

## Sulfonated polyether ether ketone (PEEK-WC)/ phosphotungstic acid composite: Preparation and characterization of the fuel cell membranes

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**Abstract:** Sulfonated poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) membranes with various degrees of sulfonation (DS) were prepared, and their electrochemical and thermal properties were studied. Composites were formed by adding the hydrated phosphotungstic acid (PWA). The membrane (DS = 0.96, PWA = 50 %) conductivity was increased to  $3.5 \times 10^{-2}$  S cm<sup>-1</sup> at room temperature and  $6.0 \times 10^{-2}$  S cm<sup>-1</sup> at 80 °C. The composite membrane with a low amount of PWA embedded, showed lower methanol crossover in comparison to Nafion<sup>®</sup>. The addition of PWA increased the water retention of the composite membrane.

**Keywords:** membranes; nanocomposites; proton conductivity; sulfonated PEEK-WC; hydrated phosphotungstic acid; direct methanol fuel cells.

### INTRODUCTION

The direct methanol fuel cell (DMFC) offers the potential of high-energy efficiency and near-zero emissions in comparison to internal combustion engine [1–3]. The proton conductive membranes play a vital role in DMFC systems. At present, the solid polymer proton conductive electrolytes used in DMFCs are exclusively perfluorinated polymers, such as the commercially available Nafion. However, the high cost of perfluorinated polymers limits the large-scale commercialization of the proton exchange membrane fuel cells [4] and the Nafion membrane is a poor barrier for methanol crossover [5]. High proton conductivity and low methanol crossover of sulfonated polyether ether ketones (PEEK) and their composites qualify these membranes to be considered as an alternative for application in DMFCs.

In the last decades, many types of arylene main-chain polymers have been developed because these polymers show the best chemical and mechanical stabilities next to the fluorinated polymer. Some of these arylene polymers have been sulfonated, such as polyether sulfone [6], polyether imide [7], and PEEK. Among them, the membranes based on aromatic PEEK were shown to be very promising for fuel cell application [8,9], since they possess good mechanical properties, thermal stability, toughness, and some conductivity, depending on degree of sulfonation (DS) [10,11].

The PEEK is insoluble in almost all the common solvents. Zhang et al. [12] reported that the poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxa-*p*-phenylene-oxy-phenylene) (PEEK-WC) is less crystalline and soluble in some polar organic solvents and chlorohydrocarbons. Dense sulfonated PEEK-

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WC (SPEEK-WC) membranes have been tested for their permeability to various gases and vapors. At 60 °C, the permeability of methanol in a sulfonated PEEK-WC membrane (with DS = 70 %) was about two orders of magnitude lower than that of a Nafion 117 membrane. The proton conductivity reaches  $2.5 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$  at 115 °C (RH = 100 %; DS = 0.82) [13]. Exceptionally high proton conductivity of heteropolyacids (HPAs) (up to  $0.1 \text{ S cm}^{-1}$  at room temperature) [14] is promising for composite membrane preparation. The Nafion composite membrane containing hydrated phosphotungstic acid (PWA) was successfully tested in a fuel cell environment at temperatures above 100 °C [15].

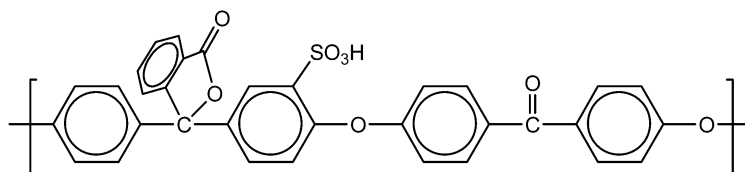
In this paper, we report the preparation of sulfonated PEEK-WC/PWA composite membranes and their characterization by electron microscopy, methanol permeability, water uptake, and proton conductivity measurements. The sulfonated PEEK-WC/PWA composite membranes were found to be suitable candidates for fuel cells. They exhibited high proton conductivity within the temperature range of fuel cell application, and its methanol crossover is lower than that of Nafion.

## MEMBRANE PREPARATION

PEEK-WC was supplied by Chan Chung Institute of Applied Chemistry (Academia Sinica, China). *N*-Methyl-2-pyrrolidinone (NMP), and PWA ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ ) were purchased from Sigma Aldrich. Chlorosulfonic acid (97.0 % synthesis grade) was purchased from Merck. All chemicals were used without further purification.

## SULFONATING THE PEEK-WC

PEEK-WC was sulfonated according to method reported by Drioli et al. [13], PEEK-WC (20 g) and chlorosulfonic acid (200 ml) were mixed by vigorous stirring at 0 °C. Polymers with various DS were obtained by differentiating a stirring time from 2 to 10 h. The polymer solution was gradually precipitated into a large excess of crushed ice. After 24 h, the polymer precipitate was filtered and washed several times with distilled water to remove the excess chlorosulfonic acid. Precipitated polymer was recovered by filtering and dried at 60 °C. Structural formula of the sulfonated PEEK-WC polymer is shown in Fig. 1.



**Fig. 1** Structural formula of the sulfonated PEEK-WC polymer [13].

The degree of membrane sulfonation was determined as follows. According to Zaidi et al. [16], there is a linear relationship between the DS and weight loss of splitting-off of  $\text{SO}_3$  group, which could be determined by thermal analysis (TGA). It was used in this work to obtain the DS. The water evaporation takes place at lower temperatures, and both processes are not overlapping. Simultaneous Thermal Analyzer STA 1500 (CCI-3, Rheometric Scientific) was used for TGA. The approximately 10–15-mg samples were first dried at 110 °C for 30 min, and then swept from 90 to 700 °C at a rate of  $10 \text{ °C min}^{-1}$  under a nitrogen atmosphere.

### Preparation of composite membranes

The appropriate amount of PWA was added to the 15 wt % sulfonated PEEK-WC polymer solution in NMP. The mixture was allowed to stir for 3 h, ultrasonicated for 0.5 h, and then cast onto a piece of glass and dried at 130 °C in order to remove the solvent. The membranes were removed from glass by immersing in water for several hours. Before measuring the proton conductivity, all membranes were kept in deionized water for 12 h. All membranes were also kept in deionized water for 2 weeks, and their conductivity was recorded in order to control the stability of the membranes.

### MORPHOLOGY

The samples were prepared by freezing the membranes in liquid nitrogen before breaking, in order to expose the membrane cross-section. The fresh cryogenic membrane fractures were then mounted upright onto aluminum stubs for cross-section analysis, and stuck flat onto the aluminum stubs for surface analysis. Prior to scanning electron microscopy (SEM) examination, the sample stubs were vacuum-sputtered with a thin layer of gold for 4 min in order to make them electronically conductive. The membrane morphology was characterized using SEM. SEM images were obtained on a Hitachi x650 (working resolution 6 nm, accelerating voltage 25 kV) attached to an energy-dispersive X-ray analyzer (EDAX) equipped with a tungsten filament and CDU "LEAP" detector.

The cross-section of sulfonated PEEK-WC/PWA composite membrane is shown in Fig. 2 (lighter area below is the surface of membrane, darker area is the background). The membrane is dense, and no porous structure is observed in the SEM picture.

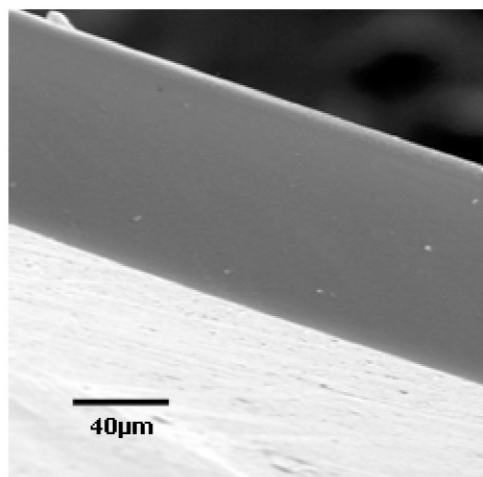
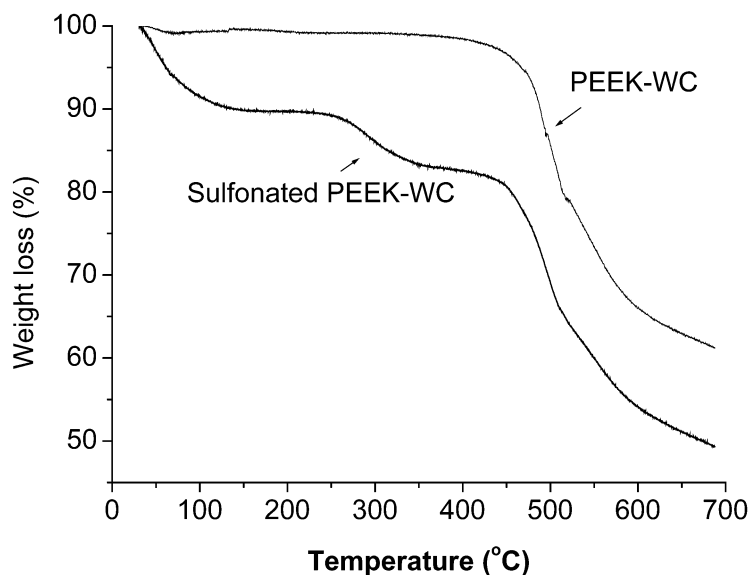


Fig. 2 SEM of cross-section of sulfonated PEEK-WC/PWA composite membrane.

### THERMAL STABILITY AND WATER UPTAKE

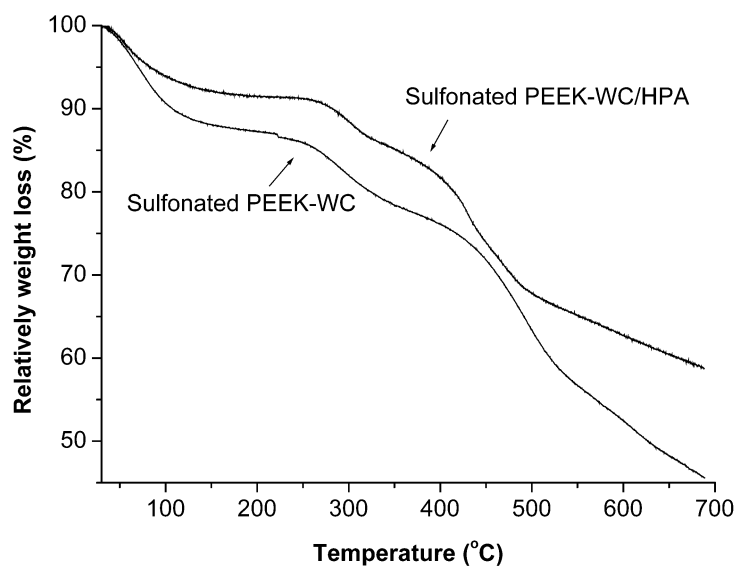
The thermal stability of membranes was analyzed by TGA. The TGA curves of one nonsulfonated PEEK-WC and one sulfonated PEEK-WC (DS = 58 %) membrane are shown in Fig. 3. The onset of weight loss for PEEK-WC takes place at about 450 °C. This weight loss is due to the main-chain decomposition, which results in the formation of phenols and benzene. In the curve of sulfonated PEEK-WC, three subsequent steps of weight loss are observed. Physically absorbed water in the porous structure of polymer causes the first weight loss. The second weight loss is related to the decomposing of the sulfonic acid groups from main chain of PEEK-WC [16]. The third weight loss is

attributed to the polymer decomposition, which shifts to a lower temperature from 450 to 390 °C as compared to the neat PEEK-WC. This shift to a lower temperature was observed also in SPEEK, comparing to PEEK.



**Fig. 3** TGA curves of nonsulfonated PEEK-WC and sulfonated PEEK-WC (DS = 58 %).

TGA curves for sulfonated PEEK-WC/PWA composite (DS = 58 %) and sulfonated PEEK-WC (DS = 58 %) membranes are presented in Fig. 4. The decomposing temperature of the main-chain PEEK-WC with the onset temperature at 250 °C is slightly affected by adding PWA. The composite membrane is thermally stable up to about 250 °C.

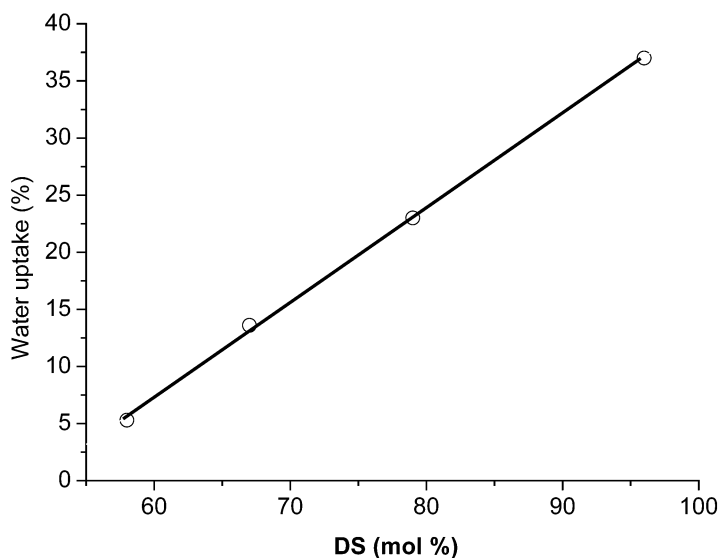


**Fig. 4** TGA curves of sulfonated PEEK-WC and sulfonated PEEK-WC/PWA membranes (DS = 58 %).

The water-swelling experiment was conducted via measuring the weight difference between the fully hydrated and the dried membrane. The membranes were equilibrated in water at various temperatures until no further weight gain was observed and weighed ( $W_{\text{wet}}$ ). The weight of the dry membrane ( $W_{\text{dry}}$ ) was obtained after drying at 110 °C. The water uptake of the membrane was calculated as follows [17]:

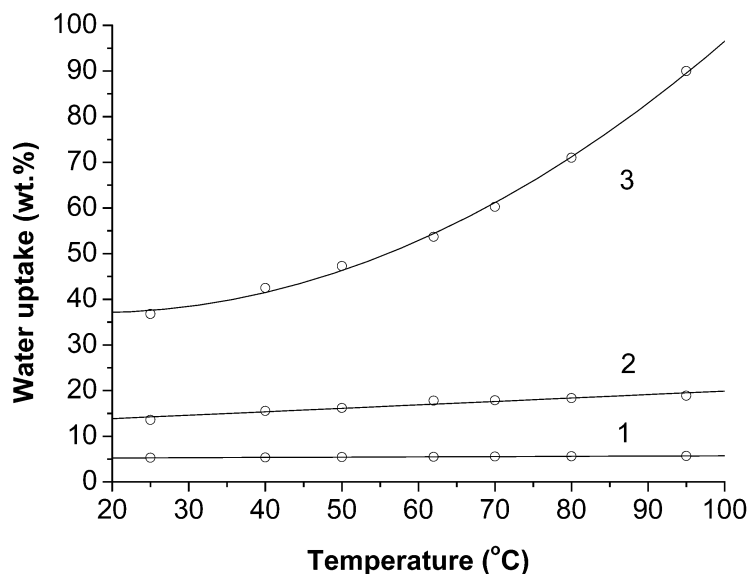
$$\text{water uptake} = \left( \frac{W_{\text{wet}}}{W_{\text{dry}}} - 1 \right) \times 100 \% \quad (1)$$

The room-temperature water uptake of sulfonated PEEK-WC membranes with different DS is presented in Fig. 5.  $\text{SO}_3\text{H}$  groups are enhancing membrane's acidity and hydrophilic properties. Therefore, the water uptake should increase with increasing the  $\text{SO}_3\text{H}$  group concentration. The results show that the water uptake of sulfonated PEEK-WC membranes increases linearly with DS (DS = 60–100 %) and reaches maximum of 37 wt % for a sulfonated PEEK-WC membrane with DS = 96 %.



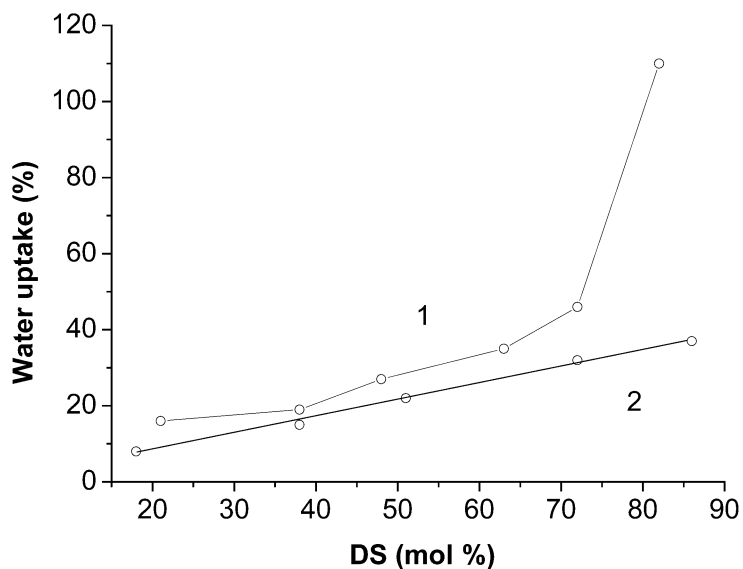
**Fig. 5** Room-temperature water uptake of sulfonated PEEK-WC membranes.

Water uptake characterizes the mechanical properties of membrane. It was reported that the membrane with high water uptake is typically fragile, and dimensional changes lead to poor mechanical properties and solubility in water at elevated temperatures [8]. The water uptake of membranes with different DS as a function of temperature is presented in Fig. 6. The water uptake of sulfonated PEEK-WC membranes increases with DS. The water uptake of sulfonated PEEK-WC membranes with lower DS (DS = 58 and 67) show very weak dependence on temperature. At the same time, the water uptake for membranes with high DS (DS = 96) strongly depends on temperature, and the increase is almost twofold in a temperature range from room temperature to 100 °C.



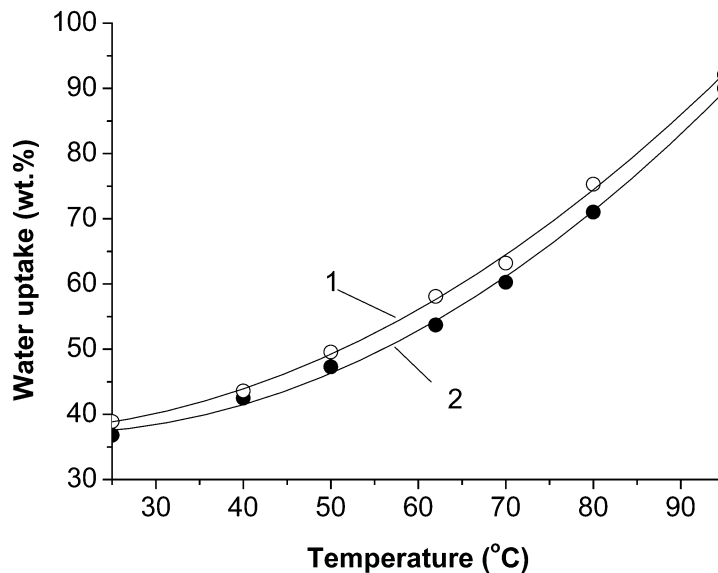
**Fig. 6** Temperature dependence of the water uptake for sulfonated PEEK-WC membranes with different DS: 58 % (1), 67 % (2), and 96 % (3).

The room-temperature water uptake of sulfonated PEEK-WC and PEEK membranes as a function of DS is plotted in Fig. 7. The water uptake of sulfonated PEEK-WC is lower than that of sulfonated PEEK membranes, and the difference is increasing at higher DS. Sulfonated PEEK membranes are less stable at high DS values, and solubility in water increases. The stability of the sulfonated PEEK-WC membrane is much higher, and suitability for practical applications is also higher.



**Fig. 7** Room-temperature water uptake of sulfonated PEEK (1) and sulfonated PEEK-WC (2) membranes.

The water uptake of sulfonated PEEK-WC/PWA and PEEK-WC composite membranes as a function of temperature is presented in Fig. 8. For both membranes, the DS is 0.72. The water uptake for both membranes increases with increasing temperature. Slightly higher water uptake can be observed for composite membranes (curve 1).



**Fig. 8** Water uptake of sulfonated PEEK-WC/PWA (1) and sulfonated PEEK-WC (2) membranes as a function of temperature.

### MEMBRANE PROTON CONDUCTIVITY

A piece of membrane with diameter 13 mm was placed in a sealed, temperature-controlled cell, where it was clamped between two blocking stainless steel electrodes with electroplated gold surface. A water recycling system with temperature controller was used to moisturize the membrane. Impedance measurements were conducted using an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie, The Netherlands) in combination with the computer-controlled frequency response analyzer (FRA) over the frequency range from 0.1 Hz to 100 kHz. The membrane (5 cm<sup>2</sup>) to be characterized was pressed between two carbon gas diffusion layers (Lydall Inc., LyFlex grade 484C) as electrodes. The volume resistance was obtained from the Cole–Cole plot by extrapolating to high frequencies using Autolab's software (linear regression analysis). The membrane conductivity was calculated using the following equation:

$$\sigma = \frac{1}{RS} \quad (2)$$

where

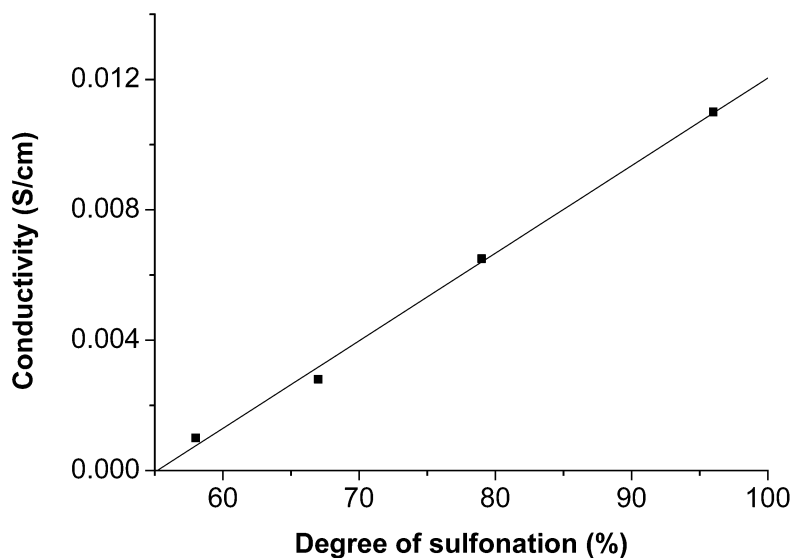
$\sigma$  = proton conductivity, S/cm;

$l$  = membrane thickness, cm;

$S$  = electrode area, cm<sup>2</sup>;

$R$  = volume resistance, Ohm.

The impact of DS on the conductivity of sulfonated PEEK-WC membrane with different DS is presented in Fig. 9.

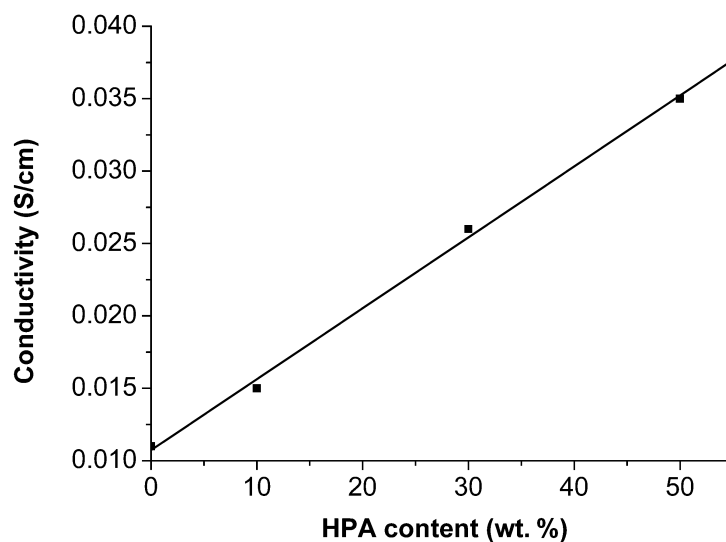


**Fig. 9** Proton conductivity of sulfonated PEEK-WC as a function of DS.

All membranes were pretreated by immersing in water for 24 h. Higher DS increases acidity and hydrophilic properties. The increase of proton conductivity with DS is related to higher proton concentration and water content. The sulfonated PEEK-WC with higher DS can absorb more water, which results in more transporting channels for protons and higher conductivity (see Fig. 5). The conductivity increases with DS and reaches a value of 0.011 S/cm for DS = 96 % (Fig. 9).

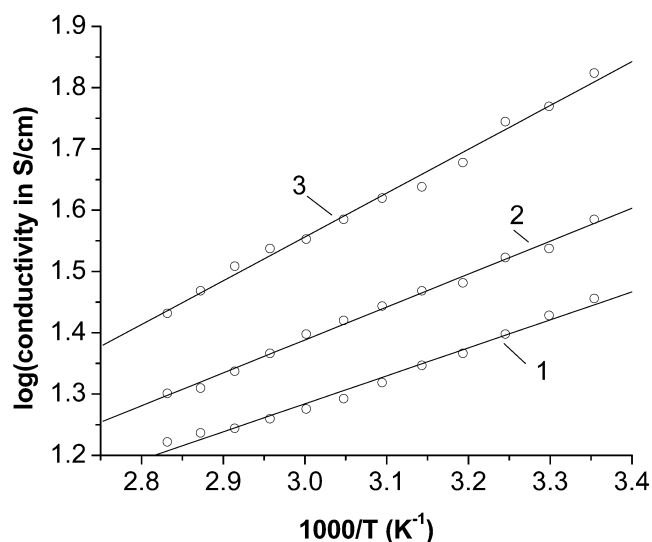
The proton conductivity as a function of PWA content is plotted in Fig. 10 (DS = 0.96 for all membranes). The conductivity measurements were performed at room temperature and at RH = 100 %. The results show that the addition of PWA can efficiently improve the proton conductivity of the composite membrane. The conductivity of the composite membrane increased linearly with increasing amount of PWA. The conductivity of the composite membrane is higher than that of the Nafion (conductivity is 0.016 S/cm) at room temperature at the content of PWA higher than 15 %.





**Fig. 10** Proton conductivity of sulfonated PEEK-WC/PWA composite membranes with various content of PWA.

The effect of temperature on the conductivity of sulfonated PEEK-WC membranes with different amount of PWA is reported in Fig. 11. Before measuring the conductivity, all the membranes were hydrated by immersing in water overnight. With increasing the PWA content in the membrane, an enhancement in the conductivity occurs. This is due to the polymer becoming more hydrophilic and absorbing more water by adding PWA, which facilitated the proton transfer. Thus, one can conclude that the conductivity increases with PWA loading and temperature. For the membrane with DS = 0.96 and 50 wt % PWA, it increased from 0.035 S/cm at 25 °C to 0.06 S/cm at 80 °C. PWA is highly water-soluble, and membranes have been tested by immersing for two weeks in distilled water and controlling stability of conductivity values. High density of the polymer membrane and large size of PWA molecule provide good stability, because the PWA is entrapped in a membrane.



**Fig. 11** Conductivity temperature dependence for composite membranes with various content of PWA: 10 (1), 30 (2), and 50 (3) wt %.

## MEMBRANE METHANOL PERMEABILITY

Methanol permeability across the membranes was obtained using a two-compartment (A and B) plastic cell. Compartment A was filled with 1 M methanol solution while compartment B was filled with ultra-pure water. The composite membrane was clamped between the two compartments. The two compartments were kept under stirring to avoid the concentration gradient. The methanol concentration changes in time in compartment B were measured using gas chromatography (GC) (Hewlett Packard 5890) at 25 °C.

The dependence of the methanol permeability through the sulfonated PEEK-WC/PWA composite membranes on PWA content has been investigated. Decreased methanol permeability is a crucial factor to achieve high efficiency of the DMFC. The permeability was determined at room temperature and DS = 0.96 (Table 1). It was about 60 times higher in Nafion as compared to sulfonated PEEK-WC composite membrane. Adding PWA to the sulfonated PEEK-WC/PWA composite membrane, the methanol permeability through composite membranes increased from  $2.3 \times 10^{-8}$  to  $8.9 \times 10^{-8}$  when the PWA in membrane increased from 0 to 30 %. At the same time, the proton conductivity is increasing. It is important for FC applications to decrease the methanol permeability maintaining high proton conductivity.

**Table 1** Methanol crossover of membranes.

Membrane type	Methanol crossover, $\text{cm}^2/\text{s}$
Nafion	$1.4 \times 10^{-6}$
Sulfonated PEEK-WC	$2.3 \times 10^{-8}$
Sulfonated PEEK-WC/PWA (10 wt %)	$3.5 \times 10^{-8}$
Sulfonated PEEK-WC/PWA (30 wt %)	$8.9 \times 10^{-8}$

## CONCLUSIONS

The water uptake, proton conductivity, and methanol permeability were studied for sulfonated PEEK-WC and PEEK-WC/PWA membranes with different DS. The composite membrane thermal stability up to 250 °C makes them suitable candidates for fuel cell applications. The proton conductivity is also sufficiently high for fuel cells. It was 0.035 S/cm at room temperature and 0.06 S/cm at 80 °C for a membrane with DS = 0.96 and 50 wt % PWA. It was demonstrated that the water uptake of the composite membranes increased with increasing temperature and DS. The addition of PWA improved the conductivity significantly. However, the methanol permeability was also increased. However, all studied composite membranes displayed a rather lower methanol crossover, as compared to Nafion. The selective solubility of sulfonated PEEK-WC membrane as compared to sulfonated PEEK is an advantage, which allows us to use the membrane preparation methods, which are easy to handle and low cost. Their high proton conductivity and low methanol crossover qualify these composite membranes to be considered for use in DMFCs.

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