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SULFONATED POLY (ETHER ETHER KETONE) (SPEEK) MEMBRANE BLEND WITH ZIRCONIUM PHOSPHATE BASED METAL ORGANIC FRAMEWORK (ZrP MOF) FOR FUEL CELL APPLICATION

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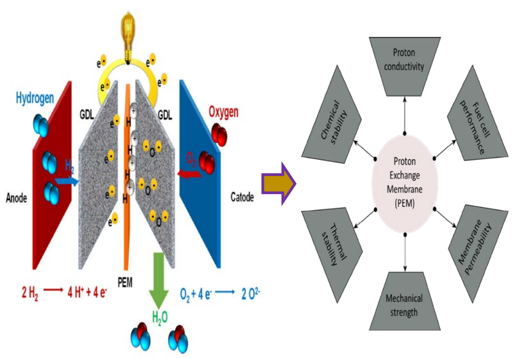
Graphical abstract



Abstract

The world is trying to switch from non-renewable energy sources to renewable ones due to the rising energy demand and environmental pollution caused by fossil fuel-based energy resources. Fuel cell, a type of renewable energy device, caught their attention due to its high energy conversion efficiency and environmental friendliness. Sulfonated poly(ether ether ketone) (SPEEK) is an alternative to the mostly used Nafion membrane in fuel cell applications due to its low cost, easy synthesis process and high thermal and mechanical strength but have lower proton conductivity than Nafion. Increasing the membrane temperature and relative humidity increases the SPEEK membrane proton conductivity but lowers the mechanical and thermal strength which influences its lifetime. Therefore, this study investigated the effect of adding proton conductive zirconium phosphate-based metal organic framework i.e $(NH_4)3[Zr(H_2/3PO_4)3$ (ZrP) (MOF) into SPEEK through solution blending methods towards its improved mechanical and thermal stability. It was determined that the addition of the stable ZrP improved the mechanical/thermal strength and dimensional stability whereas, the water uptake and swelling degree of the membrane reduced. Incorporating ZrP into the SPEEK membrane enhanced the thermo-mechanical properties thus, can be used as a stable proton conducting membrane for fuel cell that prolong the lifetime of the cell.
Keywords: Sulfonated poly(ether ether ketone), MOF, composite membrane, durability, fuel cell

1.0 INTRODUCTION

The demand for novel sources of energy that can be both sufficient as well as efficient has increased dramatically in recent years. This has been a significant source of concern and must be addressed. At the moment, hydrocarbons are the principal source of energy being researched to meet the world's energy needs. However, an issue develops when there is an over-reliance on this energy source due to the fact that it is being depleted over time. Furthermore, it is well known that the combustion of hydrocarbons contributes to a wide range of pollution, one of which is an increase in the concentration of greenhouse gases in the atmosphere. Environmental pollution, which is a major worry in today's world, is caused by the release of toxic gases such as nitrogen oxides (NOx), sulphur oxides (SOx), and carbon monoxide (CO) from the combustion of fossil fuels [1, 2]. Therefore, the research is being shifted towards renewable forms of energy such as energy from the sun, water, wind, and fuel cells (FCs) to meet the growing energy demand of the present world. Among these energy resources, FC which converts the chemical energy of the fuel into electrical energy through an electrochemical reaction, is an efficient energy resource [3, 4]. Nafion is the most used membrane in fuel cell so far as it possesses high proton conductivity at low temperatures and high humidity and shows inert chemical behaviors. However, certain disadvantages such as performance loss at anhydrous conditions, fuel permeability, and high cost limit its utilization for commercial purposes [5, 6]. Sulfonated poly(ether ether ketone) (SPEEK) being obtained through sulfonation of poly(ether ether ketone) (PEEK) with concentrated sulfuric acid (H_2SO_4) has low cost, easy synthesis process, high thermal, mechanical, and chemical strength. Additionally, It has the ability to work at low temperature and high humidity as well as high temperature and low humidity thus, is an alternative to the already available Nafion membrane [7, 8]. However, SPEEK has lower proton conductivity than Nafion. Increasing the degree of sulfonation of SPEEK elevates the proton conductivity of the SPEEK but it lowers the mechanical strength of the membrane due to excessive water uptake that causes membrane swelling. Moreover, the SPEEK mechanical strength reduces at high temperature and low humidity conditions which reduces its cell performance and durability. Therefore, the SPEEK membrane has been modified with proton conducting additives to raise its proton conductivity, single-cell performance, and membrane life time. Inorganic additives such as titanium dioxide TiO_2, zirconium dioxide (ZrO_2), carbon nanotubes (CNTs), and silicon dioxide (SiO_2) are added to SPEEK to enhance its proton conductivities, thermal, chemical, and mechanical strength [9]. However, the presence of these nano additives caused the agglomeration of nanoparticles because of the poor dispersion of these nano additives in the SPEEK matrix thus reducing the flexibility of the membrane which alternatively cracks and fracture the membrane [10].

Recently, metal organic frameworks (MOFs) composed of inorganic metal atoms and organic linkers emerged as alternative nano additives that have the ability to form both durable and high performance membranes for fuel cells. MOFs having high surface area, porous structure, and thermally and mechanically stable behaviors have been used widely to elevate the thermo-mechanical and physio-chemical properties of the SPEEK [11]. The flexible structure of MOFs can easily be changed by varying the metal ions and ligands or by post-treatment process to get the desired properties. Additionally, the high surface area and interconnected pores of MOF that provide pathways for proton transport distinguished it as one of the effective proton conductive nano additives among other nonporous nanofillers and therefore, can be used as proton conductive material in the preparation of polymer electrolyte membranes (PEMs) [12]. Based on proton conductivity, MOFs are generally classified into three distinct types. Those, that require the use of water to transfer the proton are called hydrous MOFs and operate below a temperature of 80 °C. Such types of MOFs are beneficial for low-temperature fuel cell applications. The other type that does not require the use of water for proton conduction is known as anhydrous MOF. These MOFs use a proton conducting species that has a boiling point higher than water molecules and form hydrogen bonding networks for the transport of protons. These anhydrous MOFs can function in a temperature range of 100-250 °C. For instance, a lanthanide based MOF $[Eu_2(CO_3)(ox)2(H_2O)2]\cdot 4H_2O$ [13] and imidazole added MOF (MOF@COF) [14] depicted anhydrous proton conductivities. However, MOFs that can function in both humid as well as dry conditions, the third type, are very significant. Such kind of MOFs that show both hydrous and anhydrous proton conductivity in addition to high thermal and mechanical strength have rarely been reported until now. For instance, ZrP has zirconium phosphate anions and NH_4+ cations, which form an acid-base pair in their structure and make it possible to operate at high temperatures and low humidity conditions. Thus, it has attained sufficient high proton conductivity of 1.45×10^{-3} S cm^{-1} at 180 °C. Additionally, ZrP attained elevated proton conductivity of 0.81×10^{-2} S cm^{-1} and 1.21×10^{-2} S cm^{-1} in hydrated conditions of 25 °C and 100% RH and 90 °C and 95% RH respectively [15]. Therefore, the addition of such kind of MOFs to polymer membranes will allow the electrolyte membrane to function at a wide range of anhydrous and hydrous operating conditions without sacrificing their mechanical strength and durability.

In this paper, we studied the effect of proton conductive and stable zirconium phosphate-based metal organic framework i.e $(NH_4)3[Zr(H_2/3PO_4)3$ (ZrP) as a nanofiller on SPEEK membrane characteristics such as water uptake, swelling degree, durability, and ion exchange capacity. To present time, there is no study available that demonstrates the influence of ZrP addition on SPEEK membrane properties. The addition of 2.5 wt.% ZrP into SPEEK significantly lowered the water absorbed by the SPEEK membrane and reduced the membrane swelling. Additionally, the results from the tensile test and thermal gravimetric analysis (TGA) also showed that the SPEEK/2.5%-ZrP composite membrane obtained elevated mechanical/thermal properties in terms of tensile and thermal strength and elongation at break. Thus, ZrP incorporated SPEEK blend membrane that has lower membrane swelling and superior durability made ZrP a suitable nanofiller in SPEEK composite polymer electrolyte membrane preparation that should operate at low and high temperatures of above 100 °C in fuel cell application.

2.0 METHODOLOGY

2.1 Materials

Poly(ether ether ketone) (PEEK) powder was purchased from Victrex US Inc. Ltd., 95-97% concentrated sulfuric acid (H_2SO_4) as a sulfonating agent and dimethyl sulfoxide (DMSO) (≥99.9% concentration) as a solvent were obtained from Sigma Aldrich. Similarly, zirconium (IV) chloride ($ZrCl_4$), orthophosphoric acid (H_3PO_4, 85% by weight in water), and urea (NH_2CONH_2) were supplied by VNK supply and services and are used as received. Ionic liquid 1-Butyl-2,3-dimethylimidazolium chloride ([BMMim]Cl), used as a linker and a solvent in the preparation of ZrP MOF, was also purchased from VNK supply and services.

2.2 ZrP Synthesis

ZrP was synthesized using an ionothermal method based on the published procedure [15]. Typically, a Teflon-lined autoclave was charged with 0.15 g $ZrCl_4$, 0.2 g H_3PO_4, 0.15 g $(NH_2)_2CO$, and 0.3 g 1-Butyl-2,3-dimethylimidazolium chloride ([BMMim]Cl) and heated at 180 °C for 12 hours. The product was then cooled to room temperature. Colourless block crystals of ZrP with 80% yield based on zirconium were obtained.

2.3 SPEEK Preparation

SPEEK was prepared by the reaction of PEEK and concentrated H_2SO_4. Initially, 50 g of the PEEK was dissolved carefully in 1 L of H_2SO_4 at room temperature within 1 h. The temperature was then increased to 63 °C and the mixture was stirred continuously for 3 hours. To get the SPEEK particles, the as prepared SPEEK solution was ice poured and water washed until the PH reached the neutral value. Finally, the wet SPEEK particles are oven-dried overnight at 80 °C to have the dried SPEEK particles.

2.4 SPEEK and ZrP Modified SPEEK Composite Membrane Synthesis

Neat SPEEK and SPEEK/ZrP composite membranes were prepared using the solution casting method [16]. Initially, 10 wt% dope solutions of SPEEK and SPEEK containing ZrP were prepared by dissolving the required amount of pure SPEEK and SPEEK blended with ZrP nanoparticles in 90 ml DMSO at room temperature for 48 hours. Simultaneously, the required amount of the dope solutions were poured in Petri dishes and dried at room temperature for 1 hour, followed by an oven drying for 24 hours at 80 °C. The as synthesized membranes are shown in Figure 1. To detach the membrane from the petri dish it was immersed in water for 2-3 hours. Finally, to activate the sulfonic acid group of the neat SPEEK and SPEEK/ZrP hybrid membrane they are dipped in 1 M H_2SO_4 solution for 1 day and then washed thrice with water to remove the extra acid.

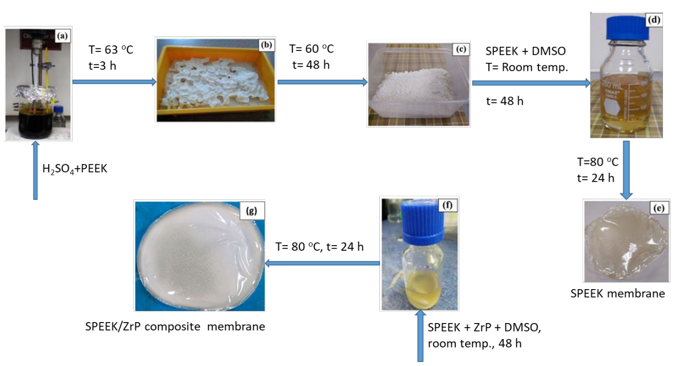


Figure 1 Schematic diagram of bare SPEEK and SPEEK/ZrP composite membrane.

2.5 Characterizations

Scanning electron microscopy (SEM) was used to analyze the structure and surface morphology of MOF powder and the membranes. Similarly, the water uptake (WU) and membrane swelling degree were measured using the procedure described by Daud et. al [17]. Mechanical testing equipment (Zwick/Roell Z020) was used to measure the mechanical properties of the synthesized bare SPEEK and SPEEK/ZrP composite membranes. The thermal stability of the samples was determined by thermal gravimetric analysis (TGA) in the temperature range of 25 to 900 °C at a heating rate of 10 °C min^{-1} using the TGA (Mettler Toledo TGA/SDTA851e) analyzer under nitrogen conditions. The ion exchange capacity (IEC) of the pure and SPEEK composite membrane was measured by the back titration method. Typically, a small piece of membrane was oven-dried and then immersed in 30 ml of 1 M NaCl solution for 24 hours. Phenolphthalein as an indicator was added to the solution and the solution was then titrated with 0.01 M NaOH solution until the PH reached to a neutral value. The IEC of the membrane samples was calculated using Equation 1.

$$IEC\,(meq/g) = \frac{C \times V}{W_d} \quad (1)$$

Where C, V and W_d are the molar concentration of the NaOH, volume of NaOH used, and dry weight of the membrane respectively.

3.0 RESULTS AND DISCUSSION

SEM was used to examine the structure and morphology of ZrP nanoparticles, neat SPEEK membrane, and SPEEK/ZrP composite membrane and the results are shown in Figure 2. Figure 2 (A) shows that ZrP has a 3D cubic structure. Figure 2 (B, C) depicts the cross-sectional images of neat SPEEK membrane and ZrP blend SPEEK membrane. The SPEEK membrane obtained a uniform dense morphology with a thickness of 63 micrometres. A typical membrane thickness for a proton exchange membrane fuel cell (PEMFC) should be around 50-250 micrometres [18]. When ZrP was loaded onto the SPEEK membrane there was not much difference in the morphology of the pure SPEEK membrane and SPEEK/ZrP composite membrane as seen in Figure 2 (C, D). This reveals that ZrP has good compatibility with the SPEEK polymer and is uniformly distributed in the polymer back bone essential for enhancing properties of polymer electrolyte membrane in fuel cell applications. Nanofillers' poor dispersion in the membrane results in agglomerate formation that reduce the flexibility of the membrane and thus causes the membrane to fracture and crack. A study performed by Dong et al [19] increased the SPEEK membrane proton conductivity, stability and fuel cell performance while, reducing fuel permeability when GO modified with ethylenediamine (EGO) was uniformly dispersed in the SPEEK backbone.

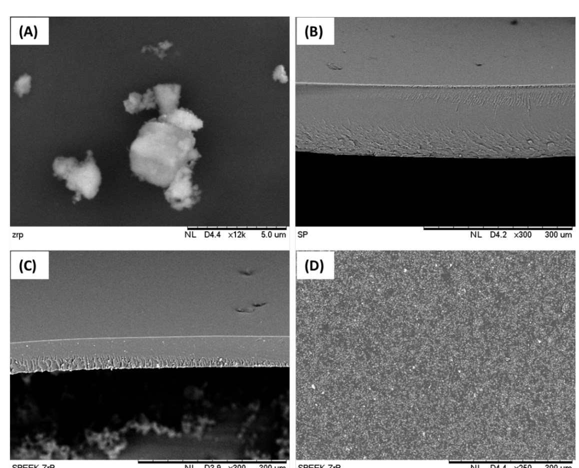


Figure 2 SEM image of (A) ZrP, crosssection of (B) neat SPEEK, (C) SPEEK/2.5% ZrP membrane, the surface image of (D) SPEEK/2.5% ZrP.

Water uptake (WU) of the polymer electrolyte membrane plays a very essential role in proton conduction. Water acts as a proton transfer carrier thus, a membrane containing a high amount of water can transfer more protons through Grotthuss and vehicular mechanisms necessary for improved single-cell performance at low temperatures operation below the boiling point of water. However, too much water present in membrane caused excessive swelling of the membrane that reduced the mechanical strength of the membrane [20]. As shown in Figure 3 (a), the WU and swelling degree of the SPEEK membrane reduced when it was added with ZrP nanoparticles. This may be attributed to the interfacial interaction of SPEEK and ZrP. ZrP contains the zirconium phosphate anions that form hydrogen bonding networks with the acidic cationic group (-SO_3H) of SPEEK. Thus, the presence of ZrP content in SPEEK reduced the overall concentration of water-attracting acidic group (-SO_3H) of SPEEK, lower the water attraction of the membrane. Alternatively, the lowered WU of the SPEEK/ZrP composite membrane decreases the SPEEK membrane swelling. Hence, the bare SPEEK membrane showed about 2 times higher swelling ratio than the SPEEK/2.5%-ZrP blend membrane. In many reports reduced membrane swelling due to lowered water uptake of the membrane has been reported. For instance, Daud et al. reduced the SPEEK membrane swelling by reducing the water uptake of the membrane [16].

Mechanical stability testing was performed to guarantee that the fabricated composite membrane is flexible, processable, and robust enough to be used in the demanding conditions of the fuel cell system. Figure 3 (b) depicts the mechanical properties of the SPEEK membrane and the SPEEK/ZrP composite membrane. It is worth noting that the incorporation of ZrP in the SPEEK matrix resulted in the greatest improvement in the mechanical properties of the SPEEK membrane. SPEEK/2.5%-ZrP exhibited a tensile strength of 56.83 MPa, meanwhile, the bare SPEEK membrane only showed 40.6 MPa. Additionally, the SPEEK/2.5%-ZrP composite membrane attained a 3.69 times elevated elongation at break contrast to the neat SPEEK membrane. The strong hydrogen bonding between SPEEK polymer and ZrP MOF crystals results in compact structure of the membrane which is responsible for the increased tensile strength [21].

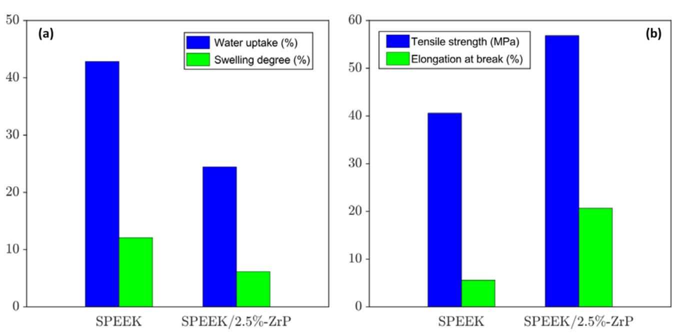


Figure 3 (a) Water uptake and swelling degree of SPEEK and SPEEK/ZrP, (b) tensile strength and elongation at break of neat SPEEK membrane and SPEEK/ZrP composite membrane

Thermal gravimetric analysis (TGA) was used to evaluate the thermal properties of ZrP nanoparticles, pure SPEEK, and SPEEK/ZrP composite membranes. From the TGA analysis, it can be seen that the introduction of the MOF nanofiller in the SPEEK polymer matrix increases the thermal stability of the SPEEK membrane thus, the SPEEK/ZrP mixed matrix membrane obtained elevated thermal strength than the neat SPEEK membrane as shown in Figure 4. Weight lost in bare SPEEK and SPEEK hybrid membranes occurred in three distinct stages. In the first stage, water elimination took place that ends above 300 °C. Similarly, weight lost in the temperature range of 300-400 °C was attributed to the degradation of the sulfonic acid (-SO_3H) group attached to the SPEEK. The weight loss occurred above this temperature was due to the SPEEK and ZrP backbone decomposition. The electrostatic interactions between SPEEK and ZrP nanoparticles increase the thermal strength of the SPEEK/ZrP membrane.

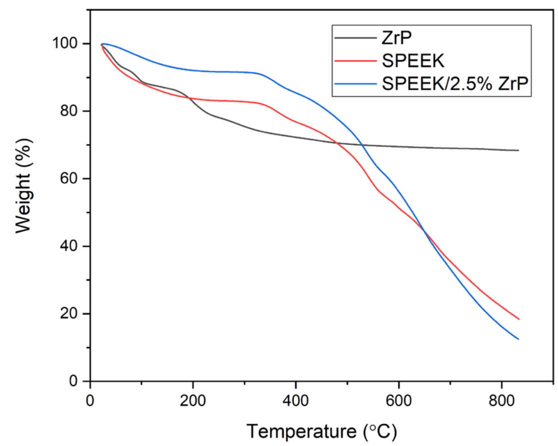


Figure 4 TGA curves of ZrP nanoparticles, neat SPEEK membrane and SPEEK/ZrP composite membrane.

Figure 5 shows the IEC the of synthesized pure SPEEK and ZrP MOF-modified SPEEK composite membrane. The IEC slightly decreased from 11.76 meq/g for pure SPEEK membrane to 11.69 meq/g for SPEEK composite membrane. This slight decrease in the IEC value is due to a lower content of the acidic sulfonic acid group (-SO_3H) of SPEEK in the SPEEK/ZrP composite membrane in contrast to the pure SPEEK [22]. However, the higher proton conductivity value of the ZrP at hydrous and anhydrous conditions itself will raise the proton conductivity and thus, the single cell performance of the composite membrane.

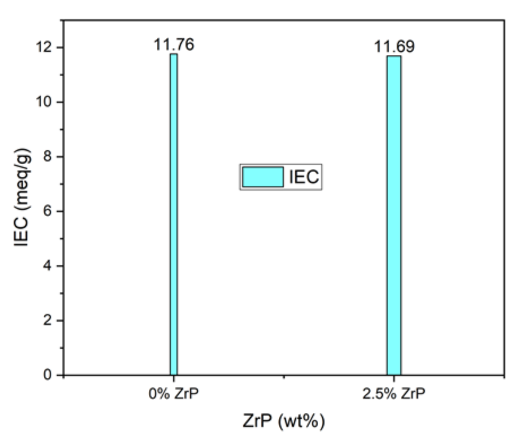


Figure 5 IEC of SPEEK and SPEEK composite membrane

4.0 CONCLUSION

In conclusion, we have described the enhancement of mechanical and thermal properties of SPEEK by incorporating a $(NH_4)3[Zr(H_2/3PO_4)3$ (ZrP) a 3D MOF into a SPEEK membrane. In the presence of 2.5 wt% ZrP in the SPEEK/ZrP composite membrane, a tensile strength of 56.83 MPa was obtained compared to 40.6 MPa of the neat SPEEK membrane. The composite membrane also obtained an overall improved thermal strength in comparison to the neat membrane. Additionally, the SPEEK/2.5%-ZrP composite membrane attained lower water uptake thus about 2 times reduced swelling than the corresponding SPEEK membrane. Therefore, based on its increased thermo-mechanical strength and lower swelling degree, it can be concluded that the SPEEK/ZrP composite membrane can be a good choice as a durable PEM in fuel cells. Further, the higher proton conductivity value of ZrP itself at humid and anhydrous conditions will significantly increase the efficiency of the fuel cell.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper

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