEK/ZrP composite membranes were semitransparent.

The SPPEK membranes were prepared by solution casting from solution of the acid form of SPPEK. The SPPEK solution of dimethylacetamide (DMAc) (20%

w/v) was stirred for 16 h at 50°C. Then, the solution was spread on a glass plate with a glass knife. The film was dried under ambient conditions for 3 days and then under vacuum at 80°C for 24 h and 120°C for 24 h. The resulting SPPEK membranes were transparent with a yellow color and a thickness of about 50 μm.

### Measurements

The membrane samples were characterized by Fourier transform infrared attenuated total reflection (FTIR-ATR), infrared spectroscopy using FTIR spectrometer (Thermo Nicolet Nexus 670) with a  $2\text{ cm}^{-1}$  resolution equipped with a Specac GS1100 ATR attachment with a KRS-5 multiple bounce crystal.

A thermogravimetric analyzer (TGA) instrument (Perkin-Elmer TGA-7) was used to measure the degradation temperatures ( $T_d$ ). TGA analysis of samples was done by heating the samples from room temperature to 850°C at 10°C/min under nitrogen atmosphere.

Tensile properties were measured by using mechanical testing machine (Shimadzu AG-1). The grip length was 20 mm, and the speed of testing was set at the rate of 5 mm/min.

The surfaces of composite membranes and their cross sections cut in liquid nitrogen (77 K), with two small nippers were characterized with a field-emission scanning electron microscope (FSEM, Sirion) using an in-lens detector at 5 kV incident beam voltage.

XRD measurements were carried out on a Rigaku D/max-rA X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15, 406\text{ nm}$ ) at 40 kV and 80 mA.

The proton conductivity was measured by alternating-current (ac) impedance spectroscopy over a frequency range of 1–10<sup>7</sup> Hz with oscillating voltage 50–

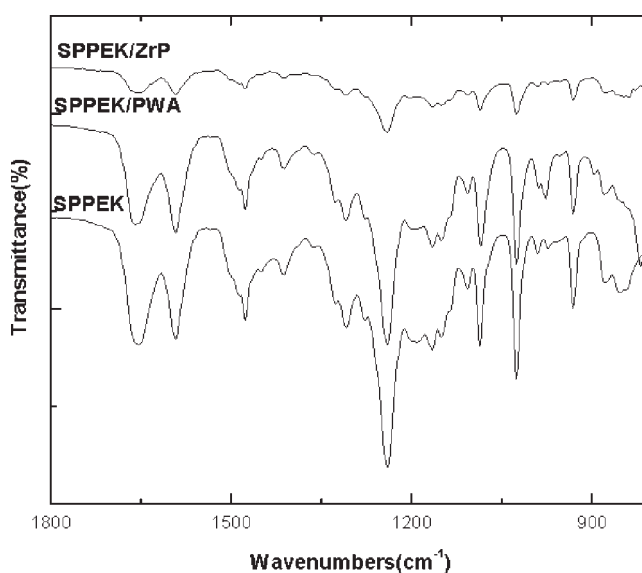


Figure 1 FTIR-ATR spectra of membranes.

500 mV, using a system based on a Solartron 1260 gain phase analyzer. A sample with size of 30 mm × 30 mm was placed in an open, temperature-controlled cell where it was clamped between two blocking stainless steel electrodes. Specimens were soaked in deionized water before the test. The conductivity ( $\sigma$ ) of the samples in the transverse direction was calculated from the impedance data, using the relationship  $\sigma = d/RS$ , where  $d$  and  $S$  are the thickness and face area of the sample, respectively, and  $R$  was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re ( $Z$ ) axis.<sup>14</sup> The test was done at 100% relative humidity.

## RESULTS AND DISCUSSION

### FTIR-ATR studies of membranes

The FTIR-IR spectra of SPPEK and composite membranes were shown in Figure 1. The absorption bands of SPPEK 1027 and 1087  $\text{cm}^{-1}$  typically indicate the presence of O=S=O and can be assigned to the symmetric and asymmetric stretching vibrations of aromatic  $\text{SO}_3\text{H}$  respectively. C=N bands at 1593  $\text{cm}^{-1}$ , carbonyl absorption at 1648  $\text{cm}^{-1}$  and aromatic C—O—C absorption at 1240  $\text{cm}^{-1}$  are characteristic absorption of SPPEK.<sup>14</sup> The bands at 810 and 894  $\text{cm}^{-1}$  of the SPPEK/PWA composite membrane are assigned to the symmetric stretch modes of W—O—W, and the absorptions at 984  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$  are assigned to the presence of W=O band and P—O band respectively. The interaction of PWA particles with the sulfonic acid moiety of sulfonated polymer have been reported in Ref. 19, which may be the reason of SPPEK/PWA membranes being transparent. The bands of the SPPEK/ZrP membrane are not obviously different from that of SPPEK membrane except for the

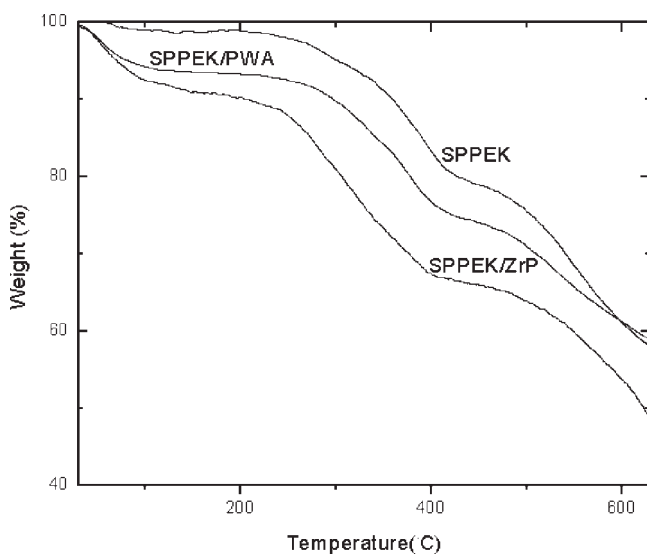


Figure 2 Thermogram of membranes.

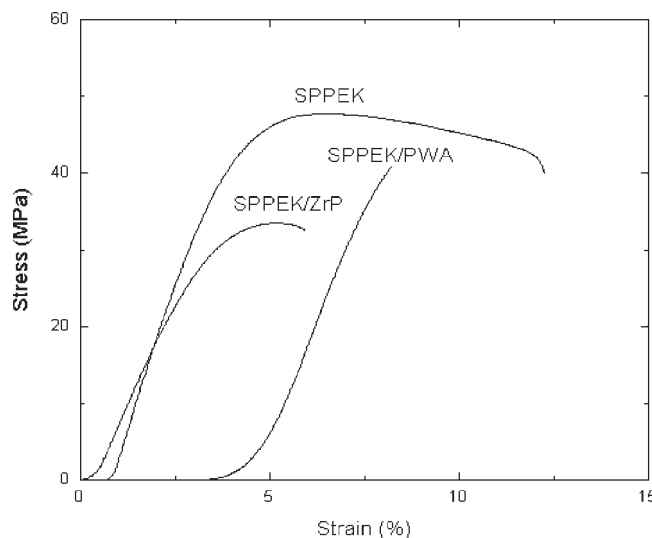


Figure 3 The stress-strain behavior of membranes at 25°C.

intensity, which can be explained by the existence of ZrP particles on the surface of SPPEK/ZrP membrane reducing the reflection of the matrix.

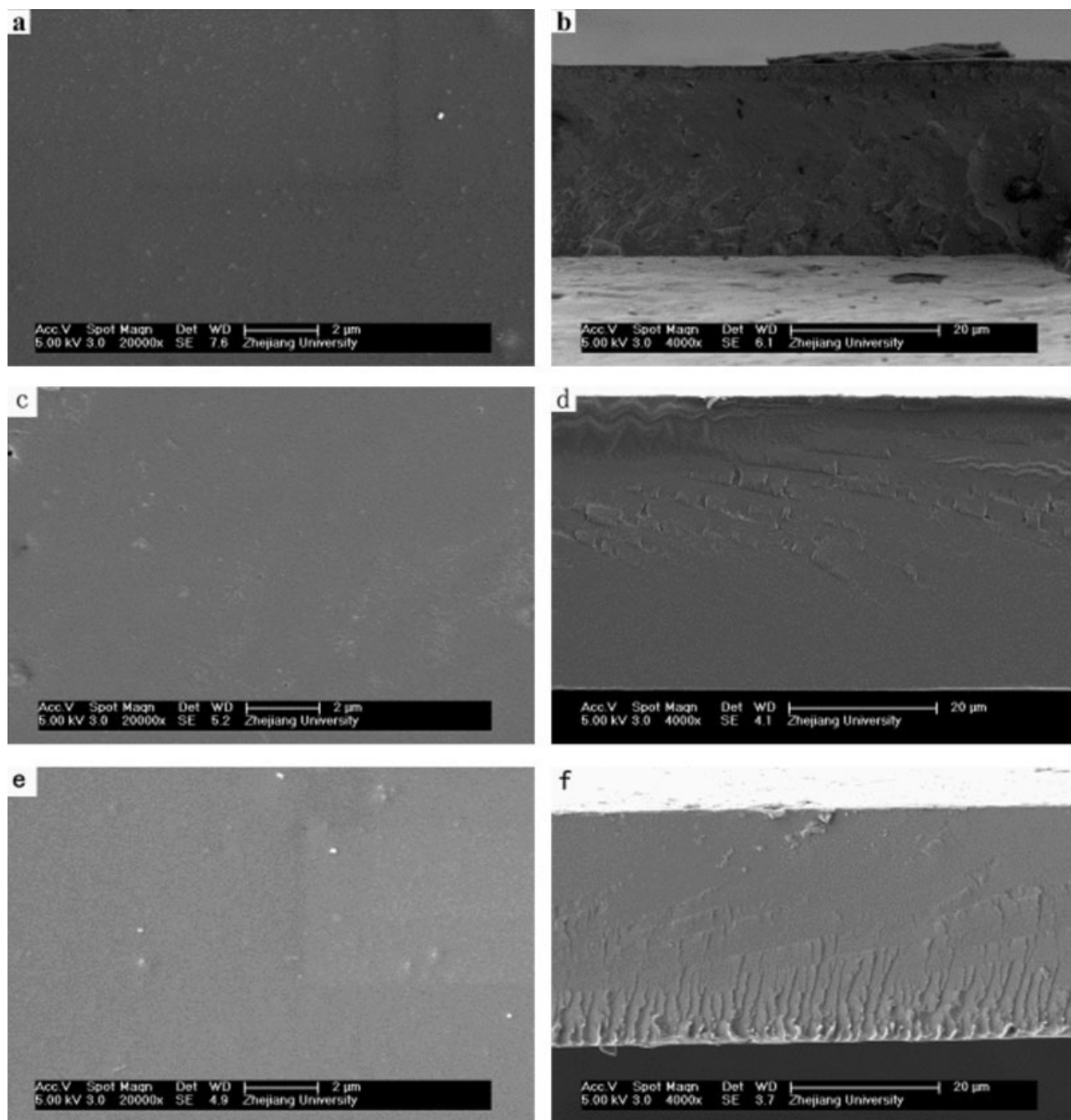
### Thermogravimetric and mechanical properties

The thermal stabilities of the SPPEK and composite membranes were measured with a thermogravimetric analyzer. The thermograms are shown in Figure 2. The TGA curves of all the membranes show the similar trend and exhibit three-step degradation patterns. The onset of weight losses occurred below 100°C, which was assigned to the moisture in the membranes and dehydration of inorganic particles. The second weight loss step beginning at around 270°C is generally correlated to the degradation of sulfonic acid group<sup>14,15</sup> which starts. But the second step of the SPPEK/PWA composite membrane starts at about 300°C, which may be assigned to the hydrogen bonding interaction between PWA particles and sulfonic acid moiety. The second step of the SPPEK/ZrP composite membrane starts near 270°C because the weak interaction between ZrP particles and SPPEK molecule is not enough to impact the degradation of sulfonic acid group from main chain. The third step of three membranes indicates the decomposition of the polymer backbone over 400°C. Considering that the PWA and ZrP are thermally resistant materials and SPPEK has a degradation in the similar temperature range, the third step degradation of the composite membranes are mainly related to the degradation of the SPPEK polymer. The composite membranes are thermally stable up to approximately 270°C and could meet the potential operation temperature in the fuel cell.

Since the membrane electrode assembly (MEA) is often assembled using a hot pressing process, a mem-

brane with excellent mechanical properties is desirable. From the stress–strain characteristics of membranes illustrated in Figure 3, it can be known that the polymer main chains of PPEK are rigid and the elongation of them must be small. The elongation of composite membranes at break decreases higher than 50% because of the brittle inorganic filler. All of the membranes show higher break stress than 30 Mpa, which is larger than that of Nafion117 (10.21 Mpa).<sup>29</sup> Such strength is enough for most possible applications. The

maximum strength of the SPPEK/PWA composite membrane (41.22 Mpa) is higher than that of the SPPEK/ZrP composite membrane (32.13 Mpa), and the maximum strength of both composite membranes is lower than that of pure SPPEK (48.15 Mpa). The decrease of the maximum strength of composite membranes may attribute to the effect of inorganic particles. In the composite membranes, the inorganic particles separate the SPPEK molecules, which leads to the decrease of the maximum strength because the



**Figure 4** FSEM images of membranes (a) surface of SPPEK/ZrP; (b) cross section of SPPEK/ZrP; (c) surface of SPPEK/PWA; (d) cross section of SPPEK/PWA; (e) surface of SPPEK; (f) cross section of SPPEK.

force between particles and SPPEK molecules is not as strong as that between SPPEK molecules. PWA particles have stronger interaction with polymer chains due to the hydrogen bonding interaction than do the ZrP particles, the SPPEK/PWA composite membrane has a higher maximum strength than that of the SPPEK/ZrP composite membrane. The Young's moduli of SPPEK, SPPEK/PWA composite membrane, and SPPEK/ZrP composite membrane are 233, 186, and 232 Mpa respectively.

### Morphology and XRD studies

From Figure 4, it can be found that the membranes of SPPEK and composite membranes have dense structure. The FSEM images, even up to magnifications of 20,000 $\times$ , do not show any evidence of the presence of a microporous structure. No agglomerate of inorganic particles is observed in the composite membranes. The particles are highly dispersed as fine particles throughout the composite membranes.

The microstructures of the composite membranes are studied with XRD. The ZrP particles show distinct reflections, but in the diagrams of SPPEK and composite membranes the inorganic peaks are overlaid by the broad SPPEK reflection. The diagrams of ZrP particles are compared with the standard data in the database with the instrument and the structure can be confirmed. The SPPEK membrane exhibits "structureless" amorphous morphology. As a whole, the XRD pattern of SPPEK is diffuse, which indicates the absence of the crystalline phase. The diagrams of composite membranes (Fig. 5) show that the impregnation of inorganic particles leads to the weak intensity of the diffuse peak of polymer matrix.

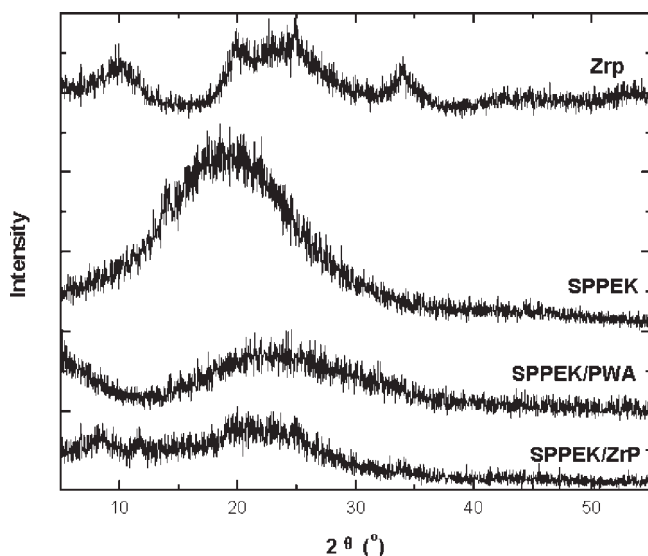


Figure 5 XRD patterns of membranes.

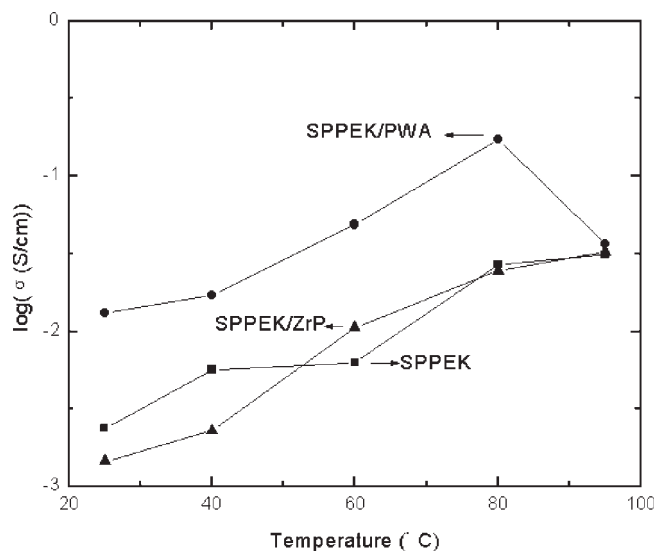


Figure 6 Proton conductivity of membranes.

### Proton conductivity

Figure 6 shows conductivities of SPPEK and composite membranes at 100% relative humidity. From Figure 6, it can be concluded that the SPPEK/PWA composite membrane shows more improved conducting properties and the SPPEK/ZrP composite membrane shows similar conducting properties with pure SPPEK membrane. The SPPEK/PWA composite membrane shows the highest proton conductivity of 0.17 S/cm at 80°C, which is in the range needed for high performance PEMFC. The difference of conducting properties between the SPPEK/PWA composite membrane and the SPPEK/ZrP composite membrane can be explained from their conduction mechanism. In the SPPEK/PWA composite membrane, the interaction between PWA particles and SPPEK chains and the water of hydrate with PWA make distance of sites for exchanging protons shorten, thus the proton transport will be more efficient. The  $\alpha$ -ZrP can conduct protons in absence of liquid solvent and the mobility of surface ions in  $\alpha$ -ZrP is  $10^4$  times higher than those of interlayer ions.<sup>21,25</sup> In the SPPEK/ZrP composite membrane, the ZrP particles and SPPEK molecules are not compatible, thus the existence of ZrP not only does not increase proton transport efficiency, but also suppresses it.

### CONCLUSIONS

The SPPEK/PWA and SPPEK/ZrP composite membranes have been successfully prepared from direct blending method. The incorporation of the PWA into the SPPEK membrane has resulted in enhanced proton conductivities without obviously weakening mechanical properties, its proton conductivity reaches 0.17 S/cm at 80°C, which is in the range needed for

high performance PEMFC. The SPPEK/ZrP composite membrane does not result in obvious improvement of conductivity of SPPEK membranes. It could be concluded that the SPPEK/PWA composite membrane should have good potential applications in proton exchange membrane fuel cell.

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