High Performance Solid Polymer Electrolyte Membranes Prepared from Polyether Ether Ketone Composites

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ABSTRACT

High performance solid polymer electrolyte membranes (SPEM) were prepared from polyether ether ketone (PEEK) with high mechanical strength and thermal stability. The sulfonation reaction improved membrane hydrophilicity and water absorbility, and thus increased ionic conductivity for the applications in direct methanol fuel cells (DMFC). The ionic conductivity has been increased from 10^{-4} to 10^{-2} S cm^{-1} while the sulfonation time was increased from 72 to 168 h. The effects of nano-SiO$_2$ composites were devoted to improved thermal and mechanical properties, and methanol permeability. The methanol permeability was decreased from 4.11×10^{-7} to 3.13×10^{-7} cm^2 s^{-1}. In addition, the ionic conductivity could be further improved by supercritical carbon dioxide (scCO$_2$) treatment under the conditions of 20 MPa at 40°C for 30 min.

Keywords: solid polymer electrolyte membrane, PEEK, ionic conductivity

1 INTRODUCTION

In order to obtain higher energy and power density, high performance solid polymer electrolyte membranes (SPEM) can replace heavy-weight aqueous electrolytes, such as non-woven PP/PE, Nafion$^{®}$ and Flemion$^{®}$. For the applicability of SPEM in direct methanol fuel cell (DMFC), it is highly demanded for low methanol permeability, high ionic conductivity and good mechanical strength. Though Nafion$^{®}$ and Flemion$^{®}$ provide good ionic conductivity, it is still concerned with the high methanol permeability and high cost for DMFC [1-2].

High performance polyether ether ketone (PEEK) has become one of the best candidate materials due to the unique combination of good thermal stability, chemical resistance and excellent mechanical performance. However, higher hydrophilicity is necessary to sustain more water electrolyte in the free volume of among polymer chains to allow the ionic transport during electrochemical cell discharge. Several researchers have studied blendings with second polymers such as polyvinyl pyrrolidone (PVP) [3], polyphenyl sulfone (PPSU) [4], polyether sulfone (PES) [5], and polyphenlyene sulfide (PPS) [6]. In addition, it was found that polyaryl ether ketones under sulfonation instead of perfluorinated polymers are durable under fuel cell conditions over several thousand hours [7-11].

This paper reveals a simple method to increase the hydrophilicity of PEEK by sulfonation in concentrated sulfuric acid at long time and high temperature. The sulfonated PEEK was incorporated with nano SiO$_2$ and further treated by supercritical CO$_2$ (scCO$_2$). The CO$_2$ molecules have a plasticizing effect by Lewis acid-base interaction between the CO$_2$ and the electron donor species on polymer chains. The T$_g$ and melting temperature (T$_m$) can be both reduced [12, 13]. The ion exchange capacity (IEC) and degree of sulfonation (DS) were studied. In addition, the methanol permeability for PEEK SPEM samples was also evaluated.

2 EXPERIMENTAL

The polyether ether ketone (PEEK, 450G, MW 34,000) was received from Victrex USA. The sulfonation reaction was conducted by dissolving PEEK granules in 98% concentrated sulfuric acid (Aldrich) with the polymer/H$_2$SO$_4$ ratio of 5% g/mL The reaction was performed under a continuous mechanical stirring from 75 to 175 h and at the temperature of 90°C. After the reaction, the marroon color sulfonated PEEK solution was then rapidly quenched in iced deionized water with mechanical agitation, and the white precipitate would appear. The sulfonated PEEK precipitate samples were repeatedly rinsed in freshly prepared D.I. water under ultrasonic vibration for several times, until the pH value of the washing water reached 6-7, and the sulfonated sample was dried at 60°C in a vacuum oven for 2 days.

The sulfonated polymer was firstly dissolved in N-methyl-2-pyrro-lidone (NMP) solvent. The appropriate amount of nano-SiO$_2$ (avg. size = 10 ± 5 nm, specific area = 640 ± 5 m^2/g) was also added to NMP solvent in another beaker under ultrasonic vibration. The two NMP solutions were then mixed under continuous mechanical agitation for 36 h. The mixture solution was then casted onto a glass plate at 90°C in a vacuum oven for 2 days to remove the residual solvent. In addition, the prepared composites could be further treated in supercritical CO$_2$ fluid (scCO$_2$) by a scCO$_2$ extraction system with a flow rate of 2 mL min^{-1} in the reactor at 40°C and 20 MPa for 30 min. The samples

were then cooled to the ambient temperature to obtain transparent composite membranes.

The glass transition temperatures (T_g) were measured by DSC (TA DSC 2010) with N_2 gas and the temperature was increased to 250°C at a heating rate of 10 $^{\circ}$C min^{-1}. The ionic conductivity measurements were carried out by an AC impedance method. The alkaline membrane samples were sandwiched between SS316 stainless steel, ion-blocking electrodes, each of surface area of 0.785 cm^2. The AC impedance measurements were carried out using an AutoLab from Eco Chemi and a computer program FRA. The frequency range from 100 Hz to 100 kHz at an excitation signal of 10 mV was recorded. The AC impedance was measured at 25°C ($\pm$0.5°C) using a convection oven.

3   RESULTS AND DISCUSSION

3.1   IEC and DS Analysis

The ionic conductivity was calculated from the equation: $\sigma = l\, R_b^{-1} A^{-1}$, where l was the thickness (cm) of the sample, A was the area of the blocking electrode (cm^2), and R_b was the bulk resistance (ohm) derived from the Nyquist plot of AC impedance analysis at low intersection of the high frequency semi-circle on a complex impedance plane.

The PEEK under different sulfonation reaction time was controlled from 75 to 175 h for the different degrees of sulfonation (DS). Fig. 1 exhibits the IEC and DS change trends with different sulfonation time for PEEK. It is suggested that the IEC and DS values were continuously increased with increasing sulfonation time, and the IEC and DS value can reach 1.9 meq g^{-1} and 68%, respectively. Fig. 2 shows the effects of nano-SiO_2 content using DS-68% PEEK sample. While the SiO_2 content was increased from 0 to 20 wt.%, the IEC value was decreased to 1.74 meq g^{-1}. This can be attributed to the interaction of hydrogen bonding between sulfonic groups and SiO_2 particles that reduces the ion exchange capability.

3.2   IR Analysis

Fig. 3 shows the FT-IR spectra for the sulfonated PEEK samples with different DS values from 0% to 70%. There are three characteristic absorption bands for -SO_3H groups which appear in the regions of 1020 cm^{-1}, 1250 cm^{-1} and 1650 cm^{-1}. They are assigned to S=O stretch, asymmetric O=S=O stretch and symmetric stretching vibration of O=S=O due to the -SO_3H groups, respectively. Substitution will preferentially take place in one of the four positions of the aromatic ring between the ether bridges, since the electron density of the other two aromatic rings in the repeat unit is relatively low due to the electron-attracting nature of the neighboring carboxyl group. The IEC analysis and IR results have proved that the sulfonic functional groups were quantitatively introduced to the PEEK polymer.

3.3   Water Absorption & Ionic Conductivity

Table 1 and Table 2 display the relationships between water absorption and ionic conductivity of the PEEK membrane samples with different degrees of sulfonation, SiO_2 content ratios and scCO$_2$ treatment effects. The water absorption was increased with increasing sulfonation time due to the improvement in PEEK hydrophilicity by grafting sulfonic groups onto the PEEK main chains. Consequently, the higher water content in the sulfonated PEEK induced the water channel formation in the free volume of the PEEK matrix between sulfonic groups and provided a smooth way for ion transport and the ionic conductivity was therefore significantly improved.

The PEEK/SiO_2 composites cannot elevate the ionic conductivity and water absorption while the content of SiO_2 is lower than 10 wt.%. The high hydrogen bonding between SiO_2 and -SO_3H groups and higher SiO_2 particles would occupy the finite free volume in PEEK to reduce the space for water content. However, when the SiO_2 content is more than 10 wt.%, the more SiO_2 particles would loose the tight PEEK polymer chain and could sustain more water content, thus the ionic conductivity and water absorption was to be elevated. When the composite membranes were conducted in super critical CO_2 fluid treatments, the interaction between SiO_2 and sulfonic groups was destroyed and the SiO_2 particles can apparently loose the tight PEEK polymer chain and largely increase the free volume to contain more water. Hence, the ionic conductivity and water absorption for the treated composite membranes were both improved, and were significantly elevated to 1.54$\times$10^{-2} S cm^{-1} and 63.1%, respectively.

4   CONCLUSION

The study provided the solid polymer electrolyte membranes with high ionic conductivity and low methanol permeability using polyether ether ketone and sulfonation. The incorporation with nano-SiO_2 and the treatment by supercritical CO_2 fluid could improve the characteristics of PEEK matrix. The infrared study verified the proper incorporation of sulfonic acid groups in the polymer chains. The improvement was attributed to both the loose-p in the rigid polymer chain and the more amorphous characteristic for the sulfonated polymer. In addition, with the higher SiO_2 content, the more complicated route would reduce methanol permeation and is beneficial to the DMFC and PEMFC applications. The super critical CO_2 fluid treatment for the PEEK composite polymer electrolytes provided a unique process to further improve the characteristics. The interaction between SiO_2 and sulfonic groups could be destroyed and the ionic conductivity and water absorption were both improved, and were significantly elevated to 1.54$\times$10^{-2} S cm^{-1} and 63.1%, respectively. Therefore, the balance between ionic conductivity and other application properties could be designed and developed to meet the requirements for different electrochemical devices.

Sample	Sulfonation time (h)	DS (%)	Absorption (%)	Ionic conductivity ($\times 10^{-3}$ S cm^{-1})
DS41	72	41.0	18.2	0.049
DS49	96	48.7	24.9	0.257
DS57	120	57.2	32.0	1.290
DS60	144	65.8	36.1	2.622
DS68	175	68.0	38.3	4.680

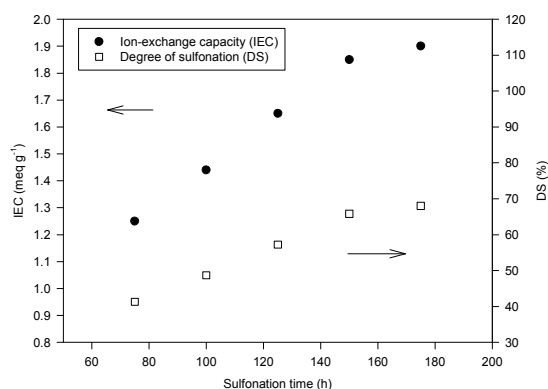Table 1: The degree of sulfonation, water absorption and ionic conductivity for the PEEK samples.

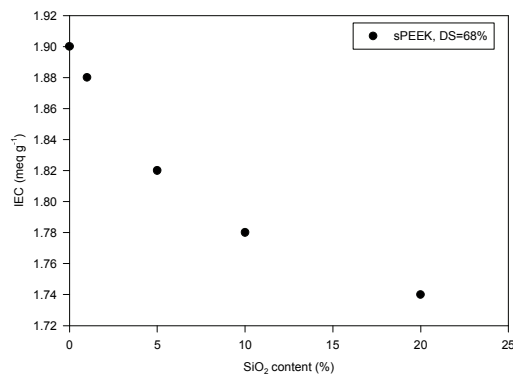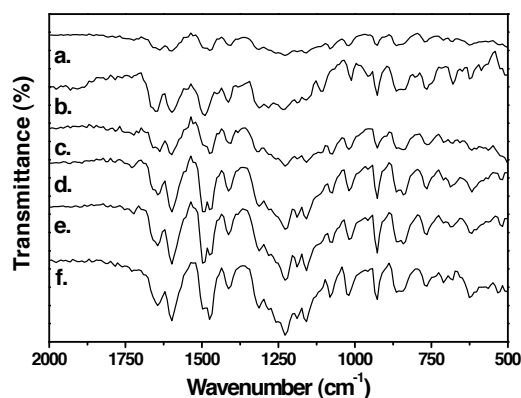Figure 1: The IEC and DS results with increasing sulfonation time for PEEK at 30°C.

Figure 3: The FT-IR spectra for the PEEK samples with different degrees of sulfonation (a) 0%, (b) 44%, (c) 51%, (d) 60%, (e) 68%, and (f) 70%.

Figure 2: The IEC results with different SiO$_2$ contents using DS-68% PEEK at 30°C.

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Sample	Sulfonation time (h)	SiO_2 content (%)	Absorption (%)	Ionic conductivity ($\times 10^{-3}$ S cm^{-1})	Supercritical CO_2 fluid treatment
DS68-S0	175	0	45.3	4.680	No
DS68-S1	175	1	44.7	3.370	No
DS68-S5	175	5	42.0	3.180	No
DS68-S10	175	10	52.6	6.460	No
DS68-S20	175	20	59.2	7.340	No
scCO$_2$-DS68-S0	175	0	56.5	9.14	Yes
scCO$_2$-DS68-S10	175	10	63.1	15.47	Yes

Table 2: The effects of nano-SiO_2 and scCO$_2$ treatment for PEEK composite membrane samples on DS, water absorption and ionic conductivity.