Fabrication of proton exchange membranes and effect of sulfonated SiO₂ (S-SiO₂) in sulfonated polyether ether ketone (SPEEK) for fuel cells applications

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Abstract. The fabrication of composite proton exchange membrane from the sulfonated polyether ether ketone (SPEEK) and sulfonated SiO₂ (S-SiO₂) have been investigated for energy production. In this work, inorganic fillers have been incorporated successfully in the organic polymer matrix. The degree of sulfonation (DS) and ion exchange capacity (IEC) were measured by back titration method and observed around 46.4 % and 1.43 mmol/gm, respectively. DS and IEC were found is increase with the increase of the amount of S-SiO₂ which reached to 56.5 % and 1.69 mmol/gm, respectively. Water uptake in percent was increased in the SPEEK/S-SiO₂ membrane due to increasing the sulfuric acid groups (-SO₃H), that lead to increasing the hydrophilic channels, the swelling ratio in percent was slightly increased. The proton conductivity of the SPEEK membrane was around 17.4 mS/cm and increased with increasing the amount of S-SiO₂. The highest proton conductivity observed at SPEEK/0.3 S-SiO₂ was around 53.7 mS/cm suggesting its use in fuel cell for energy production.

Keywords: PEEK, sulfonated SiO₂, composite membrane, proton conductivity and PEM fuel cells.

1. Introduction
Proton exchange membrane fuel cells (PEMFCs) is a device that has the ability to convert chemical energy to electrical energy with high efficiency and shows no environmental side effects [1-2]. The hydrocarbon membrane have specific benefit such as low cost but also has some disadvantage such as large water uptake, poor thermal and mechanical stability. In addition, it has poor compatibility with the electrodes present [3]. Polyether ether ketone (PEEK) shows good performance in the engineering thermoplastic as it shows good mechanical properties, high thermal stability and also has good stability under acidic conditions. Consequently, sulfonated polyether ether ketone (SPEEK) is a good material to be used in fuel cells for proton exchange membrane (PEM) applications [4-8]. SPEEK has
been broadly studied with other materials as it operates at low temperature, also have low cost, good mechanical and thermal stability, easy to functionalize, prevents the formation of useless reactions and easy to form membranes. Also incorporation of the inorganic nanoparticles such as ZrO$_2$ and SiO$_2$ with the SPEEK matrix, is convenient and presents an important approach in PEM research area [9-11]. The incorporation of inorganic materials with organic polymers (SPEEK) has many advantages like improved the mechanical properties, enhanced thermal stability and increased chemical resistance [12, 13]. On the other hand, the size of the filler is micro or nano, effective surface area of the particles and sulfonation of the particles or functionalization of the fillers, makes significant improvement in proton conductivity of the PEM [14-16]. Many modifications have already been studied to enhance the performance of the polymer electrode membrane (PEM) properties such as by radiation grafting and crosslinking [17-20]. Also organic-inorganic membranes are considered as a hybrid material known as nanocomposites, they are widely studied as they are highly effective in increasing proton conductivity [21-25]. In the present work the fabrication of composite proton exchange membrane from the sulfonated polyether ether ketone (SPEEK) and sulfonated SiO$_2$ (S-SiO$_2$) have been investigated.

2. Experimental methods

2.1 Materials and chemicals
SiO$_2$ nano particles and poly ether ether ketone (PEEK) were obtained from Sigma Aldrich, sulfuric acid H$_2$SO$_4$ with purity (95 -98%), hydrochloric acid (HCl) was obtained from Fisher Scientific, sodium hydroxide (NaOH) was purchased from Central Drug House (CDH), solvent dimethyl sulfoxide (DMSO), methanol, and hydrogen peroxide solution (H$_2$O$_2$) were used as received.

2.2 Sulfonation process of (PEEK)
Polyether ether ketone (PEEK) powder was first dried in vacuum oven at 100 °C overnight, 10 g of dried PEEK powder was dissolved in 200 ml of H$_2$SO$_4$ and appropriately stirred for 72 h at 40 °C. Afterward, the solution was gradually precipitated with the help of separate funnel into an excess of ice-cold distilled water and the product was filtered by using plastic micron filter, washed several times with distilled water until the pH became neutral. The polymer was dried under vacuum oven at 100 °C for 24 h. The final product obtained was sulfonated poly ether ether ketone (SPEEK).

2.3 Preparation of sulfonated SiO$_2$ (S-SiO$_2$)
The sulfonation of SiO$_2$ nanoparticles was done by using sulfuric acid [26]. 1 g of SiO$_2$ NPs was added to 20 ml of methanol containing 15 ml of H$_2$SO$_4$ with 0.5 M, the solution was vigorously stirred with the help of magnetic stirrer, and then, the mixture was dispersed well by using ultrasonicator for 1 h. The final mixture was put in petri dish and kept in an oven at 100 °C for 24 h. The final product was obtained sulfonated SiO$_2$ (S-SiO$_2$) white particles as shown in Fig. 1. In addition, the product was grinded by using pestle and mortar to get the powder form.
2.4. Fabrication of SPEEK and SPEEK/S-SiO$_2$ nanocomposite membrane

SPEEK sample was first dissolved in DMSO with a concentration around 10 wt. %, and stirred for 6 h at 40 °C to get a homogenous solution form. After that, homogenous SPEEK solution was cast into a petri dish and placed in a vacuum oven at 80 °C for 20 h. To prepare the SPEEK/S-SiO$_2$ membranes, a specific amount of synthesized S-SiO$_2$ was added into the homogeneous solution of SPEEK/DMSO, after that stirred with the help of magnetic stirrer for 6 h at 50 °C. The final mixture was appropriately kept in a petri dish then placed in a vacuum oven to evaporate the solvent at 80 °C for 20 h. The composite membranes were designated and maintained to be 0.5, 1, 1.5, 3, and 5 weight percentage of the S-SiO$_2$ from the total amount of SPEEK. Membranes were re-treated with H$_2$O$_2$ (30 %) and deionized water, then in 0.5 M of H$_2$SO$_4$ and finally in deionized water for 1 h.

3 Results and Discussion

3.1 Effect of sulfonation reaction on DS, IEC, water uptake and swelling ratio

Degree of sulfonation (DS %) and ion exchange capacity (IEC) were measured by back titration method [27]. Briefly, 0.1 g of the sample placed in 20 ml of 0.05M NaOH and kept for 3 days. After that, the solution was back titrated with 0.05 M of HCl with the help of phenolphthalein as an indicator. The IEC is the most important in this research area and associated with DS, known as the number of sulfonated groups per repeating units. The DS and IEC increases with the increase of the sulfonation time also with increase of the mixing temperature, that leads to increased sulfuric acid groups (-SO$_3$H) being attached to the backbone of the polymer. The DS and IEC of the SPEEK membrane were observed around 46.4% and 1.43 mmol/gm, respectively. After incorporation of the S-SiO$_2$ within the SPEEK matrix the DS and IEC were found to be increased due to the increased sulfuric acid groups and reached around 56.5 % and 1.69 mmol/gm, respectively. Water uptake and swelling ratio were determined by measuring the weight and length of the samples between fully hydrated membrane and the dried membrane [28, 29]. Water uptake increased with increasing the DS, due to increase in the hydrophilic channels as shown in Fig.2, which further leads to increasing the interaction between the water molecule and the hydrogen in the sulfuric group. Improvement in the proton conductivity was observed because of the increase in the hydrogen bond which are responsible for transporting the proton in the membrane by vehicle and hopping mechanism. The swelling ratio slightly increased with increase of sulfonation degree as shown in Table. 1. In addition, increased

![Figure 1. Visual image of S-SiO$_2$.](image-url)
water uptake and swelling ratio in weight percentage reduced the mechanical/thermal stability which made these membranes suitable for low operating temperature fuel cell.

![Figure 2. The effect of sulfonation reaction on IEC and Water uptake.](image)

**Table 1.** DS, IEC, water uptake, swelling and proton conductivity (σ).

| Sample          | DS (%) | IEC (mmol/g) | Water uptake (%) | Swelling ratio (%) | σ (mS/cm) |
|-----------------|--------|--------------|------------------|--------------------|-----------|
| SPEEK           | 46.4   | 1.43         | 34               | 3.3                | 17.4      |
| SPEEK/0.5 S-SiO₂| 48.5   | 1.47         | 37               | 5.0                | 29.5      |
| SPEEK/1.0 S-SiO₂| 49.4   | 1.51         | 39               | 6.6                | 50.5      |
| SPEEK/1.5 S-SiO₂| 50.5   | 1.54         | 45               | 3.3                | 46.1      |
| SPEEK/3.0 S-SiO₂| 53.1   | 1.60         | 48               | 5.0                | 53.7      |
| SPEEK/5.0 S-SiO₂| 56.5   | 1.69         | 51               | 3.6                | 37.4      |

### 3.2 X-Ray Diffraction (XRD) Analysis

The morphological information which is associated significantly with the crystallinity degree of the pristine membrane, as well as composite membrane, is provided by X-ray diffraction (XRD) technique [30-33]. XRD patterns show the amorphous structure in the sulfonated polymer (SPEEK) membrane, in addition, the amorphous structure was greatly observed in the SPEEK/S-SiO₂ membranes. Also, it can be realized that the crystallinity of the composite membrane SPEEK/S-SiO₂ decreased with increasing the filler (S-SiO₂) concentration from 0.5 to 5 wt. % in the SPEEK matrix due to the formation of the aggregate of the S-SiO₂ particles, which leads to changes in the crystalline properties as shown in Fig. 3. The crystallinity of the SPEEK/S-SiO₂ membranes has been decreasing with the increase of the filler up to 5 wt. % of S-SiO₂. On the other hand, the strong coordination among the functional groups of the SPEEK matrix and the particles of S-SiO₂ which can lead to increase the crystallinity, which can occur at high amount of S-SiO₂ due to the formation of a homogenous composite membrane.
3.3 Proton conductivity measurement

The proton conductivity of SPEEK and SPEEK/S-SiO\textsubscript{2} were directly obtained in a conductivity cell hardware (4-probe in-plane conductivity), along with frequency response analyser (FRA): Autolab model PGSTAT302N. Fig. 4 shows the Nyquist plot of the membrane which was obtained from FRA with frequency range from 0.1Hz to 10000 Hz. The proton conductivity of the SPEEK and SPEEK/S-SiO\textsubscript{2} were measured from the equation:

\[
\sigma = \frac{L}{RTW}
\]

Where \(\sigma\) is the proton conductivity in \((\text{mS/cm})\), \(L\) is the distance between the electrodes in \((\text{cm})\), \(R\) is the resistance in \((\text{ohm})\) and \(T\) and \(W\) are the thickness and width of the specimen in \((\text{cm})\) [34]. The specimen area was \((3\times1)\). Table 1, shows the proton conductivity of the SPEEK and SPEEK/S-SiO\textsubscript{2} membranes with a various weight percentage of the S-SiO\textsubscript{2}. The proton conductivity of the SPEEK membrane was found to be around 17.4 mS/cm. The proton conductivity was found to be increased with increasing the amount of S-SiO\textsubscript{2}. The highest proton conductivity was observed at SPEEK/0.3 S-SiO\textsubscript{2} around 53.7 mS/cm. The effective surface area of the incorporated filler may be decreased with the increase of the amount of the S-SiO\textsubscript{2} owing to the aggregation may be more than of 5 wt. %, which might explain the interaction of S-SiO\textsubscript{2} particles which has been incorporated in the polymer matrix.
3.4 Fourier Transform Infrared (FT-IR) spectroscopy

FT-IR analysis was successfully used to study the sulfuric acid group in the synthesized SPEEK polymer and also used to confirm the filler, which was incorporated with the SPEEK. Fig. 5, shows the spectra of FT-IR and illustrate the (O-H) vibration associated with the sulfuric acid group and a broad band about 3412 cm\(^{-1}\) in the sulfonation of PEEK polymer. The symmetry of (S=O) in the sulfuric acid group (-SO\(_3\)H) showed absorption peak at 1079 cm\(^{-1}\) and 1023 cm\(^{-1}\). The peaks at 1591 cm\(^{-1}\) and 1640 cm\(^{-1}\) for sulfonated PEEK were assigned to carbonyl groups [35, 36]. The peak at 1471 cm\(^{-1}\) refers to (-SO\(_3\)H) which increases with increased degree of sulfonation [37]. Subsequently, it was a little difficult to realize the structure changes in the SPEEK and the SPEEK/S-SiO\(_2\) membranes, because of the difficulty in the identification of sulfuric acid groups that was attached on the surface of SiO\(_2\) particles [33].

![Figure 4. Nyquist plots of (a) SPEEK and (b) SPEEK/5 wt. % S-SiO\(_2\) membrane](image)

![Figure 5. FT-IR spectrum of SPEEK, SPEEK/0.5 wt. % S-SiO\(_2\) and SPEEK/5 wt. % S-SiO\(_2\)](image)
4 Conclusions
Sulfonated polyether ether ketone (SPEEK) and sulfonated SiO\(_2\) (S-SiO\(_2\)) have been prepared by using the sulfuric acid. The synthesized SPEEK and SPEEK/S-SiO\(_2\) membranes showed comparable result with the various amount of S-SiO\(_2\) doped well in the SPEEK matrix. The results revealed an increased in DS and IEC with increasing the amount of S-SiO\(_2\), and also increased in the water uptake and swelling ratio. The morphological information was obtained by using XRD. The proton conductivity of the SPEEK membrane was increased with increasing the amount of S-SiO\(_2\). The highest proton conductivity was observed at SPEEK/0.3 S-SiO\(_2\) around 53.7 mS/cm. FT-IR analysis was successfully used to examined the sulfuric acid group in the synthesized SPEEK polymer and also used to confirm the filler (S-SiO\(_2\))which was used in the SPEEK membrane.

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