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ELECTROSPUN STRONTIUM CROSS-LINKED SULFONATED POLY (ETHER ETHER KETONE) SPEEK NANOFIBER FOR PROTON EXCHANGE MEMBRANE FUEL CELL

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Graphical abstract

Abstract

Strontium (Sr) cross-linked nanofibrous membranes of sulfonated polyether ether ketone (SPEEK) were successfully prepared using the electrospinning technique. Metal-polymer physical cross-linked has been proposed as a way to improve the mechanical and chemical stabilities of the electrospun SPEEK membrane which we found in this finding can help to reduced water uptake compared with the non-crosslinked membrane. Physical cross-linked of Sr-SPEEK membranes were fabricated by immersion process which were than electrospun into nanofibrous membranes. The morphologies of electrospun Sr-SPEEK membrane, fabricated under different concentrations of Sr were presented which show up to 6% concentration of Strontium was able to be electrospun. On the electrical properties of the electrospun membrane, conductivity for the sample with 6% Sr weight percentage has given 0.188 S/cm which is about 80% higher than the film cast Nafion-117 at 80°C as cited before. This particular result is a hallmark of the studies as it shows that a combination of nanostructured with crosslink is proven to work in favor of producing proton exchange membrane fuel cell (PEMFC) which performed much better than Nafion based membrane.

Keywords: Electrospinning, crosslinking, nanofibers, polymer electrolyte membrane, SPEEK

Abstrak

Membran gentian nano SPEEK (sulfonated polyether ether ketone) yang telah di silang sambungkan dengan bahan logam strontium (Sr) dan seterusnya di 'electrospinning'kan telah berjaya dihasilkan. Kaedah silang sambung antara logam-polimer dalam membran telah dicadangkan berupaya meningkatkan kestabilan mekanikal dan kimia membran serta mengurangkan sifat serap air bahan membran. Kaedah sambung silang bahan Sr terhadap membran SPEEK ini dihasilkan dengan proses rendaman dan seterusnya diikuti dengan proses elektrospin bagi menghasil bahan membran bergentian yg bersaiz nano. Kajian terhadap morfologi membran elektrospun Sr-SPEEK dengan kepekatan Sr yang berbeza telah menunjukkan sehingga 6% kepekatan Sr dapat dihasilkan. Seterusnya, kajian sifat elektrik terhadap bahan membran elektrospun telah menunjukan konduktiviti untuk sampel dengan nisbah peratusan 6% Sr memberikan bacaan 0.188 S/cm iaitu 80% lebih tinggi daripada filem tulen Nafion-117 pada suhu 80°C seperti yg dilaporkan sebelumnya. Dapatan kajian konduktiviti ini sangat signifikan dan merupakan ciri penting yang menunjukkan gabungan struktur bahan nano dan kaedah silang sambung terbukti dalam menghasilkan bahan membran pertukaran proton fuel cell yang lebih baik dari bahan asas membran Nafion.

Kata kunci: Elektrospinning, silang sambung (crosslinking), nanofiber, membran pertukaran proton (PEM), SPEEK

1.0 INTRODUCTION

A proton exchange membrane fuel cell (PEMFC) also known as polymer electrolyte membrane fuel cells (PEMFC) is one of the cleanest and most efficient energy conversion devices. Conventional PEMFC operates at relatively low temperatures, between 80°C to 100°C while for high-temperature PEMFC, its operating temperature is above 150°C. Polymer electrolyte membrane (PEM) is the center in PEMFC and as a key component of PEMFC, it is functioning as an electrolyte to transfer protons as well as providing a barrier to the crossover of fuel between cathode and anode [1], [2], [3]. Perfluorosulfonic acid-type electrolytes, Nafion, produced by Dupont is one of the most widely used commercial polymer electrolyte membranes due to its excellent properties such as high chemical and physical stabilities as well as high proton conductivity at ambient temperature.

However, Nafion is not possible to operate at high temperatures (above 80°C) and low humidity due to its low stability and decrease in conductivity [4]. Hence, more studies on developing an alternative to Nafion membranes that are capable of operating at higher temperature [5]. Sulfonated aromatic poly (ether ether ketone) (SPEEK) has received more attention due to its low methanol permeability, high chemical, mechanical, and thermal resistances, and more importantly, low cost and good processability [6], [7]. Unfortunately, the SPEEK membrane also has a weakness which are poor mechanical strength in hot water (over 80°C) associated with high swelling, when the degree of swelling (DS) is higher than 65%. Several ways have been used to overcome this problem such as grafting and blending but crosslinking appears to be an efficient and simplest approach. In recent years, crosslinking based on SPEEK has been widely researched and the results indicated crosslinking seems to be an attractive method to restrict and limit the water uptake [8] and improve mechanical properties and tensile strength of the membrane. According to Dinh Xuan Luu [9], physical crosslinking is more feasible than the covalent crosslinking in SPEEK which provides the proton transport properties. The metal-polymer crosslink is introduced based on the interaction between a sulfonic group of SPEEK and earth metal ions where cationic earth metal ions make strong bonds with the sulfonic group. The choice of strontium (Sr) earth metal ion as a crosslinking agent in this study is based on its bonding strength which is not too strong that makes the polymer chain inflexible in-turn hinder proton transport and not too weak that would weaken the membrane mechanical properties[9].

Several approaches have been used to stabilize proton exchange membranes and to improve their properties for fuel cell application. The development of nanostructured systems comprising electrospun nonwoven mats has emerged to be a promising strategy. 1-D structures of nanofibers (NFs) can provide interconnected ionic conductive channels, providing long-range ion trajectories by spanning PEMs with their high aspect ratios [10]. Electrospinning is a simple and reliable technique to produce smooth nanofibers from a variety of polymers with nanosized diameter involving an application of a high electric field to generate nanofibers from a charged polymer solution. Electrospinning is capable of producing the electrospun nanofibers with many properties such as large specific area, superior mechanical properties [11]. Besides, electrospinning is incredible, straightforward, simple, and cost-effective in producing polymeric nanofiber and Ballengee & Pintauro [12] reported that the nanofiber membrane exhibited impressive mechanical properties and proton conductivity in a fuel cell.

SPEEK membrane was synthesized first followed with the incorporating of Sr by immersion technique for crosslink effect. Prepared solutions were then undergone an electrospinning technique. Nanofiber membranes were evaluated by investigating their morphology, functional group entity, and electrical properties by field emission scanning electron microscope (FESEM), Fourier transforms infrared (FTIR) spectroscopy, and electrical impedance spectroscopy respectively. Water uptake testing was also performed on all prepared NF membranes.

2.0 METHODOLOGY

2.1 Chemicals and Materials

In this experiment, Poly (ether ether ketone) (PEEK) grade 90p was obtained from Victrex® PEEK™ polymer (England), 95-98% concentrated sulfuric acid (H_2SO_4) from Sigma-Aldrich (USA), dimethylacetamide (DMAc), Strontium acetate ($C_4H_6O_4Sr$) from Sigma-Aldrich (USA).

2.2 Sulfonation of PEEK

The starting material of PEEK in powder form was dried for 48 hours in the vacuum oven. The sulfonation process with the slow mixing of the dried PEEK (10.0 g) with 250 mL concentrated sulphuric acid (H_2SO_4) at room temperature under constant stirring for 60 hours. After completion of the sulfonation reaction, SPEEK was washed with distilled water. During this process the fibrous yellowish SPEEK needs to be stirred until it turns white.

The fiber is then filtered and washed several times with distilled water until the pH close to 7. Finally, the resulting fibers of SPEEK were dried in a vacuum oven for 48 hours at 40°C.

2.3 Preparation of SPEEK-Sr Membrane

The process was started by first dissolving the SPEEK membrane (prepared in 2.2) in dimethylacetamide (DMAc) with the predetermined concentration of 30

wt.% of SPEEK in 10 mL of DMAc. The solution was stirred at room temperature until a homogeneous phase was achieved. The SPEEK solution was cast on a glass Petri dish and then dried for 10 hours at 100°C in an oven then followed by 2 hours in a vacuum oven at 120°C. Separately, the strontium acetate solution was prepared by dissolving 2g $SrC_4H_6O_4$ in 50 mL of deionized water, which is a predetermined concentration. SPEEK membranes were immersed in the Sr solution and after soaking it for 5 hours at room temperature, the membrane was washed with deionized water to remove trace of free strontium.

2.4   Preparation of SPEEK-Sr Nanofiber Membrane

The SPEEK-Sr membrane prepared (in 2.3) was dissolved in DMAc and stirred for 5 hours at room temperature to obtain a homogeneous solution. The solution is kept for 24 hours to clear up air bubbles in the sol after vigorous stirring before taken into the electrospinning process. The solution was held inside a plastic disposable syringe and the needle with the inner diameter is 0.6 mm. The distance between the tip of the needle and collector was maintained (in the range 12 -15 cm) and the feed rate was maintained at 0.25 mL/h and an electrical potential was applied to the polymer solution. The nanofiber then collected on the aluminum foil at the grounded collector. Spinning was continued for 8 hours per day to get the desired thick membrane, which was peeled off from the drum winding collector for characterizations.

2.4   Characterization of Membranes

2.4.1   *Field Emission Scanning Electron Microscopy (FESEM)*

The morphologies of all samples were examined by a Field emission scanning electron microscope (FESEM). All membranes samples were coated first with gold-coating for 3 minutes to form a conductive layer on-top to avoid charging effects.

2.4.2   *Fourier Transformation Infrared (FTIR) (Structural)*

The structure and functional groups of both electrospun membrane crosslinked and non-cosslinked were characterized by Fourier transform infrared spectrophotometry (FTIR). Transmission spectra of the samples were recorded on Perkin-Elmer 1700X FTIR spectrometer in the range 4000-450 cm^{-1}, at the resolution of 2 cm^{-1}.

2.4.3   *Water Uptake*

The membranes were cut into a circular-shape and oven dried at 80°C for 24 h under vacuum and finally weighed when it dried off (W_{dry}). The samples were then soaked in a water for 12 h to promote the swelling. When the samples were swollen to equilbrium and after removing surface water with tissue paper, the wet membranes were quickly weighed again (W_{wet}). The water uptake is calculated using the following equation:

Water swelling (%) = [(W_{wet} - W_{dry}) / W_{dry}] x 100%   (1)

where W_{wet} and W_{dry} are the weight of swollen and dry membranes, respectively.

2.4.4   *Proton Conductivity Study*

The proton conductivity measurements were carried out using the electrode AC impedance spectroscopy method (HIOKI 3531-01 Hi-tester) over a frequency range of 50 Hz to 1 MHz. The membranes were measured at varying temperatures from 30 °C to 80°C and constant humidity of 80%. Before each measurement, the sample was immersed in de-ionized water for 24 h. The ion conductivity was calculated from the ohmic resistance by the equation:

$$\sigma = L/(R \times A)$$ (2)

where L is the thickness of the sample; R is the resistivity obtained from EIS and A is an area of the membrane sample.

3.0   RESULTS AND DISCUSSION

Table 1 shows the observation for nanofibers formation with different concentrations of Strontium (Sr). Based on the results below, a low concentration of Strontium (4% - 6%) favors the formation of nanofibers while higher concentration (8% - 10%) leads to the inability to collect a fiber mat.

Higher concentrations of Sr (above 6%) may hinder formation of nanofibers due to the surface tension of the sol has become much stronger. As expected, the metal–polymer crosslink is based on the interaction between earth metal ions and sulfonic groups where the cationic earth metal ions make very strong bonds with the anionic sulfate or sulfonic groups of the SPEEK.

**Table 1** Nanofibers formation for different concentration of Sr

Samples	Formation of Nanofiber
Pure SPEEK	+ve
4% Sr-SPEEK	+ve
6% Sr-SPEEK	+ve
8% Sr-SPEEK	-ve
10% Sr-SPEEK	-ve

## 3.1	The Change of Fiber Diameter

FESEM (Figure 1a) was used to investigate the cross-sectional morphology of the pristine SPEEK and crosslinked Sr-SPEEK membranes. Along with the FESEM micrographs is the diameter distribution histograms of electrospun mats. The electrospun membrane of both pristine and Sr-crosslinked SPEEK (Figure 1a) shows regular, unwelded, and randomly oriented nanofibers obtained for all conditions of electrospinning sol. The fiber diameter size distribution ranged from 100 to 170 nm with an average value of around 104 nm, 144 nm, and 167 nm for pristine SPEEK and both crosslinked 4% and 6% Sr-SPEEK membrane respectively. Electrospun fibers with different average diameters were obtained probably due to the different electrospinning conditions and the higher functionalization. FESEM results indicated that the addition of Strontium led to a tendency of higher average fiber diameter with random diameter distributions. Increasing of the Strontium concentration into the SPEEK leads to the thicker formation of nanofibers. The electrospun membrane of 4% Sr-SPEEK and 6% Sr-SPEEK shows the improvement in the morphology as a smooth single fiber without beads were produced. These findings were very important since fabricating NFs based PEM membrane is crucial in which conductivity of the proton can be badly affected by defects fibers such as beaded NFs.


(b)

(c)

(a)
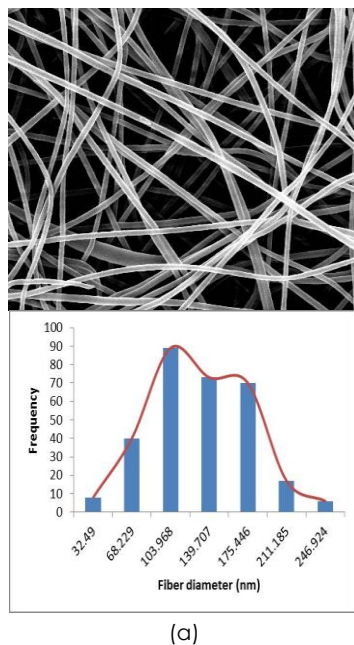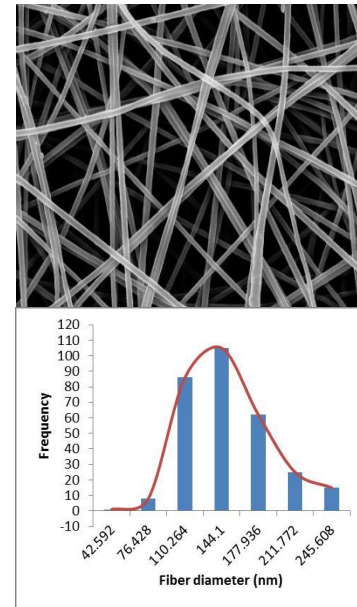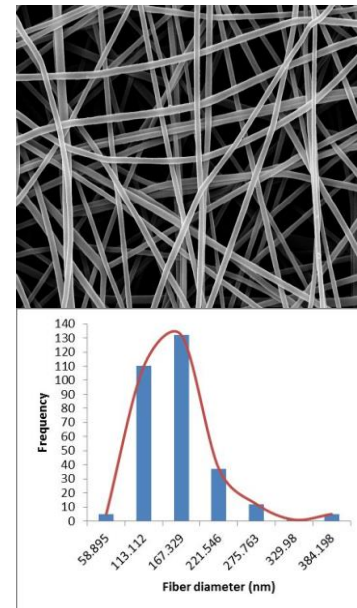
Figure 1 FESEM images of the electrospun membranes together with diameter distributions charts beside for :(a) Pristine SPEEK , (b) 4% Sr-SPEEK , and (c) 6% Sr-SPEEK

## 3.2	FTIR Analysis

Figure 2 shows the FTIR spectra for sulfonated PEEK, 4% Sr-SPEEK, and 6% Sr-SPEEK. The presence of functional groups in the electrospun NFs can be determined based on the FTIR spectrum shown in Figure 2. The presence of the sulfonic group in SPEEK was confirmed by the sharp peak at 1250 cm^{-1}, due to asymmetric O=S=O stretching vibration [12]. Transmittance peaks at 3476 cm^{-1} and 1640 cm^{-1} were observed, corresponding to O-H stretching

vibrations and the bending vibrations of adsorbed water, respectively [9]. These peaks which correspond to O-H vibration which is adsorbed water due to interacting with sulfonic groups become broader after the addition of Strontium. The hydrophobic nature of the samples in this instance was thought to be enhanced by the crosslinking of Sr. Specific peak attributed to the ionic bonding of crosslinked Sr-SPEEK cannot be conclusively determined here since metal-polymer is a physical crosslinking type and not a chemical (covalent) crosslinking. The interaction between metal ions and sulfonic groups resulted in the strong bonds of cationic metal ions and the anionic sulfonic groups of the SPEEK cannot be shown by the FTIR analysis.
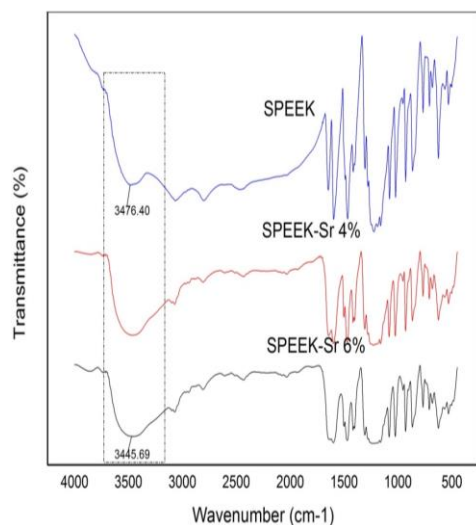

Figure 2 FTIR spectrum for SPEEK, 4% Sr-SPEEK and 6% Sr-SPEEK

3.3   Water Uptake

Water uptake is one of the important parameters for PEM. The dissociation of protons from $-SO_3^-$ ionic groups causes the conductivity of the acidic membrane to depend on water uptake [13][14]. Protons within PEMs could not be conducted, as stated in the "vehicle mechanism" of proton conduction unless they are hydrated by water. However excessive water leads to deterioration of the dimensional stability thus lose their mechanical properties [15]. The values of the water uptake obtained for all studied membranes in room temperature are given in Figure 3.

The water uptake for the pristine SPEEK nanofiber membrane is considerably low compared to SPEEK film as SPEEK film obtained above 40% [9]. At a higher concentration of Strontium which was 4% and 6%, the water uptake reduces to 28.1% and 20.2% respectively. The effect of crosslinking on electrospun NF SPEEK can be observed from water uptake as water uptake decreased considerably with increasing strontium content [9]. These experimental

results showed that cross-linking not only limited the mobility of the polymer chains plus decreased the water uptake of the membranes [16].
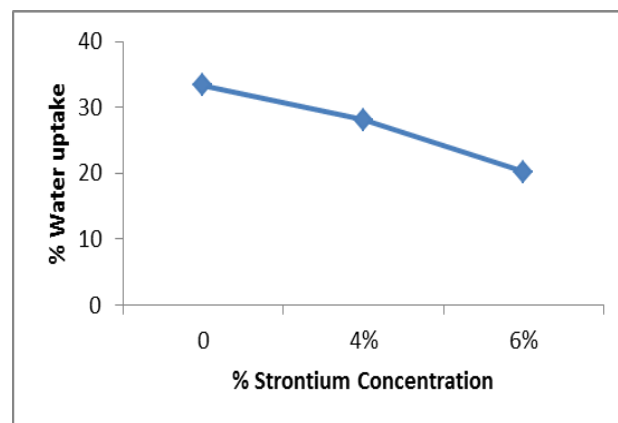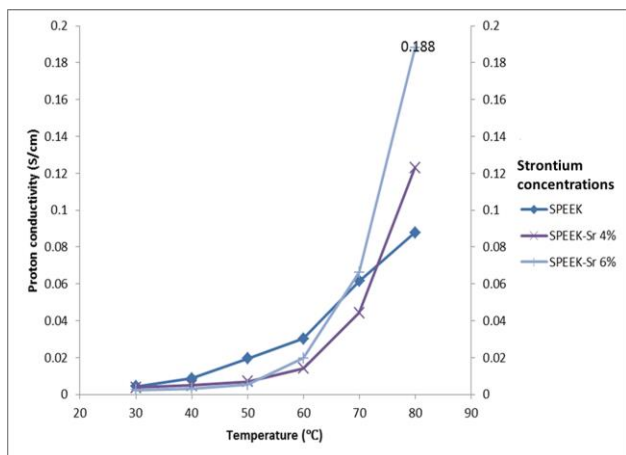

Figure 3 Effect of different concentration of Strontium on Water uptake for pristine SPEEK and crosslinked membrane

3.3   Proton Conductivity

Proton conductivity is probably the most important property of a PEM's. Performance of a PEMFC is mainly dependent on how well it deals especially at medium and high temperatures. Figure 4 shows the proton conductivities of electrospun SPEEK membranes with different concentrations of Strontium over the range of temperatures between 30˚C to 80˚C. As discussed earlier in water uptake, protons within PEM could not be conducted unless they are hydrated by water. The combined factors of high proton conductivity and lower water uptake are ideal for PEM [17]. As shown in Figure 4, at temperature 30˚C the conductivity for pristine SPEEK and electrospun NF Sr-SPEEK are both low. This result suggests the formation of continuous proton transferring channels was limited which happens at lower water uptake [15].

All membranes show positive conductivity-temperature dependencies. An improvement of about one order of magnitude as compared with Nafion® at 80 °C was achieved [9] for both electrospun SPEEK-Sr samples. The crosslinking ions of Sr in the polymeric chain of the electrospun SPEEK membranes were proven to have further improved the conductivity of SPEEK based membrane [9]. These results were in stark contrast where an increased percentage amount of Sr in SPEEK had resulted in the decrease of proton conductivity at a temperature above 70oC due to a reduced number of proton ions and less flexible molecular structure [9]. The increase of conductivity in electrospun NFs Sr-SPEEK compared to the pristine electrospun NFs SPEEK could be explained by the large-aspect-ratio of NFs interconnecting the absorbed water and proton channels, in-turn creating continuous proton transfer networks [11], [18]. All these make the proton

transfer distance and barrier closer and resulted in much faster proton transportation across the membrane. The reductions of mobile proton ions in the NFs Sr-SPEEK were compensated by the above-mentioned mechanism.

Figure 4 Effect of different concentration of Strontium on the temperature dependence of proton conductivity

4.0 CONCLUSION

In this work, we prepared electrospun mat nanofibers membrane of pristine SPEEK and crosslinked SPEEK with Strontium (Sr) through electrospinning technique. The morphologies of electrospun Sr-SPEEK membrane, fabricated under different concentrations of Sr were presented which show up to 6% concentration of Strontium was able to be electrospun. Results as a whole can be concluded that additions of Sr via ion covalent crosslinks have been able to increased proton conductivity in the electrospun PEM membrane. While the conductivity of pristine SPEEK decreases at the temperature above 70˚C, the increase of conductivity in electrospun NFs Sr-SPEEK compared to the pristine electrospun NFs SPEEK could be explained by the large-aspect-ratio of NFs interconnecting the absorbed water and proton channels, in-turn creating continuous proton transfer networks.

References

[1] J. Wang *et al.* 2010. Novel Covalent-ionically Cross-linked Membranes with Extremely Low Water Swelling and Methanol Crossover for Direct Methanol Fuel Cell Applications. *J. Memb. Sci.* 363(1): 112-119.

[2] S. J. Peighambardoust, S. Rowshanzamir, and M. Amjadi. 2010. Review of the Proton Exchange Membranes For Fuel Cell Applications. *International Journal of Hydrogen Technology.* 35(17): 9349-9384.

[3] N. Intaraprasit and P. Kongkachuichay. 2011. Preparation and Properties of Sulfonated Poly(ether ether ketone)/Analcime Composite Membrane for a Proton Exchange Membrane Fuel Cell (PEMFC). *J. Taiwan Inst. Chem. Eng.* 42(1): 190-195.

[4] K. Charradi *et al.* 2019. Amelioration of PEMFC Performance at High Temperature by Incorporation of Nanofiller (sepiolite/layered double hydroxide) in Nafion Membrane. *Int. J. Hydrogen Energy.* 44(21): 10666-10676.

[5] S. K. Kamarudin, F. Achmad, and W. R. W. Daud. 2009. Overview on the Application of Direct Methanol Fuel Cell (DMFC) for Portable Electronic Devices. *Int. J. Hydrogen Energy.* 34(16): 6902-6916.

[6] K.-J. Chae *et al.* 2014. Sulfonated Polyether Ether Ketone (SPEEK)-based Composite Proton Exchange Membrane Reinforced with Nanofibers for Microbial Electrolysis Cells. *Chem. Eng. J.* 254: 393-398.

[7] N. N. Ramly, N. A. Aini, N. Sahli, S. F. Aminuddin, M. Z. A. Yahya, and A. M. M. Ali. 2017. Dielectric Behavior of UV-Crosslinked Sulfonated Poly (ether ether ketone) with Methyl Cellulose (SPEEK-MC) as Proton Exchange Membrane. *Int. J. Hydrogen Energy.* 42(14): 9284-9292.

[8] Y. Ye, Y. Yen, C. Cheng, W. Chen, L. Tsai, and F. Chang. 2009. Sulfonated Poly (ether ether ketone) Membranes Crosslinked with Sulfonic Acid-containing Benzoxazine Monomer as Proton Exchange Membranes. *Polymer (Guildf).* 50(14): 3196-3203.

[9] D. X. Luu and D. Kim. 2011. Strontium Cross-linkeded SPEEK Proton Exchange Membranes for Fuel Cell. *Solid State Ionics.* 192(1): 627-631.

[10] C. Dong *et al.* 2017. Facile Synthesis of Metal Oxide Nanofibers and Construction of Continuous Proton-conducting Pathways in SPEEK Composite Membranes. *Int. J. Hydrogen Energy.* 42(40): 25388-25400.

[11] R. Sood, S. Cavaliere, D. J. Jones, and J. Rozière. 2016. Electrospun Nanofibre Composite Polymer Electrolyte Fuel Cell and Electrolysis Membranes. *Nano Energy.* 26: 729-745.

[12] J. B. Ballengee and P. N. Pintauro, 2013. Preparation of Nanofiber Composite Proton-Exchange Membranes from Dual Fiber Electrospun Mats. *J. Memb. Sci.* 442: 187-195.

[13] S. Mollá and V. Compañ. 2011. Polyvinyl Alcohol Nanofiber Reinforced Nafion Membranes for Fuel Cell Applications. *J. Memb. Sci.* 372(1): 191-200.

[14] H. Hou, M. L. Di Vona, and P. Knauth. 2012. Building Bridges: Crosslinking of Sulfonated Aromatic Polymers—A Review. *J. Memb. Sci.* 423-424, 113-127.

[15] G. Li, C. Zhao, Y. Cui, T. Rong, C. Zhu, and H. Na. 2016. Intermolecular Ionic Cross-linked Sulfonated Poly(ether ether ketone) Membranes with Excellent Mechanical Properties and Selectivity for Direct Methanol Fuel Cells. *RSC Adv.* 6(27): 23025-23032.

[16] S. Zhou, J. Kim, and D. Kim. 2010. Cross-linked Poly(ether ether ketone) Membranes with Pendant Sulfonic Acid Groups for Fuel Cell Applications. *J. Memb. Sci* 348(1–2): 319-325.

[17] J. Mengbo and Z. Wei. 2009. *A Review of Water Management in Polymer Electrolyte Membrane Fuel Cells.* Energies. 2009; 2(4): 1057-1106.

[18] B. Dong, L. Gwee, D. Salas-De La Cruz, K. I. Winey, and Y. A. Elabd. 2010. Super Proton Conductive High-purity Nafion Nanofibers. *Nano Lett.* 10(9): 3785-3790. DOI: 10.1021/nl102581w.