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ORIGINAL PAPER

Improved properties of sulfonated octaphenyl polyhedral silsequioxane cross-link with highly sulfonated polyphenylsulfone as proton exchange membrane

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Abstract

This study explored the concept of improving the properties of the cross-linked membrane using a 1.5-nm closed cage octaphenyl polyhedral silsesquioxane (POSS) form of nanosilica carrying the sulfonic acid group. POSS functioned with SO_3H groups (SPOSS) at 0, 1, 2, and 5 wt% were cross-linked with water-soluble sulfonated polyphenylsulfone (SPPSU) polymer. The cross-linking between SPPSU and SPOSS was accomplished through the interchain condensation of sulfonic acid functionalities initiated by thermal curing treatment. In this study, a covalently cross-linked membrane was obtained under stepwise thermal curing from 80 to 180 °C. Upon curing at 180 °C, the SPPSU-SPOSS showed considerable improvement on the membrane proton conductivity under low and high RH (%) conditions compared with the pristine SPPSU membrane. The membrane proton conductivity shows similar patterns with the membrane water uptake as the presence of water greatly influences the cross-linked membrane. The proton conductivity of the SPPSU cross-linked with 1 wt% SPOSS that was conducted under low RH (%) and at elevated temperature exhibited about six times higher proton conductivity as compared with pristine SPPSU membrane. However, increasing the loading of SPOSS beyond 1 wt% significantly dropped the membrane water uptake and proton conductivity due to SPOSS aggregation, blocking the hydrophilic domains in the polymer matrix. The results indicated that the incorporation of SPOSS in the SPPSU membrane by curing at 180 °C exhibit improvement on membrane water management and proton conductivity as compared with the pristine SPPSU membrane.

Keywords Sulfonated PPSU · Proton exchange membrane · Sulfonated POSS · Cross-linking · Fuel cell

Introduction

The scarcity of fossil fuel as energy sources, together with the destruction of environmental issues due to the emission of toxic gasses, has raised the adopted need for clean and green technologies for power generation. Fuel cells are nowadays becoming a rising technology that has been widely explored due to promising clean and efficient energy conversions. Despite modern world technology, fuel cells have known to science for more than 150 years. Though generally considered a curiosity in the 1800s, fuel cells became the subject of intense research and development during the 1900s [1]. Fuel cells offer several advantages over conventional power sources include reducing dependence on fossil fuels, long useful life, high efficiency, relatively safe, essential zero toxicity, minimal maintenance costs, and carbon emission–free. This cell system also prepared a platform for a clean, quiet, and highly efficient process in the conversion of the fuel to

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energy via an electrochemical process. In addition to low or zero emissions, benefits include high efficiency and reliability, multi-fuel capability, flexibility, durability, scalability, and ease of maintenance [2].

The fuel cell system is classified primarily by the type of electrolyte that has employed. The type of electrolyte used will determine the type of electrochemical reaction that happens in the cell, the catalyst needed, the operating temperature, and the reactant required in the cell [3, 4]. Polymer electrolyte membrane fuel cells employed proton exchange membrane (PEM) as an electrolyte that is operating at intermediate temperature (80 to 120 °C), and low relative humidity (% RH) conditions have been extensively studied to be applied in automobile transportation. Since the radiators for automobiles are designed to operate at an intermediate temperature, designed PEM should be complying with the same temperature range. Nafion (perfluorosulfonic acid)-based polymer electrolyte membrane by DuPont is the most and common commercially available PEM in the market that has high hydrolytic and oxidative stability also excellent proton conductivity [5]. The state of the art of the PEM fuel cell–based perfluorosulfonic acid ionomer that has lower proton conductivity along with rising temperature and water management issues has limited the application of the Nafion to be applied at intermediate temperature ranges [6]. A series of studies have been performed for the development of alternative PEMs using sulfonated hydrocarbon polymer for the application at intermediate temperature applications with excellent proton conductivity and water mobility.

Polyphenylsulfone (PPSU) represents a family of hydrocarbon polymer that has been widely explored as an alternative to proton-conducting membrane instead of expensive perfluorinated membranes. PPSU has excellent thermal stability and appropriate mechanical strength with high proton conductivity, which increases along the degree of sulfonation [7]. Unfortunately, highly sulfonated materials suffered from mechanical and chemical deterioration due to excess membrane swelling in water causing a reduction in proton conductivity [8]. The mechanical weaknesses of the highly sulfonated PPSU have initiated several attempts to prepare a more stable proton-conducting membrane. Recently, the cross-linking process has been studied to improve the poor dimensional stability and mechanical properties of the highly sulfonated PPSU through bridging links to the reactive sulfonic acid functions without deterioration of proton conductivity [9]. It is practicable to improve the mechanical strength and surpass membrane swelling in water by cross-linking technique. However, the cross-linking between sulfonic acid groups has reduced the acid function of the proton transport channel [10]. The formation of micro-phase-separated morphology with nanochannel for improving proton conductivity has obtained by blending ionomeric polymers with organic-inorganic hybrid materials.

This study explored the properties of composite sulfonated polyphenylsulfone (SPPSU) membrane blending with organic-inorganic hybrid materials. The composite membrane having inorganic materials is believed to avoid the trade-off between the water swelling and mechanical properties of the membrane. 1.5-nm closed cage polyhedral oligomeric silsesquioxane (POSS) form of nanosilica is one kind of organic-inorganic hybrid material that becomes attractive materials to be explored as filler. POSS is an organic-inorganic hybrid material that combines the inorganic characteristics presented by the siloxane bond (Si–O–Si) with silica as the main chain [11]. POSS has a general formula of $RSiO_{1.5}$ where R may be hydrogen or organic functional group that attaches to the Si. POSS particles that are dispersed in the polymer matrix can produce a nanoscale organic-inorganic interface that influences the hydrophilic channel of PEM. POSS molecules that carry different types of organic substituents on its outer surface make this nanostructure compatible with many polymers. The organic substituents can also be modified to enhance the compatibility with a specific polymer matrix. In this study, the water management and physicochemical characteristics of the composite SPPSU-SPOSS–cross-linked membrane comprising different loading of sulfonated POSS are presented and discussed.

Experimental procedure

Materials

The commercial polyphenylsulfone (PPSU, Solvay Radel R-5000 NT, MW ~ 50,000) purchased from Solvay Specialty Polymers, Japan, was used as the polymer backbone in the membrane formation. Highly sulfonated PPSU polymer was sulfonated using sulfuric acid (H_2SO_4, ~ 98%) purchased from Sigma-Aldrich as a sulfonating agent. Meanwhile, the commercial polyoctahedral silsesquioxane (POSS, Hybrid Plastics Inc., U. S, FW ~ 1033.53) was used as an inorganic filler. Chlorosulfonic acid was used as a sulfonating agent to develop sulfonated POSS.

Preparation of highly sulfonated polyphenylsulfone

PPSU polymer was first dried in an oven at 80 °C for about 48 h to remove moisture contents. Dried PPSU polymer was added into 1 L of sulfuric acid (H_2SO_4, ~ 98%) at 60 °C in an oil bath. The solution was continuously stirred for 48 h and maintain at 60 °C. The sulfonated polymer was recovered by precipitating the sulfonic acid solution into the huge excess of ice. The resulted precipitate sulfonated PPSU was then filtered using mild vacuum filtration and then was subjected to neutralize by excess amounts of deionized water in a dialysis-tubing cellulose membrane until pH 7. The resulting SPPSU

polymer was then dried at 80 °C until it was completely dried and ready to use. The ion exchange capacity (IEC) value of the prepared SPPSU polymer was estimated using titration technique to determine the degree sulfonation of SPPSU. The degree sulfonation of prepared SPPSU corresponds to 1.86 in which there are about two sulfonic acid groups attached to one repeating unit of the SPPSU polymer matrix.

Preparation of sulfonated POSS

Octaphenyl-POSS (3 g, 2.9 mmol) was first dried in an oven at 80 °C for more than 24 h to remove moisture content. Chlorosulfonic acid ($ClHO_3S$, 60 mL, 900 mmol) was added to dried POSS and was stirred for 24 h at 50 °C in an oil bath under Ar gas conditions. Unreacted $ClHO_3S$ was removed by vacuum distillation at 110 °C. The crude products were washed with water several times, and the excess water was evaporating under normal heating. The brownish liquid products designated as SPOSS were formed, and the IEC values using the titration method show a value of 7.84 meq/g.

SPPSU-SPOSS–cross-linked membrane preparation

The SPPSU-SPOSS–cross-linked membrane was prepared under a single casting step using a slow evaporation technique to develop a dense membrane structure. The dope solution for membrane preparation was carried out by varying the different SPOSS wt% loading. Firstly, 10% of SPPSU was dissolved in DMSO, and the dope solution was continuously stirred for 24 h until it became homogeneous. Then, different wt% of SPOSS were mixed in the solution and stirred for another 24 h to produce a homogenous solution. In the preparation of the cross-linked membrane, the SPPSU-SPOSS dope solution was first spread in the glass petri dish that acquires the membrane thickness about ~ 70 μm. The cast membrane was dried in the drying oven at 80 °C for 24 h until the solvent was completely removed. The nanocomposite membrane was then undergoing the thermal cross-linking process to improve the mechanical properties of the membrane. The membranes were further heated in air at 120 °C (24 h), 160 °C (24 h), and 180 °C (24 h). After the thermal cross-linking process, the membrane was then activated in a different solution. The residual acids and water-extractable molecules will be removed from the post-activation step. The cross-linking membrane was then immersed in 0.5 M of NaOH (80 °C, 2 h), boiling water (2 h), 1 M of H_2SO_4 (80 °C, 2 h), and boiling water (2 h). Then, the activated membrane was dried at room temperature for further characterizations.

Characterizations

Fourier transform infrared spectroscopy (FTIR) of the prepared membrane was obtained by attenuated total reflection (ATR) with an infrared (IR) spectrophotometer (Nicolet-6700, Thermo Scientific) in the frequency range of 4000–400 cm^{-1}. The IEC values of the sulfonated POSS were determined using the titration method. SPOSS was mixed in 20 mL of 2 M NaCl for about 24 h under continuous stirring to replace the protons with sodium ions. The solution was then titrated with 0.01 M NaOH solution until the pH turned to 7. The IEC value of the test sample was calculated using the following Eq. (1):

$$\mathrm{IEC}\ (\mathrm{meq/g}) = cv/w_{\mathrm{dry}} \tag{1}$$

where c (molar) is titration solution (0.01 M), v (mL) is the volume of the neutralized NaOH, and W_{dry} (g) is the dry weight of the sample tested.

Meanwhile, the water uptake of the prepared membrane was determined by the membrane weight variation before and after hydration. The membrane was first dried in the oven at 80 °C for 24 h. The dry membrane was weighted and denoted as W_{dry}. Then, the dry membrane was immersed in boiling water for 1 h. After that, the wet membrane was removed from boiling water, and the membrane was mopped with blotting paper to remove the excess water on the membrane surface. The wet membrane was weighed and denoted as W_{wet}. The water uptake of the prepared sample was calculated as the following Eq. (2):

$$\text{Water uptake}\ (\%) = \left[\left(W_{\mathrm{wet}} - W_{\mathrm{dry}}\right)/W_{\mathrm{dry}}\right] \tag{2}$$

The hydration number of the membrane (λ) which was classified as the average number of water molecules per conducting functional group was calculated using the next Eq. (3):

$$\text{Hydration number}\ (\lambda) = \frac{\text{mol } H_2O}{\text{mol acid groups}} = \frac{1000\left(W_{\mathrm{wet}} - W_{\mathrm{dry}}\right)}{18\ W_{\mathrm{dry}}\mathrm{IEC}} \tag{3}$$

The swelling ratio of the prepared sample was determined based on the membrane variation before and after hydration on the membrane thickness and dimensions. The swelling ratio was determined based on the following Eqs. (4) and (5):

$$\text{Thickness, S.R}(\%) = \left[\left(t_{\mathrm{wet}} - t_{\mathrm{dry}}\right)/t_{\mathrm{dry}}\right] \times 100 \tag{4}$$

$$\text{Dimensions, S.R}(\%) = \left[\left(l_{\mathrm{wet}} - l_{\mathrm{dry}}\right)/l_{\mathrm{dry}}\right] \times 100 \tag{5}$$

where t_{wet} and l_{wet} was the membrane thickness and length after immersing in boiling water for 1 h while t_{dry} and l_{dry} were the membrane thickness and length in dry conditions.

The mechanical properties were measured by determining the tensile strength and elongation at the break of cross-linked membranes. The measurement was performed by using a tension test machine (Shimadzu, EZ-S) at room temperature with a load cell of 100 N at a displacement rate of 0.5–1.0 mm/min. The samples were cut by using a super dumbbell cutter SDMP-1000 (Dumbbell Co.) having a width around 2.7–4.8 mm. At least three sample measurements were conducted for each sample.

Thermal properties of the SPPSU and SPPSU-SPOSS–cross-linked membrane was analyzed using thermogravimetry analysis (TGA, STA 8000, Perkin Elmer) with alumina pans at a heating rate 10 °C/min from 30 to 800 °C under flowing of nitrogen gas. The membrane was dried at 80 °C for about 24 h before measurement.

The proton conductivity of the SPPSU membrane was measured using a 4-point probe impedance spectroscopy by MTS 740 test system (Scribner Associates, Inc.) with a phase-sensitive multimeter (model PSM1735, Newtons4th Ltd.) combined with an impedance analysis interface. The conductivities were measured at a temperature of 80 °C and 120 °C at different % RHs (40, 60, 80, 90). Frequency ranges of 1 Hz to 1 MHz and a peak-to-peak voltage of 10 mV were used for the impedance measurements.

Single-cell performance test

The thickness of the tested membrane was approximately 42 μm. 0.5 mg/cm^2 40 wt% Pt/C was used as a single-cell electrode catalyst, and an active electrode area is 2.25 cm^2. The membrane electrode assembly (MEA) was prepared by hot pressing the membrane between the anode and cathode layer at 75 kg/cm^2 at room temperature for 1 min. The I–V polarization curves were recorded by a single-cell test at 80 °C under 60% RH and 100% RH. The flow rate of hydrogen was fixed at 100 mL/min and 100 mL/min for the pure oxygen. The backpressure was atmospheric pressure. The I–V performance was compared with commercial Nafion 117 (Sigma-Aldrich; thickness, 177.8 μm).

Results and discussions

The prepared sulfonated SPPSU polymer in this study was highly soluble in water. It is well understood that a highly swelled membrane is troublesome to the mechanical stability of a membrane. In order to overcome the issue, highly sulfonated PPSU polymer was cross-linked with SPOSS by heat treatment. Figure 1 a and b show the photographic images of the SPPSU membrane heating at 80 °C and 180 °C. SPPSU membrane heating at 80 °C, resulting in a transparent membrane while the color of the SPPSU membrane heating at 180 °C turns to light brown. After heating at 80 °C and 180 °C, the membrane was smooth and very flexible. The membrane solubility in water was tested by immersing both membranes in the water at room temperature. SPPSU membrane heated at 80 °C was immediately dissolved in water while the SPPSU membrane heated after 180 °C showed no difference in the membrane appearance. The improvement in the mechanical strength and dimensional stability of the membrane heating at 180 °C suggested that heat promoted the cross-linking between the SPPSU polymer matrixes. The cross-linking SPPSU membrane further illustrated by the FTIR spectra shown in Fig. 1c. IR spectra displayed a broad peak around 3411 cm^{-1} assigned to O–H stretching, and 1693 cm^{-1} of O–H bending vibration from sulfonic acid groups interacts with water molecule for SPPSU-80 °C. The O–H peak of hydroxyl groups was decreased for SPPSU-180 °C, indicating that dehydration of water as the cross-linking temperature increased. The characteristic peak at 1411 cm^{-1} and 1376 cm^{-1} was attributed to SO_3H vibration. The intensity peak of SO_3H for the SPPSU-180 °C was reduced compared with SPPSU-80 °C. These indicate that SPPSU heat at 180 °C has promoted the cross-linking within the SPPSU polymer matrix that simultaneously improves the mechanical strength and dimensional stability of the membrane.

The FTIR spectra were measured to explore the structural properties of the SPPSU-SPOSS cross-linking membrane. The IR spectra of the cross-linked membrane are illustrated in Fig. 2. The absorption peak of the SPPSU-SPOSS–cross-linked membrane shows almost identical spectra with pristine SPPSU-cross-linked membrane. The characteristic peak at 1488 cm^{-1}, 1411 cm^{-1}, and 1373 cm^{-1} attributed to the stretching vibration of the C=C bond of aromatic PPSU. As SPOSS was incorporated into the SPPSU polymer matrix, the densities of the C=C vibration peak were reduced. The strong signal at 1010 cm^{-1} assigned to the vibration peak of symmetric stretchings of the sulfonic acid group. The densities of the characteristic peak of the symmetric sulfonic acid group decreased as the SPOSS loading was increased. It might be due to the higher number of sulfonic acid groups taking part in cross-linking reaction during heat treatment. Although it is not quantitatively reported, the spectroscopic observation indicates that there is some modification in the SPPSU polymer matrix chemical structure with the incorporation of SPOSS. The chemical structure of highly sulfonated PPSU and possible cross-linking mechanism of SPPSU and SPOSS are illustrated in Fig. 3. The unique structure of organic and inorganic hybrid of SPOSS with its nanosized structure and rich surface functional sulfonate group can improve the number of chemical bonding between SPOSS and SPPSU as a cross-linking reaction under heat treatment occurs mainly between the sulfonic acid groups.

The most important characteristic that can reflect the performance of a PEM is proton conductivity conducted through

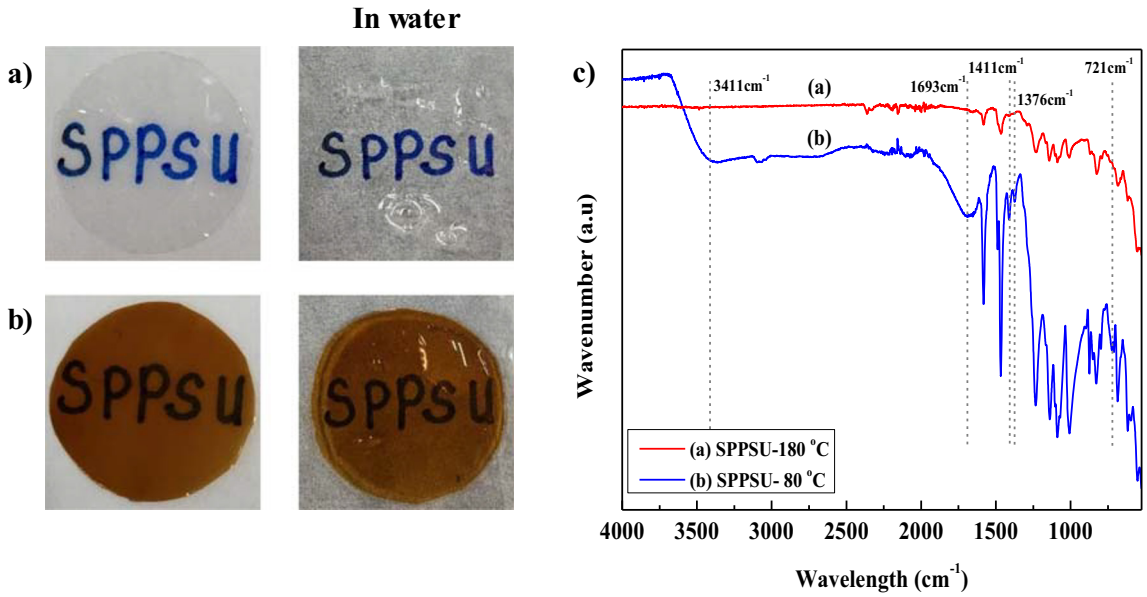

Fig. 1 Photographic image of SPPSU membrane after heating at **a** 80 °C, **b** 180 °C, and **c** FTIR of SPPSU membrane

the water content of a membrane. The proton conductivity is especially dependant on the water content and water uptake of the membrane. Proton transportation through the PEM is fundamentally dependent on the content and distribution of water within the membrane since the dominant proton transportation required water as a medium [12]. The water contents in the membrane affect the rate of proton transfer and hydrogen permeability throughout the electrolyte layer. Lower water uptake and excess water uptake can cause reduction of the proton transportation rate at lower humidity conditions and deteriorate mechanical strength, respectively. Thus, the optimum amount of membrane water uptake is required to give a balance between those properties. Figure 4 shows the water uptake and water content of the SPPSU-SPOSS cross-link membranes. The water uptake for SPPSU-0% SPOSS, SPPSU-1% SPOSS, SPPSU-2% SPOSS, and SPPSU-5% SPOSS was determined to be 43.0%, 127.7%, 79.8%, and 33.1%, respectively. Adding 1 wt% of SPOSS can cause water uptake of more than 100% in the cross-linked membrane. However, increasing the SPOSS loading of more than 1 wt% contributes to a significant reduction in water uptake. It is indicated that the particles are aggregated and blocking the hydrophilic domains in the polymer matrix [13]. Hydration number was calculated as a parameter to define the number of water molecules for each sulfonic acid groups. As can be seen in Fig. 4, the hydration number of SPPSU-incorporated SPOSS content was higher than the pristine SPPSU. It was advocated that the SPOSS was bearing a sulfonic acid group, enhancing the number of water content inside the cross-linked membrane for better proton transportation.

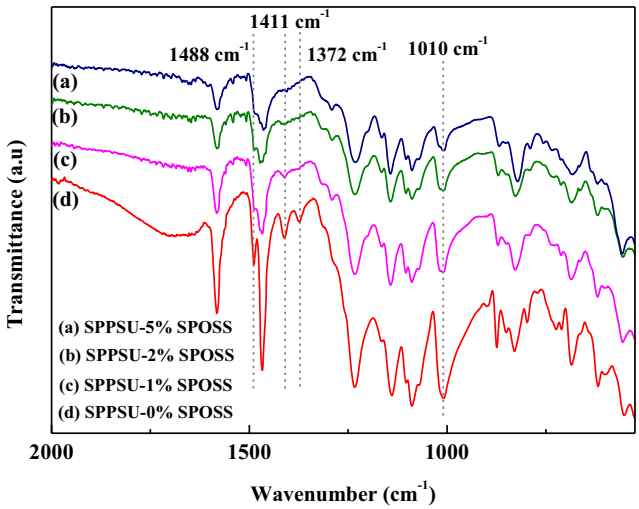

Fig. 2 IR spectra of SPPSU-SPOSS–cross-linked membrane at 2000–525 cm^{-1}

Meanwhile, ion exchange capacity (IEC) of the cross-linked membrane depends on the content of the active sulfonic acid group for proton transportation [14]. Table 1 shows the IEC, swelling ratio, and conductivity values of the cross-linked membrane. When the SPOSS was incorporated into the SPPSU, there is a significantly decrease in the IEC. It could be related to the decrease of the available number of the sulfonic acid group per unit mass due to the $–SO_3H$ group taking part in cross-linking reaction under thermal treatment. It leads to having the lower availability of the exchangeable proton transport. Despite having lower IEC with increasing loads of SPOSS, all the composite membranes show a higher value of hydration number compared with pristine SPPSU. Water uptake and membrane swelling become essential parameters that need to be determined in which this property is directly affecting almost entire membrane properties [15]. Although water uptake of the SPPSU-SPOSS membrane is higher than the pristine SPPSU membrane, the swelling on

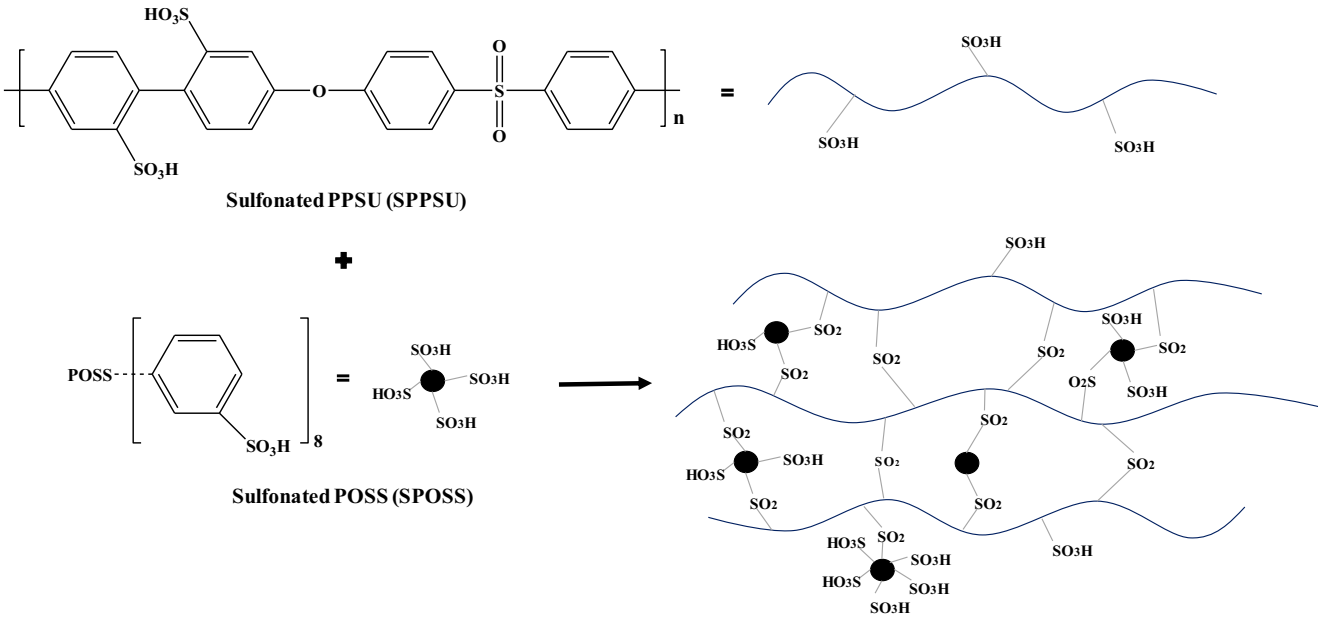

Fig. 3 Chemical structure of highly sulfonated PPSU with the possible cross-linking structure of the cross-linked membrane during thermal treatment

the membrane dimension is not so much different. It might be due to accumulation and the cross-linking effect of SPOSS in the SPPSU polymer matrix that prevents the membrane from swelling. This characteristic has confirmed with the mechanical strength properties that will be further discussed in Fig. 5.

The SPPSU-SPOSS–cross-linked membrane was further characterized for its mechanical properties. Proton-conducting membrane should have excellent mechanical stability as high temperature and humidity in an operating cell system significantly make a change in membrane mechanical properties due to degradation or aging [16]. Figure 5 shows the stress-strain curve of the SPPSU-SPOSS–cross-linked membrane. The mechanical strength and ultimate elongation of the SPPSU membrane are 47.77 MPa and 74.11%, respectively. SPPSU-cross-linked membrane shows a characteristic of an elastomeric membrane with significantly lower strength but more excellent elongation. Meanwhile, the membrane strength and ultimate elongation at break of the SPPSU-SPOSS–cross-linked membrane lie between 26.62 to 52.30 MPa and 36.06 to 72.98%, respectively. The mechanical properties of the SPPSU-cross-linked membrane were found to be affected by the chemical composition of SPOSS and cross-linked structure. From Fig. 5, 2 wt% of SPOSS loading behaved like elastomeric materials with lower strength but mostly excellent in membrane strain. Meanwhile, when the loading increased up to 5 wt% SPOSS, the membrane shows tough characteristics and visibly more rigid compared with lower SPOSS loading. The mechanical behavior indicates that SPOSS effectively suppresses excessive water absorption and increases the tensile strength of the cross-linked membrane [17].

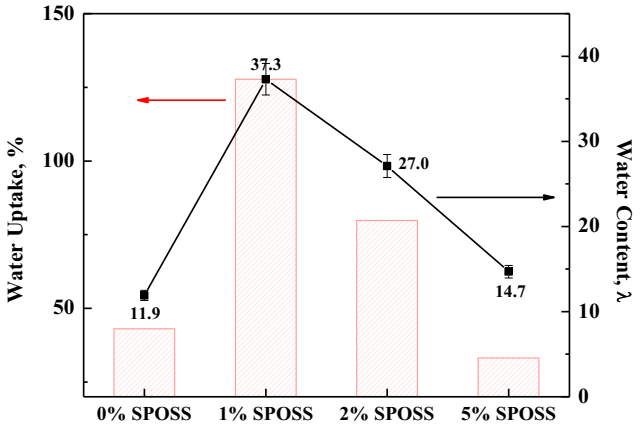

Fig. 4 Water uptake and water content of the SPPSU-SPOSS–cross-linked membrane

Thermal management is one of the critical characteristics for longer terms, and stable performance in PEM fuel cell (PEMFC) as membrane materials sometimes loses their performance due to thermal degradation. Generally, the thermal analysis could provide information on the temperature-dependent properties of the membrane. The thermal properties of the SPOSS- and SPPSU-SPOSS–cross-linked membranes were measured using the TGA analysis. Figure 6 illustrates TG curves for SPOSS- and SPPSU-SPOSS–cross-linked membranes obtained under the nitrogen gas atmosphere. The temperature at 5% mass loss ($T_{d5\%}$) was determined to measure the resistance of the material towards initial thermal degradation [18]. The $T_{d5\%}$ of SPOSS measured by TG analysis was 265 °C. The TG curves of SPOSS are illustrated in Fig. 6a. SPOSS is bearing silica as the main chain having higher thermal retention as the materials decompose only about 38.6% after being heated up to 800 °C. Higher thermal

Table 1 IEC, water uptake, swelling ratio, and conductivity of the cross-linked membranes

Sample	IEC (meq/g)	SR (t/l) (%)	Conductivity, S/cm at 80 °C		Conductivity, S/cm at 120 °C	
			40% RH	90% RH	40% RH	90% RH
SPPSU-0% SPOSS	2.00	16.4/11.0	0.0011	0.0112	0.0006	0.0131
SPPSU-1% SPOSS	1.90	26.2/40	0.0065	0.0379	0.0066	0.0498
SPPSU-2% SPOSS	1.64	23.6/30	0.0042	0.0313	0.0037	0.0361
SPPSU-5% SPOSS	1.25	11.1/7.7	0.0009	0.0094	0.0006	0.0103

degradation of SPOSS offers advantages over the cross-linked membrane as it can improve the thermal properties of the SPPSU polymer [19].

SPPSU membrane without incorporating SPOSS filler shows obviously two steps of degradation. The first degradation temperature is around 267.9 °C and the second is at 501.6 °C. These degradation steps depicted towards the substitution of SO_3H groups and thermal degradation of the polymer backbone, respectively. These thermal characteristics are comparable with the previously reported study [20]. The temperature at which a $T_{d5\%}$ mass loss of SPPSU-0% SPOSS was 300.6 °C. As 1 wt% of SPOSS was incorporated, the $T_{d5\%}$ degradation was increased to 330.6 °C. The existence of SPOSS within the SPPSU polymer matrix had slightly delayed the oxidative degradation of the polymer matrix in situ with improving the thermal stability of the cross-linked membrane [15]. This might be due to the nano reinforcement effect of SPOSS that is responsible for increasing the initial decomposition of the cross-link membrane [21]. As the SPOSS loading increased, the $T_{d5\%}$ reduced to 312.3 °C and 311.5 °C for SPPSU-2%SPOSS and SPPSU-5%SPOSS, respectively. There were not many significant changes in the thermal degradation of the SPPSU-SPOSS–cross-linked membrane compared with the SPPSU membrane. The TGA curves are illustrated in Fig. 6b. The thermal degradation temperature of the cross-linked membrane due to the evaporation of water molecules interacting with sulfonate groups was higher than the pristine SPPSU membrane which might be due to the cross-linking effect between SPOSS and SPPSU polymer that resists the degradation of the water molecule.

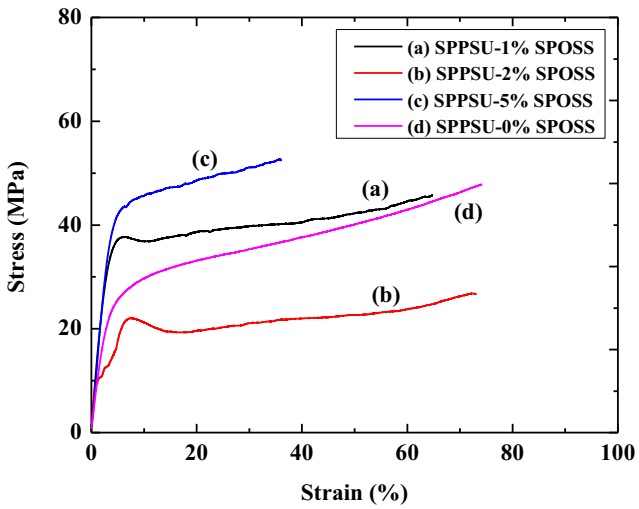

Fig. 5 Stress-strain of SPPSU-SPOSS–cross-linked membrane with different loadings of SPOSS

A polymer electrolyte membrane having high proton conduction properties is in strong demand to be applied in the fuel cell system [22]. In particular, the high proton conductive membrane is needed to obtain high voltage per current density in the unit cell [23]. The proton conductivity was measured from the resistance of the membrane against the current flow. In this study, the proton conductivity of the cross-linked membrane was measured using the 4-point probe impedance spectroscopy under different relative humidity (% RH) conditions. The proton conductivity of the cross-linked membrane carrying different loadings of SPOSS is illustrated as in Fig. 7. The proton conductivity was enhanced about six times at 40% RH at 80 °C over 1 wt% of SPOSS incorporated into the SPPSU polymer. At a higher temperature of 120 °C, the proton conductivity of SPPSU-1% SPOSS enhanced more than ten times at low relative humidity. Alternatively, POSS grafted with sulfonic acid groups can provide external proton channels for nanocomposite membranes which has resulted in improvements on the proton conductivity values of the membrane [24].

Unfortunately, as the loading of the SPOSS increased, the proton conductivity values gradually decreased. It is suggested that higher content of SPOSS resulting in particle aggregation corresponds to reduce the active site for proton transportation [25]. These results of proton conductivity are equivalent to the membrane water uptake in which the conductivity decreased upon higher SPOSS loading. It suggested that the proton conduction requires water-assisted pathways for proton transportation, and water acts as a proton carrier. The proton will travel along with the hydrogen-bonded ionic channels, and proton conductivity highly depends on the connectivity of the hydrated domains [26]. Therefore, it resulted in proton conductivity values of the SPPSU-SPOSS composite membrane following the same trend, based on the water

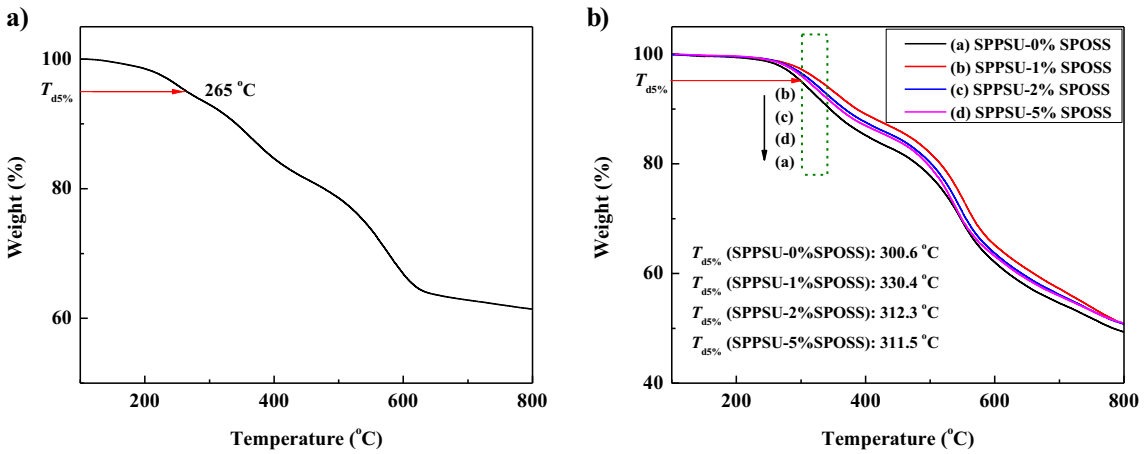

Fig. 6 TGA curves for **a** SPOSS- and **b** SPPSU-SPOSS–cross-linked membranes

uptake results in which higher membrane water uptake resulted in higher proton conductivity. From the obtained results, incorporating SPOSS in the SPPSU polymer matrix indeed greatly improved the properties of the highly sulfonated PPSU as a proton-conducting membrane.

Based on the physicochemical properties of the membranes, SPPSU-2% SPOSS nanocomposite membrane generated a significant improvement as a proton exchange membrane compared with SPPSU-1% SPOSS and SPPSU-5% SPOSS. Therefore, the performance of SPPSU-2% SPOSS nanocomposite membrane was further characterized in terms of its cell voltages and power densities as a function of current density in a single-cell PEMFC. In this study, the single-cell performance was tested at the standard operating temperature of the PEMFC system, which is at 80 °C. The effect of the different % RH conditions (60% RH and 100% RH) on the cell performance was also analyzed. Figure 8a shows the single-cell voltages and power density of SPPSU-2% SPOSS concerning the current density under 60% RH and 100% RH conditions. At 100% RH, SPPSU-2% SPOSS nanocomposite membrane showed better performance as compared with 60% RH. The collected voltage potential of the cell at 200 mA/cm^2 is 0.48 V and 0.56 V for 60% RH and 100% RH, respectively. The fact is that the decreasing output voltage was due to significant ohmic losses in the MEA, in which increasing ohmic losses caused the drop in output voltage [27]. The ionic resistance dominates the ohmic losses in the PEM fuel cell, representing resistance against proton transfer from anode to cathode due to the membrane interfaces [28]. Ionic resistance is closely related to the membrane thickness and proton conductivity in which ionic resistance increased when the proton conductivity is reduced [29]. Thus, these behaviors are consistent with the lower proton conductivity values of SPPSU-2% SPOSS nanocomposite membrane measured at low % RH conditions resulting in lower potential voltage. The peak current density of the cross-linked membrane at fully hydrated conditions reached up to 244.44 mA/cm^2 and 297.75 mA/cm^2, respectively. The maximum power density of the cross-linked membrane at 100% RH conditions exhibited as high as 133.51 mW/cm^2, which are higher than at 60% RH conditions (101.84 mW/cm^2). Low-humidity conditions in the cell may increase the resistance in the membrane that can restrict transportation, causing performance degradation.

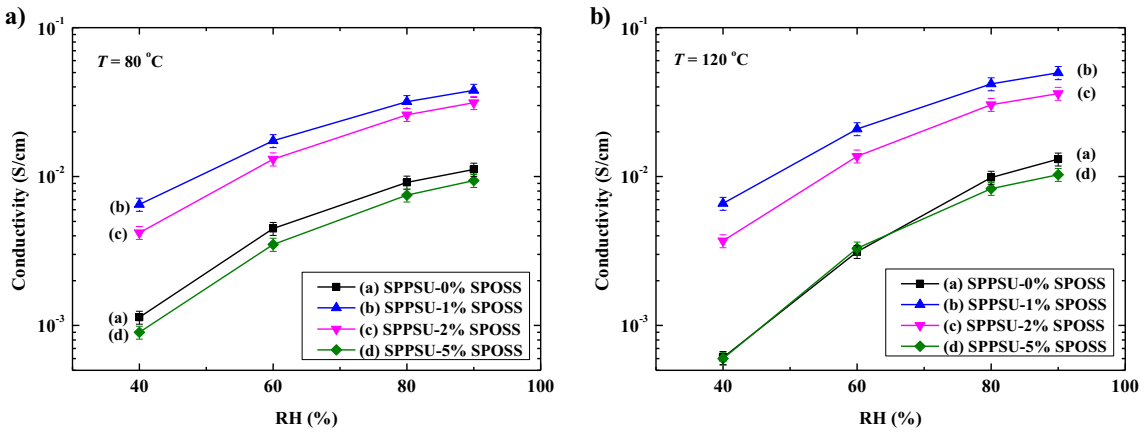

Fig. 7 Proton conductivity of the SPPSU-1%, SPPSU-2%, and SPPSU-5% SPOSS membranes at **a** 80 °C and **b** 120 °C

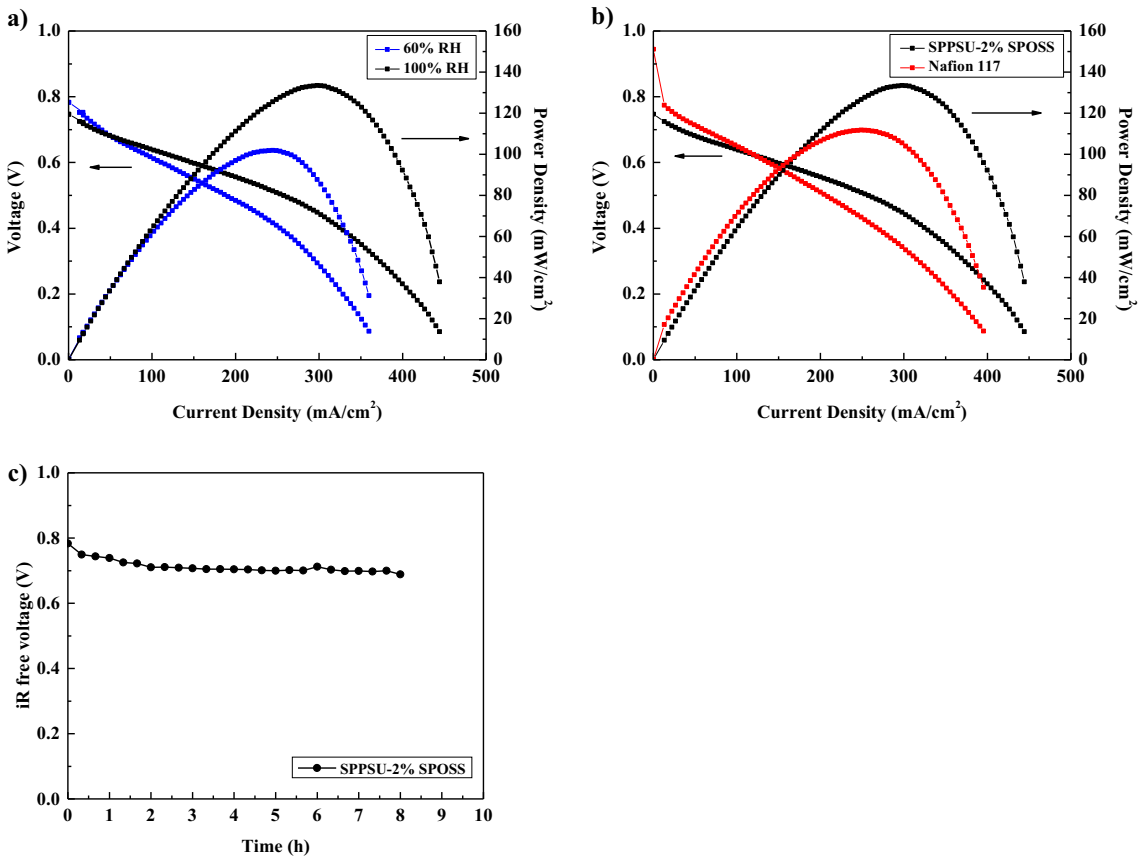

Fig. 8 Polarization curves of **a** SPPSU-2% SPOSS nanocomposite membrane at 80 °C, 60% RH and 100% RH. **b** Comparison between SPPSU-2% SPOSS with commercial Nafion 117 at 80 °C under 100% RH conditions. **c** Voltage stability of SPPSU-2% SPOSS nanocomposite membranes under 0.1-A constant current for 8 h

Under optimized conditions of single-cell PEMFC performance test, the I–V polarization curves of SPPSU-2% SPOSS nanocomposite membrane were compared with the commercial Nafion 117 and illustrated as in Fig. 8b. From Fig. 8b, SPPSU-2% SPOSS nanocomposite membrane showed good performance compared with Nafion 117 measured at 80 °C under fully hydrated conditions. The peak current density of SPPSU-2% SPOSS nanocomposite membrane reached up to 297.80 mA/cm^2 compared with 257.8 mA/cm^2 for Nafion 117. The maximum power density of SPPSU-2% SPOSS exhibited about 133.51 mW/cm^2, which is higher than the maximum power density for Nafion 117 (111.76 mW/cm^2). The performance of the SPPSU-2% SPOSS nanocomposite membrane was further tested under the long-term durability of the MEAs to predict the feasibility of the prepared membrane towards fuel cell applications. The potential voltage against times of the SPPSU-2% SPOSS membranes is illustrated in Fig. 8c. It shows that SPPSU-2% SPOSS nanocomposite membrane exhibited good electrochemical stability under constant current (0.1 A) at operating conditions of 80 °C and 100% RH. Only small voltage drop was observed after 8 h of operations. It is interesting to state that the MEA using SPPSU-2% SPOSS nanocomposite membrane shows good electrochemical properties under operating conditions of 80 °C and 100% RH, which are comparable with commercial Nafion 117.

Conclusions

The research results on the effect of various loadings of SPOSS in highly sulfonated PPSU membrane subjected under thermal cross-linking reaction as the proton-conducting membrane was studied. The properties of the SPPSU-SPOSS-cross-linked membrane was studied by varying the loading of the SPOSS (1%, 2%, and 5%). SPPSU-SPOSS–cross-linked membrane shows higher water uptake compared with pristine SPPSU-cross-linked membrane. Increasing SPOSS loading of more than 1 wt%, the water uptake and IEC values were decreased. The mechanical characteristics of the SPPSU-SPOSS–cross-linked membrane were found to be affected by the chemical composition of SPOSS as the mechanical strength was improved with the incorporation of SPOSS.

The proton conductivity of the SPPSU-SPOSS–cross-linked membrane also improves compared with pristine SPPSU membrane, indicating that adding SPOSS contributes to more significant numbers of available sulfonic acid groups for proton transportation. The PEMFC performance of SPPSU-2% SPOSS nanocomposite membrane showed a good performance compared with Nafion 117 measured at 80 °C under fully hydrated conditions. Based on these findings, the SPPSU-SPOSS–cross-linked membrane yielded a significant improvement, which improves in membrane mechanical strength and higher proton conductivity as compared with the SPPSU-cross-linked membrane.

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