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Preparation and characterization of zeolite polymer composite proton exchange membrane

Anis Nurdhiani Rosdi[a], Yee Li Kang[a], Monash Purushothaman[b], Shaliza Ibrahim[a], Saravanan Pichiah[a,*]

[a]*Environmental Engineering Laboratory, Department of Civil Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia, Tel. +60 379677678; Fax: +60 379675318; email: saravananpichiah@um.edu.my (S. Pichiah)*
[b]*Centre for Separation Science & Technology, Faculty of Engineering, Department of Chemical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*

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ABSTRACT

Sulfonated polystyrene (SPS) and sulfonated polystyrene zeolite composite (SPS-Z) membranes were prepared by solution casting technique. SPS was synthesized using acetyl sulfate as a sulfonating agent in a reflux condenser under nitrogen atmosphere. The membrane casting was done without isolating the SPS. The SPS-Z membrane was fabricated by adding the zeolite to the SPS solution by the same technique. The synthesized SPS and SPS-Z membranes were characterized with Fourier transform infrared spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, and atomic force microscopy to identify the $-SO_3H$ functional group attached onto the polymer membrane, thermal stability, and surface morphology. The membranes were further examined for their water uptake capacity, swelling behavior, and degree of sulfonation. In addition, the performance of the fabricated membranes was examined based on their ion exchange capacity (IEC) and proton conductivity. The results revealed that both the membranes have good thermal and surface properties. The SPS-Z membrane has less swelling tendency than the SPS membrane due to lower water uptake capacity of SPS-Z membrane (2.5%) than the SPS membrane (3.5%). The proton conductivity of the SPS-Z membrane (1.11×10^{-5} S/cm) is higher than the SPS membrane (1.68×10^{-6} S/cm). The IEC capacity of SPS and SPS-Z membranes is found to be 0.03 and 0.17 meq/g, respectively. The proton conductivity of SPS and SPS-Z membranes is comparable with the Nafion 117® membrane (5.32×10^{-6} S/cm) under the same experimental conditions indicates that the fabricated membranes have the good potential for membrane applications, especially for fuel cell applications.

Keywords: Membrane; Sulfonated polystyrene; Polymer zeolite composite; Proton exchange membrane

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*Corresponding author.

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1. Introduction

Environmental issues and the subsequent effort to rectify these problems lead to the application of many types of treatment technology for pollutant removal. One of the major types of treatment is chemical treatment which includes filtration, chemical precipitation, electroflotation, ion exchange, and reverse osmosis [1]. Membrane plays an important role in certain chemical treatment such as ion exchange and reverse osmosis. Additionally, membrane is also useful for processes other than wastewater and water purification.

Membranes also play an important role in fuel cell application. The typical membrane used in fuel cell is proton exchange membrane (PEM). PEM plays a dominant role in fuel cell applications such as electric vehicle applications, portable electronics, and residential power generation [2]. PEMs have been demonstrated as a potential candidate because of their greater capability to pass through the protons produced in the cathode [3]. Among the various PEMs, Nafion is the most common and well known commercial PEM owing to their chemical, mechanical, and thermal stability as well as high proton conductivity [2,4]. The amphiphilic nature (i.e. possess both hydrophilic and lipophilic nature) of Nafion, attributed to the polytetrafluoroethylene primary structure and perfluorinated vinyl ether as side chains, allows the nanophase separation that makes the Nafion as a strong candidate for PEM fuel cell applications [2,5,6]. However, due to its high cost and detrimental environmental impact due to tetrafluoroethylene elicited researchers to search for alternative PEM for fuel cell applications [7,8].

Several membranes have been examined as an alternative for the Nafion membranes and polystyrene PEM has been found to be one of the potential substitutes [9,10]. The major factor that must be the foremost concern during the synthesis of PEM are the proton conductivity, water uptake, and swelling properties. Proton conductivity of Nafion PEM must be in the order of 10^{-2} S/cm [11]. Such high order of proton conductivity is very hard to achieve using a pure polymeric membrane alone. Hence, most of the membranes are sulfonated to increase the proton exchange capacity [11]. The inclusion of this $-SO_3^-$ ion helps in promoting the proton transfer across the electrode through the membrane [9,12]. Other than proton conductivity, cross-linked network was produced by sulfonation reactions that increase the thermal stability of the membrane [9,13]. The proton conductivity is also highly influenced by the degree of sulfonation (DS). High DS leads to higher proton conductivity and vice versa. On the other hand, higher DS leads to swelling [11]. Hence, an optimum DS would compromise the proton conductivity, swelling, and stability of the PEM membrane.

Several researchers incorporated inorganic aids, especially aluminosilicates, to enhance the proton conductivity and stability of the PEM membrane such as sulfonated poly(arylene ether sulfone)/sulfonated zeolite composite membrane [14], sulfonated polystyrene (SPS) butadiene rubber [11], and cross-linked SPS [9]. The portable cation framework functions as an ion exchange network in the aqueous phase that makes zeolite as an excellent PEM. Therefore, polymer–zeolite composite makes a successful combination as zeolite will enhance the proton-exchange properties while the base polymer will provide a flexible polymer matrix [15,16]. Yu et al. [14] have successfully synthesized sulfonated poly(arylene ether sulfone)/sulfonated zeolite made for PEM application for temperature condition above 100°C. Both zeolite and poly(arylene ether sulfone) were sulfonated first before it has been combined as a membrane by varying the ratios of sulfonated zeolite into sulfonated poly(arylene ether sulfone). The addition of 5 wt% sulfonated zeolite increase the proton conductivity from 0.022 to 0.030 S/cm [14].

Most literatures reported that the fabrication of the membrane by isolating the SPS after sulfonation reaction and the casting solution was prepared by dissolving the SPS in solvent. Hence, the present study focused on the preparation of polymer–zeolite composite PEM using polystyrene as a precursor. The SPS and sulfonated polystyrene zeolite composite (SPS-Z) membrane was fabricated by solution casting technique without isolating SPS from the sulfonation reaction. The fabricated membranes are examined for their characteristics and potential use in membrane applications by various analytical and experimental techniques.

2. Material and methods

2.1. Material

Polystyrene beads ($M_w = 350{,}000$ g/mol, $M_w/M_n = 2.06$) purchased from Sigma-Aldrich is used as polymeric precursor. Sulfuric acid (98%), acetyl sulfate, acetic anhydride, dichloroethane, chloroform, and zeolite powder (<45 μm) were also purchased from Sigma-Aldrich and used as received.

2.2. Membrane synthesis

Polystyrene beads were used as a precursor for the SPS using a modified synthesis procedure reported by Xu et al. [9]. A 5.2 g of polystyrene beads was dissolved in 40 ml of chloroform with constant stirring under nitrogen atmosphere in a three-necked-round bottom flask with reflux condenser. Fresh acetyl sulfate solution of 0.5 ml was added as a sulfonating agent to the homogeneous polystyrene solution and the reaction was continued for 6 h at 50˚C. The fresh acetyl sulfate solution was prepared by mixing 1 ml of acetic anhydride and 5 ml of dichloroethane in an ice bath followed by dropwise addition of 7 mL of concentrated sulfuric acid. After 6 h of sulfonation, the SPS polymer solution from the round-bottom flask was removed carefully. Without terminating the reaction and isolating SPS, a requisite amount of casting solution is poured at the center of a flat petri glass dish of 90 cm placed in a surface plate. The plate was kept as it is to allow surface evaporation at room temperature for 24 h. After that, the membrane was dried at 60˚C for 12 h in a controlled hot air oven. The obtained membrane was designated as SPS membrane. Similar casting technique was applied for the preparation of polymer–zeolite composite membrane by adding 1 g of zeolite powder to the SPS polymer solution and casted in glass petri dish kept on the surface plate. The membrane prepared with zeolite was designated as SPS-Z membrane.

2.3. Membrane characterization

Fourier transform infrared (FT-IR) spectroscopy analysis was performed using Nicolet iS10 FT-IR spectrometer with diamond ATR crystal (Thermoscientific, USA) under the wavenumber ranging between 800 and 3,500 cm^{-1}. Thermogravimetric analysis (TGA) was performed between 28 and 500˚C at a heating rate of 10˚C/min under nitrogen atmosphere in STA 449 F3Jupiter, Netzsch (Germany). The surface morphology of the prepared membranes was investigated using field emission scanning electron microscope (FESEM) (LIBRa 200 FE, Carl Zeiss, Germany). Surface roughness of the membranes was captured using atomic force microscopy (AFM) (Ambios Technology, USA).

2.4. Membrane performance experiments

2.4.1. Water uptake

The water uptake and the number of water molecules per sulfonic group are calculated using the mass of dry and wet membrane. The SPS and SPS-Z membranes were cut into 5 × 5 cm using doctor's blade and dried at 60˚C for 2 h. The membranes were then kept in a desiccator to cool to the room temperature and the dry mass of the membrane was measured. The membranes were then immersed in DI water for 24 h at room temperature. The membranes are taken out and the surface water was removed by careful and quick blotting with Kimwipes®. The mass of the wet membranes were measured. The water uptake capacity of the membranes was calculated using the following equation:

$$\text{Water uptake } (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{1}$$

where W_{wet} (g) and W_{dry} (g) is the mass of wet and dry membranes, respectively. The reported water uptake is the average of three SPS and SPS-Z membranes, respectively.

The number of water molecules absorbed per sulfonic group (ionic site) was calculated using Eq. (2).

$$\lambda_{\text{w}} = \frac{\text{Water uptake}}{M_{\text{w}} \times \text{IEC}} \tag{2}$$

where λ_{w} is the number of water molecules adsorbed, IEC is the ion exchange capacity (value obtained from ion exchange experiment) and M_{w} is the molecular weight of the immersed liquid (i.e. water, $M_{\text{w}} = 18$ g/mol).

2.4.2. Swelling ratio

After measuring the mass of membranes during water uptake experiments, the change in dimensions (length and width) of the membranes are measured. The extent of swelling is measured in terms of swelling ratio using the following equation:

$$\text{Swelling ratio} = \frac{D_{\text{wet}} - D_{\text{dry}}}{D_{\text{dry}}} \times 100 \tag{3}$$

where D_{wet} and D_{dry} are the average dimensions of wet and dry membranes. The average dimension refers to the geometric mean of wet ($D_{\text{wet}} = (L_{\text{wet1}} \times B_{\text{wet2}})^{1/2}$) and dry ($D_{\text{dry}} = (L_{\text{dry1}} \times B_{\text{dry2}})^{1/2}$), respectively, where L and B denotes length and breadth of the membrane. Square (5 × 5 cm) samples are used in this work, L_{dry1} and B_{dry2} are the same.

2.4.3. Ion exchange capacity

The IEC of the SPS and SPS-Z membranes were determined by the back-titration method. A known mass of the membrane sample (≈0.3 g) was soaked in 1 M NaCl aqueous solution for 24 h to convert the acid form (H^+) of the membrane to sodium form (Na^+). Then, the exchanged H^+ ion in the solution was titrated with 0.01 M NaOH solution using methyl orange as an indicator. IEC is a measure of number of exchangeable protons per unit mass of dry polymer and the value is obtained by the following equation:

$$\text{IEC (in milliequivalents)} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \times 1{,}000 \quad (4)$$

where C_{NaOH} is the concentration of NaOH (mol/L) and V_{NaOH} is the volume of NaOH used in the titration (ml) and W_{dry} is the mass of the dry membrane before immersed in NaCl (g).

2.4.4. Degree of sulfonation

The DS is the average number of sulfonic groups (SO_3H) per repeating unit in a polymer and estimated by rearranging the theoretical relationship between IEC and DS as shown in the following equation:

$$\text{IEC} = \frac{\text{DS}}{M_{\text{monomer}} + M_{\text{sulfonicgroup}} \times \text{DS}} \quad (5)$$

where M_{monomer} is the molecular weight of the monomer (g/mol) and $M_{\text{sulfonic group}}$ is the molecular weight of the sulfonic group. Molecular weight of styrene monomer (C_8H_8) is 104 and the molecular weight of sulfonic group (SO_3H) is 81. Applying these values and rearranging Eq. (5) will obtain the equation for DS as shown in the following equation:

$$\text{DS} = \frac{104(\text{IEC})}{1 - 81(\text{IEC})} \quad (6)$$

2.4.5. Proton conductivity

Proton conductivity (σ) of full hydrated SPS and SPS-Z membranes was measured at room temperature by the two-probe alternating current impedance method (Autolab PGSTAT128 N, Netherlands). A 5 × 5 cm hydrated membrane of SPS or SPS-Z was clamped between two chambers (each chamber has 125 ml capacity) containing DI water as electrolyte. Two carbon cloth electrodes were used as electrodes to measure the proton conductivity at room temperature (30 ± 2°C) with relative humidity of $55 \pm 5\%$. Resistance of the membrane was measured by recording the voltage (V) for a known applied current (A). The actual resistance offered by the membrane was obtained by subtracting cell resistance from total resistance (i.e. $R_{\text{total}} = R_{\text{membrane}} + R_{\text{cell}}$). Cell resistance, R_{cell} was measured without the membrane under the same operating condition. The proton conductivity (σ in S/cm) of membrane is determined from the following equation:

$$\sigma = \frac{T}{RS} \quad (7)$$

where T is the membrane thickness of the membrane (cm), S is the surface area of membrane (cm^2), and R is membrane resistance (Ω). The thicknesses of the membranes are measured using a dial gauge (precision of ± 0.01 mm) and the thickness used in the calculation is the average of 12 measurements (four measurements on each membrane for the three different membranes of Nafion 117, SPS, and SPS-Z membranes, respectively).

3. Result and discussions

3.1. FT-IR spectroscopy

Polystyrene is a thermoplastic and hydrophobic polymer with aromatic backbone. To obtain ionic conductivity of polystyrene membranes, sulfonic acid groups (SO_3H) are introduced to polystyrene backbone through an electrophilic substitution reaction. Fig. 1(a) and (b) show the FT-IR spectra of SPS and SPS-Z membranes, respectively. FT-IR spectra were used to identify the substitution of sulfonic group (SO_3H) with the hydrogen and aromatic groups. Sulfonic group vibration bands are detected between 1,000 and 1,080 cm^{-1} for both the prepared membranes [17]. Absorption band at 1,027 cm^{-1} corresponds to the symmetric stretching vibration of SO_3H group and S–O vibration band at 1,180 cm^{-1}. Aromatic C–H deformation bands are found at wavenumbers ranging between 750 and 850 cm^{-1}. The band at 1,154 cm^{-1} corresponds to sulfonate anion attached to aromatic rings. Both membranes recorded almost similar spectrum for wavenumber below 3,000 cm^{-1}. This confirms that the sulfonation was successful and not disturbed by the incorporation of zeolite powder to the sulfonated polymer solution. However, the broad band between 3,100 and 3,700 cm^{-1} present in SPS-Z membrane is attributed to the hydroxyl groups (>3,500 cm^{-1}) associated with the zeolite metal ion and C–H stretching bonds of the zeolite as shown in Fig. 1(b).

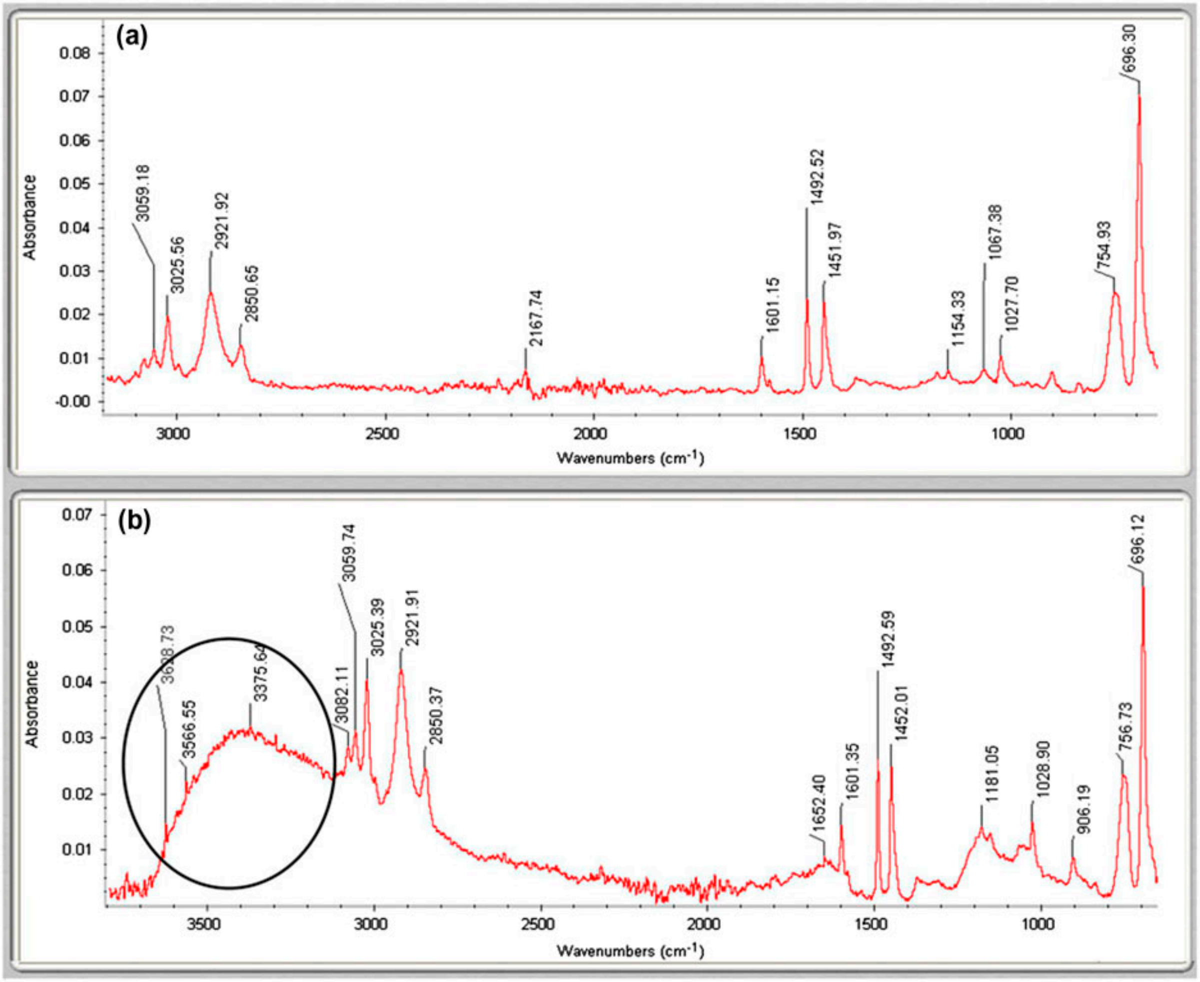

Fig. 1. FT-IR spectra of (a) SPS and (b) SPS-Z membrane.

3.2. Thermogravimetric analysis

The thermal stability of both SPS and SPS-Z membranes are investigated by TGA and depicted in Fig. 2. The addition of zeolite on SPS-Z might cause structural modification and will affect the membranes' degradation behavior [18]. The onset of weight loss process for SPS and SPS-Z membranes is found to be at 380 and 400˚C, respectively. A minor difference in the overall weight loss of SPS and SPS-Z membranes is attributed to the physisorbed moisture present in the zeolite powder. The high value of degradation temperature (>380˚C) indicates the structural rigidity of SPS and SPS-Z membranes. A significant decrease in the thermal stability of SPS-Z does not affect its use in microbial fuel cell (MFC) applications, since the operation is carried out at lower temperatures than the degradation temperature of SPS-Z membrane. In addition, the zeolite incorporation would improve the surface properties but has detrimental effect in the proton exchange capacity.

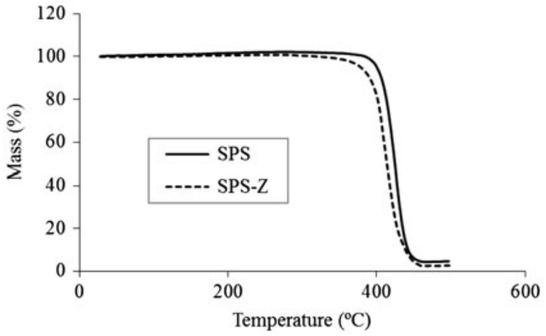

Fig. 2. TGA analysis of SPS and SPS-Z.

3.3. Surface morphology characterization

Surface morphology of the SPS and SPS-Z membranes is observed using FESEM and AFM micrographs and is depicted in Figs. 3 and 4, respectively. Both membranes show similar surface morphology and the variation in the surface texture is probably due to the presence of aggregates of sulfonic groups or zeolite at the film surface. The AFM analysis showed a considerable increase in the roughness of the SPS-Z membranes.

3.4. Water uptake

In general, a PEM should absorb sufficient water to assist the transportation of protons from the anode to the cathode. However, excessive absorption of water would induce the loss of the dimensional stability and mechanical properties. Hence, a good PEM should possess high water uptake and low swelling ratio. The water uptake of the SPS and SPS-Z membranes for different days of immersion in DI water is depicted in Fig. 5. The results confirm that both the membranes are saturated within 24 h of immersion and the water uptake capacity remains constant. The water uptake capacity of SPS membrane is found to be higher (3.5%) than that of SPS-Z (2.5%) membrane. The water uptake is due to the hydration of the sulfonic groups. In general, high value of water uptake leads to higher proton conductivity attributed to the water residing in the hydrophilic domains of the membranes that facilitates the transport of protons. However, the high value of water uptake has a negative effect attributed to swelling that reduces the mechanical stability as well as the performance of the membrane. Incorporation of zeolite to SPS reduces the polymer chain mobility and free volume that leads to more rigid and compact structures of the SPS-Z membranes, thus reduces the water uptake capacity. This is confirmed with the hydration number (λ_w) that is the number of absorbed water molecules per sulfonic group. The λ_w of SPS and SPS-Z membranes are found to be 6.48 and 0.82, respectively. In general, the addition of zeolite increases the hydrophobicity of the membrane that would be helpful in reducing membrane fouling. The 28.5% reduction in water uptake of SPS-Z membrane than the SPS membrane has detrimental effect in proton exchange capacity; however, this can be compromised with reduction in fouling. In general, the hydration of the sulfonic acid group during water uptake causes swelling of the ionic clusters. The swelling ratio of SPS and SPS-Z membrane measured at room temperature is found to 10 and 6%, respectively. Lower percentage of swelling obtained for SPS-Z membrane is due to increased hydrophobicity. The low swelling ratio of both SPS and SPS-Z membranes compared to Nafion 117® membrane (18%) indicates that the prepared membranes have good mechanical stability.

3.5. Ion exchange capacity

The IEC represents the amount of exchangeable ions in unit grams of the dry polymer and depends on the number of sulfonic acid groups present in the membrane [9,11]. The IEC of SPS and SPS-Z membranes is found to be 0.03 and 0.17 meq/g, respectively. The results indicate that the addition of zeolite enhanced the IEC. In general, the IEC strongly depends on DS. Since the sulfonation time is fixed for both the membranes, the DS is same for both the

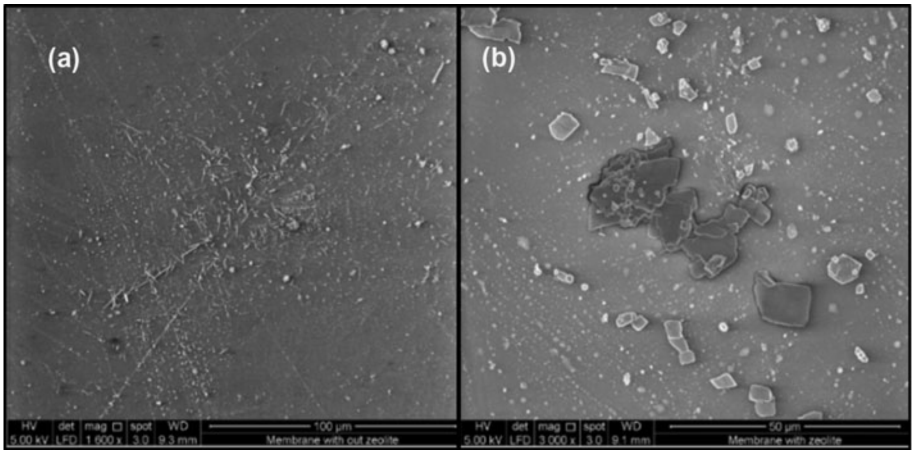

Fig. 3. FESEM image of (a) SPS and (b) SPS-Z.

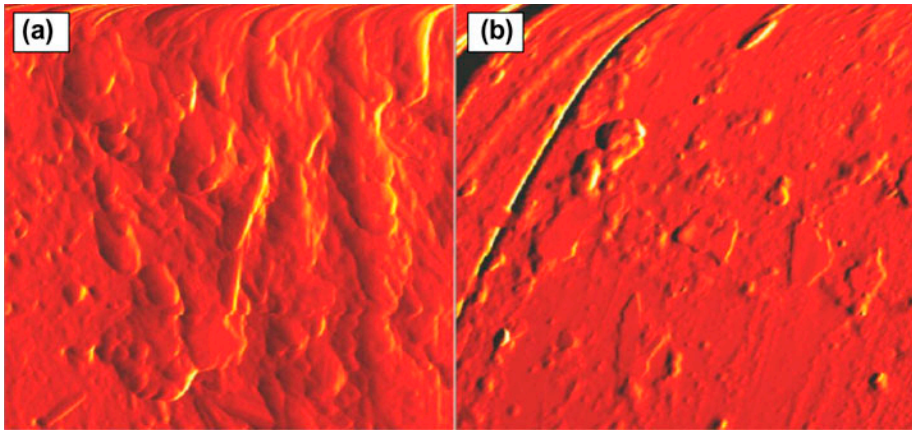

Fig. 4. AFM image of (a) SPS and (b) SPS-Z.

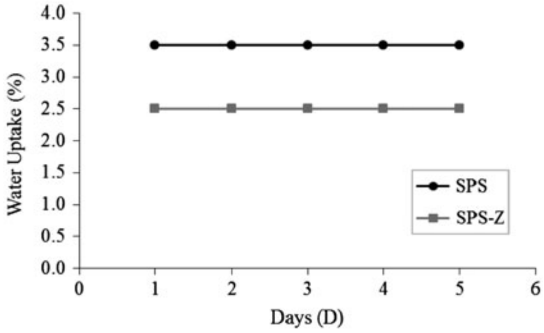

Fig. 5. Water uptake of SPS and SPS-Z membrane.

membranes. However, the addition of zeolite to the SPS polymer solution reduces the reduction in sulfonic acid group in the unit volume of the casting solution. This would actually decrease the IEC of SPS-Z membrane than the SPS membrane. However, the increased IEC of SPS-Z membrane is attributed to the ions released by the zeolites. In general, the movement of the ionic groups from one cluster to another in SPS membrane is responsible for the transportation of ions. The lower value of IEC of SPS membrane might be attributed to the lower level of connectivity of the ionic groups compared to that of SPS-Z membrane under the same fabrication conditions. The higher value of connectivity between the regularly spaced styrene side chains and sulfonic acid groups because of zeolite addition might also be a reason for high IEC of SPS-Z membrane. The IEC values of SPS-Z membrane is comparable or higher than the Nafion 117® membrane (IEC = 0.16 meq/g) under the same experimental conditions. This suggests that the SPS-Z membrane have potential for proton exchange and can be used in fuel cell applications.

3.6. Degree of sulfonation

After 6 h of sulfonation reaction, the DS of the formed SPS membrane is found to be 0.31%. The DS of the SPS-Z membrane is assumed to be the same due to the addition of zeolite was done after the sulfonation process. SPS-Z membrane is a SPS zeolite composite membrane and not SPS membrane on zeolite surface. The degree of polymerization can be controlled by the reaction time and temperature. Since the membrane is prepared without isolating the sulfonation reaction, a lower DS is chosen to reduce the swelling behaviour of the membrane. Optimization of reaction time and concentration will be reported in succeeding manuscript.

3.7. Proton conductivity

Proton conductivity of SPS and SPS-Z membranes at 55% relative humidity and at room temperature (30 ± 2°C) are estimated from the measured resistance and

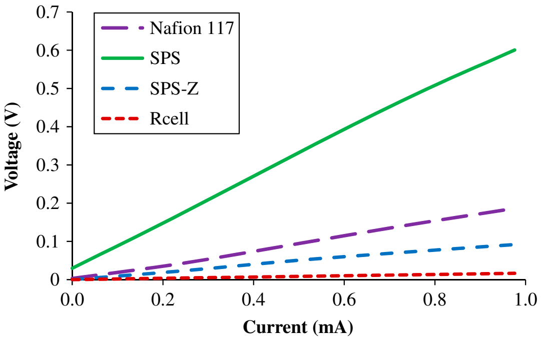

Fig. 6. Current–voltage characteristic curves of Nafion 117®, SPS and SPS-Z membranes.

Table 1
Proton conductivity of Nafion 117®, SPS, and SPS-Z membranes

Membrane	Resistance (Ω)	Thickness ($\times 10^{-2}$ cm)	Area (cm^2)	Proton conductivity (S/cm)
Nafion 117®	162.21	2.159	25	5.32×10^{-6}
SPS	544.61	2.286	25	1.68×10^{-6}
SPS-Z	82.31	2.286	25	1.11×10^{-5}

the current–voltage characteristic curves of the membranes are presented in Fig. 6. The details of the conductivity experiments of SPS and SPS-Z are tabulated in Table 1. The addition of zeolite onto SPS membrane increased the proton conductivity by one order of magnitude confirms that the role of zeolite in enhancing proton conductivity of SPS membrane. This is contradictory with the water uptake result, where higher absorption of water usually leads to higher proton conductivity. Although SPS-Z membrane has lower water uptake, it has higher proton conductivity compared to SPS membrane. The SPS-Z membrane showed lower resistance than the SPS membrane attributed to the larger average separation of neighboring sulfonic acid group and hydrophilic/hydrophobic interface of the zeolite in the SPS-Z membrane, which reduces the resistance for proton transport to pass through the membrane.

In addition, the conductivity of a Nafion 117® membrane at the same experimental conditions is measured for reference. The conductivity obtained for Nafion 117® agrees well with literature values [19,20]. Thus, it can be inferred that zeolite enhanced the properties of the membrane through other means instead of increasing the water uptake of the membrane. Bae and Kim [19] reported that the proton conductivity increased linearly with the sulfonation time to 6 h, beyond which no distinguishable increase of proton conductivity was observed. The proton conductivity of the SPS and SPS-Z membranes is comparable or higher than the Nafion 117® membrane under the same experimental conditions indicates that the fabricated membranes have good potential for membrane applications. The ranges of proton conductivity result based on the references are in the range of 10^{-8}–10^{-2} (S/cm). Higher conductivity values reported in literatures are usually conducted at 100% relative humidity and at high temperature (>80˚C).

4. Conclusion

In this work, SPS and SPS-Z composite membranes were successfully prepared by solution casting technique without isolating the sulfonation reaction. The sulfonic groups are identified in FT-IR analysis and increase in the hydroxyl groups by the addition of zeolites is also identified in the FT-IR spectrum. TGA and swelling ratio confirmed that both the membranes have good thermal and mechanical stability, respectively, which is suitable for MFC application. The surface morphology of both membranes has the aggregates of sulfonic groups at the film surface. The water uptake and swelling behavior of SPS membrane is marginally higher than the SPS-Z membrane. However, the IEC and proton conductivity of SPS-Z membrane is higher than that of SPS membrane confirms the addition of zeolite improves the performance of the membranes. In major aspects, the SPS-Z membrane has better performance than the SPS membrane. The proton conductivity of both the membranes (SPS = 1.68×10^{-6} S/cm and SPS-Z = 1.11×10^{-5} S/cm) compared to Nafion 117® membrane (5.32×10^{-6} S/cm) suggests that both the membranes could be used for fuel cell applications.

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Symbols and abbreviations

λ_w	—	hydration number
σ	—	proton conductivity (S/cm)
AFM	—	atomic force microscopy
B	—	breadth of membrane
C_{NaOH}	—	concentration of NaOH (mol/L)
D	—	average dimension of membrane (mm)
DS	—	degree of sulfonation
FESEM	—	field emission scanning electron microscopy
FT-IR	—	Fourier transform infrared
IEC	—	ion exchange capacity (meq/g)
L	—	length of membrane
MFC	—	microbial fuel cell
M_{monomer}	—	molecular weight of the monomer (g/mol)
M_{n}	—	number average molecular weight (g/mol)

$M_{\text{sulfonic group}}$ — molecular weight of the sulfonic group (g/mol)
M_w — molecular weight (g/mol)
PEM — proton exchange membrane
PS — polystyrene
R — resistance (Ω)
S — surface area of membrane (cm^2)
SPS — sulfonated Polystyrene
SPS-Z — sulfonated Polystyrene Zeolite composite
T — thickness of membrane (cm)
TGA — thermogravimetric analysis
V_{NaOH} — volume of NaOH used in the titration (ml)
W — mass of membrane (g)

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