Journal of Environmental Chemical Engineering 9 (2021) 105641

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

A novel imogolite-reinforced sulfonated polyphenylsulfone as proton exchange membrane in fuel cell applications

Nor Azureen Mohamad Nor [a,b,d], Kenji Tamura [c], Juhana Jaafar [d,*], Je-Deok Kim [a,b,*], Ahmad Fauzi Ismail [d], Mohd Hafiz Dzarfan Othman [d], Mukhlis A. Rahman [d]

[a] Hydrogen Production Materials Group, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[b] Polymer Electrolyte Fuel Cell Group, Global Research Center for Environmental and Energy based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[c] Functional Clay Materials Group, Research Centre for Functional Materials, National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[d] Advanced Membrane Technology Research Centre (AMTEC), School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

ARTICLE INFO

Editor: Dr. G.L. Dotto

Keywords:
Highly sulfonated polyphenylsulfone
Inorganic clay
Imogolite
Crosslinking
Proton exchange membrane

ABSTRACT

The high ion exchange capacity of sulfonated polyphenylsulfone (SPPSU) consists of nanotubular inorganic clay that was developed as a proton exchange membrane for fuel cell application. The nanotubular imogolite (Im) was incorporated into SPPSU polymer matrix under various loading (0.5 wt%, 1 wt%, and 2 wt%) and subjected to thermal annealing up to 180 ℃. Upon heat treating at 180 ℃, SPPSU-Im nanocomposite membranes showing homogenous membrane structure and improved water uptake at higher water temperature compare to pristine SPPSU membrane. The strength of the nanocomposite membrane is decreasing upon the incorporation of the imogolite fillers. Hence, at lower relative humidity conditions, the SPPSU-Im nanocomposite membrane resulting in six times higher proton conductivity than the SPPSU membrane. Furthermore, at 80 °C under fully hydrated conditions, 1 wt% of Im incorporate into the SPPSU matrix can achieve the maximum power density up to 89.8 mW/cm^2, which is about 16% higher than the maximum power density produce by SPPSU membrane in single-cell proton exchange membrane fuel cell (PEMFC) system. The results indicating that the imogolite reinforced SPPSU polymer matrix shows significant improvements on the SPPSU polymer matrix as PEM in fuel cell applications.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a type of fuel cell being developed mainly for transport applications as well as for stationary and portable fuel cell applications. PEMFC is a leading technology that can replace the aging alkaline fuel cell (AFC) technologies used in a space shuttle. PEMFCs work with a polymer electrolyte in the form of a thin, permeable sheet [1]. The system efficiency is about 40–50% under an operating temperature of 80 °C. The cell outputs generally range from 50 W to 250 kW. The solid and flexible electrolyte will not leak or crack. This kind of system operates at a low enough temperature to make them suitable for homes and car applications [2]. However, cost, performance, and durability are still crucial challenges in the fuel cell industry. Universities, laboratories, and industries are working closely to overcome critical technical barriers to fuel cell development.

Electrolyte layer materials based on perfluorinated ionomer membranes such as Nafion® are widely practiced in both industry and research. Nafion® membranes are classified as one of the most common and commercially available polymer electrolyte membranes in the market. Despite having excellent fuel cell performance and stability, their high cost makes it unpractical to be commercially practiced [3]. New anhydrous proton conductor membranes are actively studied for the development of suitable PEM with excellent cell performance.

* Corresponding author.
* Corresponding author at: Hydrogen Production Materials Group, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
E-mail addresses: juhana@petroleum.utm.my (J. Jaafar), KIM.Jedeok@nims.go.jp (J.-D. Kim).

https://doi.org/10.1016/j.jece.2021.105641
Received 30 November 2020; Received in revised form 20 April 2021; Accepted 4 May 2021
Available online 10 May 2021

Recent research has been devoted to developing PEM using non-fluorinated polymer materials as an alternative to Nafion®, which would be less expensive and counter the drawbacks of perfluorinated membranes [4,5]. Polyphenylsulfone (PPSU) is one of the sulfone polymers types that are commercially available in the market and being studied for fuel cell application purposes [6].

PPSU has excellent thermal stability, appropriate mechanical strength, and high proton conductivity that is increasing along the degree of sulfonation [7]. Generally, alternative PEM based on PPSU polymers only reaches high proton conductivity at high ion exchange capacity (IEC) values. However, at higher IEC, the mechanical and chemical properties of the hydrocarbon polymer become unstable due to excess membrane swelling in water [8]. Many studies have reported on the polymers modifications with inorganic materials to design PEM with controllable mechanical properties to counter the drawbacks. For example, Hou et al., (2013) apply thermal to crosslink the nanodiamond particles with highly sulfonated PEEK (DS=81%). The developed nanodiamond particles show excellent mechanical and chemical stabilities with high proton conductivity values [9]. Other than that, Lee et al., (2019) reported on the incorporation of sulfonated poly(arylene thioether sulfone)-grafted graphene oxide (SATS-GO) into highly sulfonated polyphenylsulfone to control the excessive swelling of SPPSU polymers. The addition of SATS-GO into SPPSU polymers greatly enhanced the mechanical, dimensional stability as well as excellent proton conductivity [10]. The production of composite membrane materials by bridging organic polymers and inorganic chemistry at the molecular level is a fascinating field of investigation.

Inorganic clays such as montmorillonite [11–13] or laponite [14,15] have also been evaluated based on their possible inorganic materials bridging with the polymer matrix. Beauger et al. [16] developed Nafion® composite membrane by introducing the fibrous sepiolite for mechanical resistance purposes. The introduction of sepiolite in the Nafion® membrane greatly improved mechanical properties and water uptake for better proton conduction [16]. Porous aluminosilicate materials are also gaining attraction as an additive in polymer matrix due to their textural and surface features, namely highly ordered structures, high surface area, and wide pore-range/pore size distribution. The porous morphology of aluminosilicate facilitates specific ionic interactions with the host matrix. It enhances water uptake and other related properties such as mechanical and thermal properties of the composite membrane. Imogolite is an aluminum silicate clay mineral with the general formula [Al_2O_3. SiO_2.$2H_2O$] [17]. The fascinating structure of nanotubular imogolite with high surface area, length about nanometers to micrometers, and unique physicochemical properties are expected can improve the SPPSU membrane properties. The wall structure of imogolite comprises a layer of aluminum hydroxide on the outer wall and a silicate layer on the inner wall.

Since clay reinforced polymer composites are well known for their excellent mechanical strength, dimensional and chemical stability, SPPSU-clay composite membrane is expected to improve membrane properties as a proton exchange membrane. As far as the subject is concerned, few studies have reported on the imogolite reinforce polymer matrix as proton exchange membranes despite having great potential as polymer membrane additives. In this study, the high IEC SPPSU was modified by incorporating the imogolite nanotubes. Imogolite nanotubes with various loadings were incorporated into the SPPSU polymeric solution and then undergone thermal treatment from 80 ℃-180 ℃ to promote crosslinking chain between the SPPSU polymer chain and imogolite nanotube. This double reinforcing strategy of thermal crosslinking is expected to improve bonding between imogolite nanotubes with SPPSU based PEM significantly. The properties of the nanocomposite membranes on mechanical strength, dimensional stability, oxidative resistance, proton conductivity, and single-cell PEMFC test were studied and discussed.

Table 1
Designation for SPPSU-Im dope solution.

Varied parameter	Variable parameter	Membrane designation
Im loading (wt%)	0.5	SPPSU-Im0.5
	1	SPPSU-Im1
	2	SPPSU-Im2

2. Experimental procedure

2.1. Preparation of highly sulfonated polyphenylsulfone (SPPSU)

The commercial polyphenylsulfone (PPSU, Solvay Radel R-5000 NT, MW~50,000) purchased from Solvay Specialty Polymers Japan, was used. The preparation of highly sulfonated PPSU polymers is similar to the method that has been reported previously, and the evaluated IEC value by titration for SPPSU polymer is about 3.2 meq/g correspondents about 2 for a degree of sulfonation (DS) [18]. In detail, the SPPSU polymers were sulfonated by direct sulfonation reaction using concentrated sulphuric acid (H_2SO_4, Aldrich~98%). The PPSU was first dried in an oven (80 °C) for about two days to remove moisture content. Then, the PPSU was dissolved in the H_2SO_4 in an oil bath under stirring at 60 °C for two days. The molar ratio of the PPSU polymer to the H_2SO_4 content was 1: 225. The produce solution was then poured in significant excess of ice, and the resulting white precipitate was collected using mild vacuum filtration. The precipitate was subjected to neutralization by an excess amount of deionized water in dialysis tube cellulose membrane (MWCO~14,000, Sigma Aldrich Co., Ltd.) until pH 7 was achieved. The resulting SPPSU polymer was then subjected to freeze-drying to yield solid SPPSU polymer for further use.

2.2. Preparation of Imogolite (Im)

Imogolite was synthesized from a dilute solution containing sodium orthosilicate (Na_4O_4Si, Kishida Chemical Co., Ltd) and Aluminium chloride ($AlCl_3.6H_2O$, Kanto Chemical Co. Inc.) as silica and aluminum sources, respectively. Sodium hydroxide (NaOH, Nacalai Tesque, Inc.) and hydrochloric acid (HCl, Nacalai Tesque, Inc.) was used to control the pH of the solutions. All the reagents employed in this study were used as received without further purification. An aqueous solution was prepared by mixing aqueous Na_4O_4Si and $AlCl_3$ solutions with initial concentrations of 73 mM and 182 mM, respectively. Then, the 1 M NaOH was slowly dropped into the mixed solution to reach a pH 6. After free ions were removed by washing with pure water three times, the precursor solution was formed. Finally, 1 M HCl was added to the precursor solution. The mixture was heated at 100 °C for four days to obtain an imogolite suspension. The imogolite was further suspense in water for further use.

2.3. SPPSU-Imogolite (SPPSU-Im) composite membrane preparation

The SPPSU-Im nanocomposite membrane was prepared using the slow evaporations technique to develop a dense membrane structure. Various loading of imogolite nanotubes was incorporated into the dope solution. 0.1 wt% Im in water was mixed with 10 mL DMSO, and the dope solution was continuously stirred until it became homogeneous. Due to the large amount of water presence mixed with DMSO, the dope solution was heated at 80 °C to remove excess water. It is estimated to remain about 10–12 mL volumes of the total solution after heated since it is tough to completely remove water content. Then 10 wt% of SPPSU polymer was mixed inside the solution and continually stir until homogenous for 24 h. The membrane dope solution was prepared at different loading and is tabulated in Table 1.

The dope solution was cast into a petri dish and heated to remove the solvent by drying in the oven at 80 °C for 24 h. The membranes were further heated in air at 120 °C (24 h), 160 °C (24 h), and 180 °C (24 h).

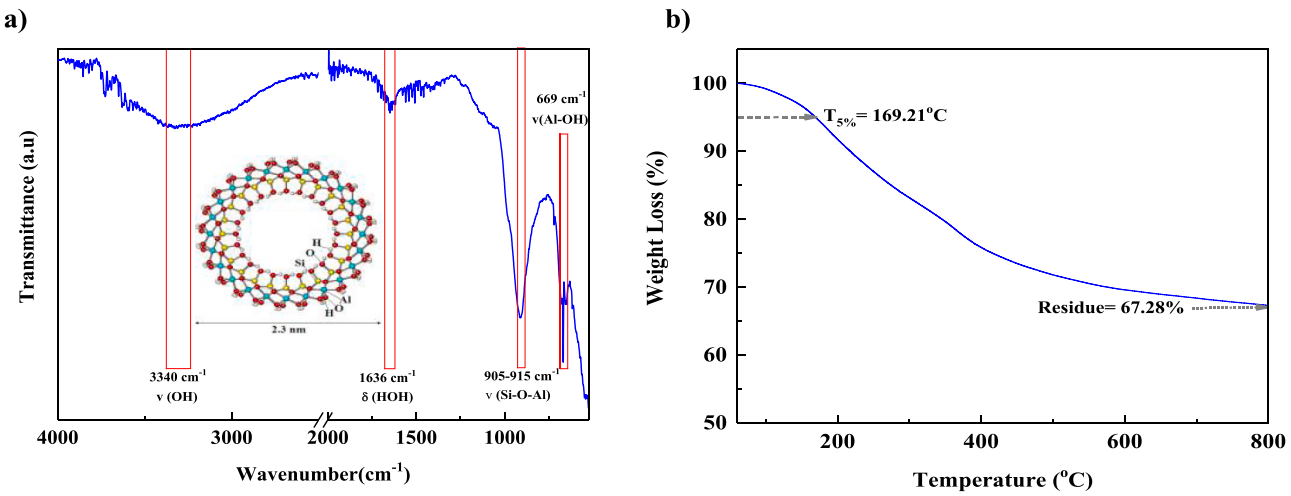

Fig. 1. (a) FTIR spectra together with chemical structure [22], and (b) TGA curves for imogolite.

After the heated process, the membrane was then activated in a different solution. The post-activation step removed the residual acids and water-extractable molecules. The crosslinked membrane was then immersed in 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.

2.4. Characterizations

2.4.1. Structural characterization

Fourier Transform Infrared (FTIR) Spectroscopy is an effective analytical instrument to detect functional groups and identify chemical bonds in a sample by producing an infrared absorption spectrum. The molecular structure of Imogolite was characterized using FTIR spectra obtained from a (Nicolet-6700, Thermo Scientific) using an attenuated total reflection (ATR) with an infrared (IR) spectrophotometer. The sample was scanned within the wave range of 550–4000 cm^{-1}.

2.4.2. Thermal properties

Thermal properties of the Imogolite were analyzed using thermogravimetry analysis (TGA, STA 8000, Perkin Elmer) with alumina pans at a heating rate 10 °C/min from 60 °C to 800 °C under flowing of nitrogen gas. Imogolite was dried at 80 °C for about 24 h before measurement.

2.4.3. Morphological structure

The surface and cross-sectional morphology of the SPPSU-Im nanocomposite membrane was studied using a scanning electron microscope (SEM, Hitachi Model TM 3000). Samples are coated with gold under vacuum for about 3 min at 20 mA.

2.4.4. Mechanical properties

The mechanical properties were determined by measuring the tensile strength and elongation at the break of the membrane samples. The measurement was performed using a Tension Test Machine (Shimadzu, EZ-S) at room temperature with a constant crosshead speed at 5 mm/min.

2.4.5. Water uptake, the swelling ratio in thickness, ion exchange capacity, and hydration number (λ)

The membrane weight variation determined the water uptake of the prepared membrane before and after hydration. The membrane was first dry in the oven at 80 °C for 24 h. Then, the dry membrane was immersed in different water temperatures (RT, 40 °C, 60 °C, 80 °C, and 90 °C,) for 1 h. The wet membrane was removed from the water, and the membrane surface was wiped with blotting paper to remove excess water. The water uptake of the prepared sample was calculated as the following equation (Eq. (1)):

$$WU(\%) = [(W_w - W_d)/W_d] \times \quad 100 \tag{1}$$

Where W_w refer to the weight of the wet membrane and W_d for the weight of the dry membrane.

The swelling ratio of the prepared sample was determined based on the membrane variation before and after hydration on the membrane thickness in various water temperatures. The swelling ratio was determined based on the following equation (Eq. (2)):

$$Thickness, \quad S.R(\%) = [(T_w - T_d)/T_d] \times 100\% \tag{2}$$

Where T_w was the membrane thickness after immersed in water for 1 h while T_d was the membrane thickness in dry conditions.

The IEC values of the nanocomposite membranes were determined using the back titration method. The membrane sample was dried in an oven at 80 °C for 24 h to remove moisture content. Dry membrane samples were then soaked 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 pH 7. The IEC value of the test sample was calculated using the following equation (Eq. (3)):

$$IEC\left(meq.g^{-1}\right) = cv/w_{dry} \tag{3}$$

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

The hydration number was calculated to determine the number of water molecules per sulfonic acid site. In these stages, the hydration numbers were calculated using membrane water uptake at 90 °C. The calculation was as follows (Eq. (4)):

$$\lambda \quad = \quad \frac{WU}{18 \quad (Mwof H_2O) \quad \times IEC} \tag{4}$$

2.4.6. Proton conductivity

The proton conductivity of the SPPSU membrane was measured using four-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 40 °C, 60 °C, and 80 °C at 90% RH conditions. A frequency ranges of 1 Hz to 1 MHz and a peak-to-peak voltage of 10 mV were used for the impedance measurements.

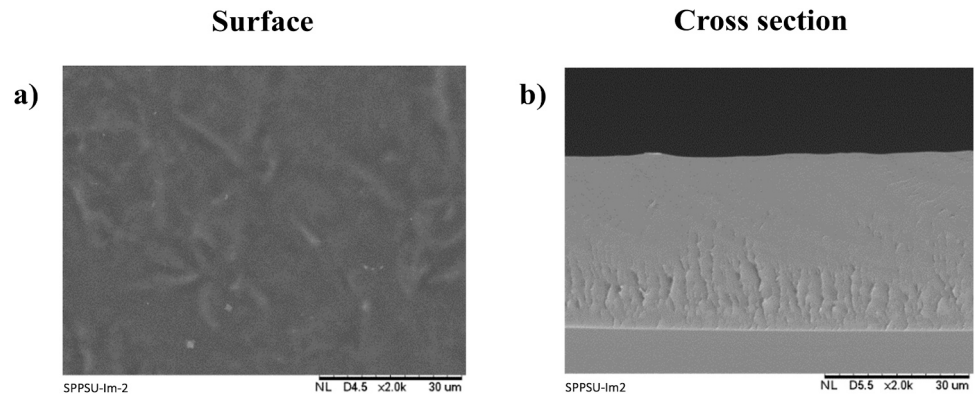

Fig. 2. SEM images of SPPSU-Im2 (a) surface and (b) cross-section.

2.4.7. Long term oxidative stability

The oxidative stability of the nanocomposite membrane was tested under harsh oxidative conditions by immersing the small pieces of the sample into Fenton's reagent. Fenton's reagent was prepared using 5 wt % H_2O_2 and 3 ppm Fe (II) (added as $FeCl_2.4H_2O$). The sample membrane was immersed in Fenton reagents at RT for 14 days. After the reaction, the conditions of the membrane sample were recorded.

2.4.8. Single cell performance test

The Membrane Electrode Assembly (MEA) active surface area was 2.25 cm^2 and comprised of 0.5 mg/cm^2 40% Pt on carbon cloth (Fuel Cell Earth LLC, US) for both anode and cathode. The MEA cells were constructed by the hot-pressing of the membrane assembled with an anode and a cathode electrode 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 fully hydrated conditions. The flow rate of hydrogen was fixed at 100 mL/min and 100 mL/min for oxygen. The backpressure was

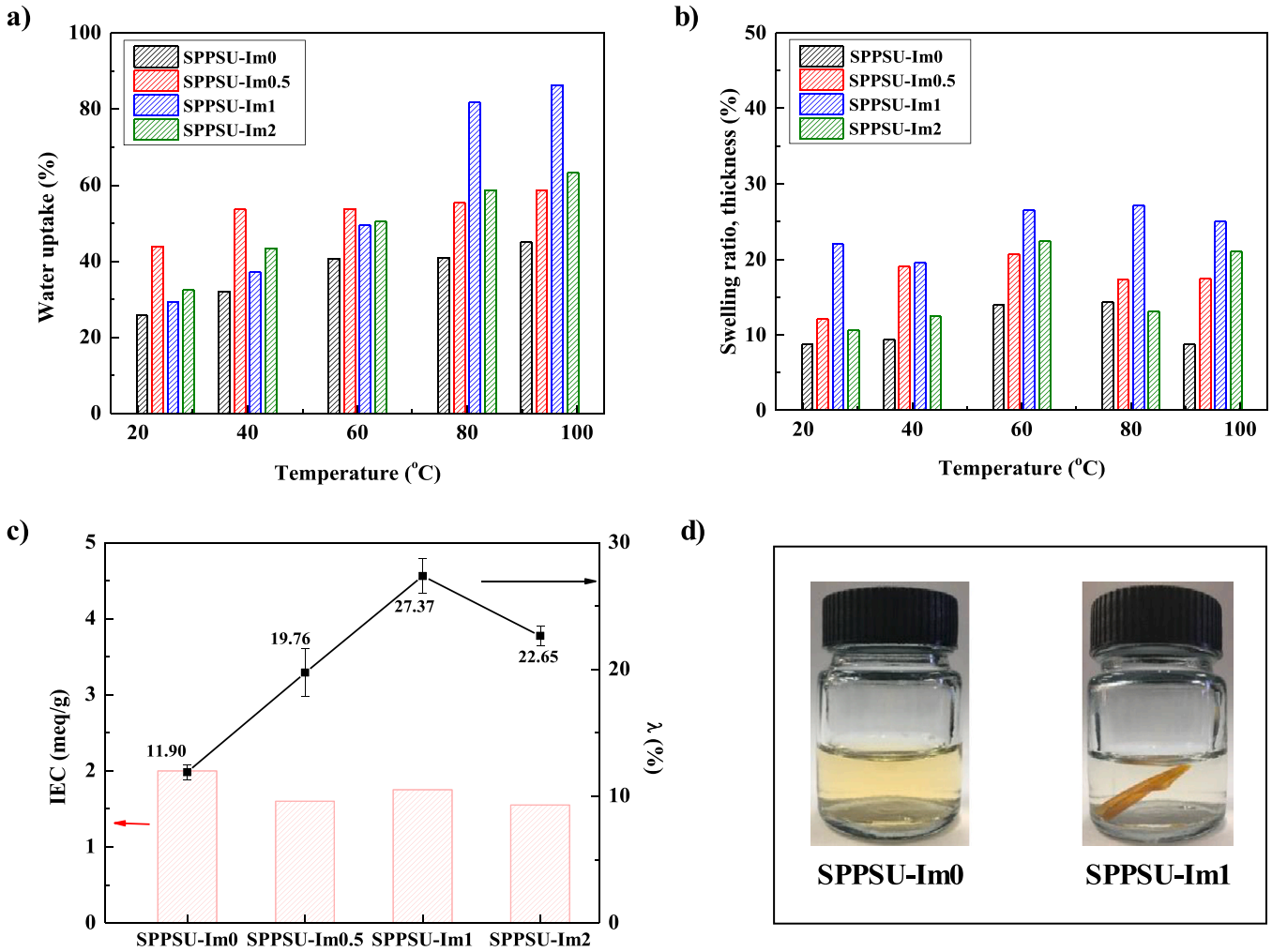

Fig. 3. (a) water uptake and (b) swelling ratio of membrane thickness after immersed in different temperature of the water, (c) IEC and hydration number of SPPSU-Im nanocomposite membranes, and (d) oxidative stability (Sample after immersed in Fenton reagents (5 wt% of 30 wt% H_2O_2 + 3 ppm Fe (II)) at RT for 14 days).

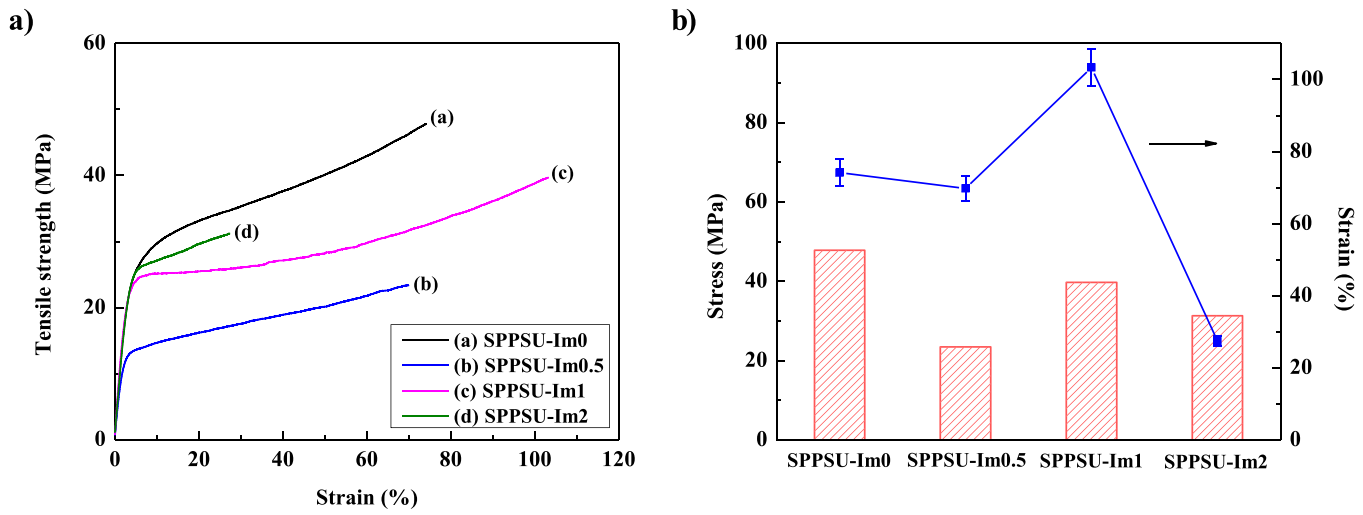

Fig. 4. (a) Stress strain curve and (b) stress strain values for SPPSU and SPPSU-Im nanocomposite membranes.

atmospheric pressure.

3. Results and discussions

Imogolite is hydrated aluminosilicate clay minerals with the general formula [Al_2O_3. SiO_2.$2H_2O$]. Fig. 1(a) shows the FTIR spectra and schematic representation of the cross-sectional structure of the imogolite. Generally, imogolite forms a hollow nanotube with an internal diameter of below 1 nm and lengths ranging from several hundred nanometers to micrometers. The outer surface of the imogolite is composed of hydrophilic Al-OH groups that can be dispersed in water at low acidic conditions [19]. This was proven with the more significant broad peak of the O-H stretching band around 3340 cm^{-1} assigns to the interaction of imogolite with water molecules. The wall structure of the imogolite comprises a layer of aluminum hydroxide on the outer wall and a layer of silicate on the inner wall. The spectrum shows the stretching vibration band at 915 cm^{-1} and 905 cm^{-1}, indicating the function of Si-O-Al groups in the imogolite structure. Hence, a sharp peak presence at 669 cm^{-1} showing the stretching band of Al-OH in the imogolite materials. This FTIR spectrum of this imogolite structure is similar to the study reported before [20].

TGA measurements were conducted from 60 °C to 800 °C under a heating rate of 10 °C/min. Fig. 1(b) shows the TGA curves for the imogolite nanotube used in this study. Two steps of weight loss profile were illustrated, which is similar to the reported previously [21]. The first 5% weight loss was observed to determine the initial resistance for imogolite nanotubes towards initial thermal degradation that was happening at 169.21 °C. The initial thermal degradation might be due to the elimination of the adsorbed water and structural water in the imogolite interlayer [19]. The total residue of 67.2% total mass after heating up to 800 °C, showing the higher resistance of imogolite nanotubes towards thermal degradation.

The structural properties of the SPPSU-Im nanocomposite membrane were further determined by characterized the morphological structure using SEM analysis. Fig. 2(a) and (b) show the SEM images on the surface and cross-section of the SPPSU-Im2 nanocomposite membrane. The SPPSU-Im2 nanocomposite membrane shows a dense membrane structure with no defects that can be observed on the membrane cross-section images in Fig. 2(b). The surface of the SPSU-Im2 shows a rough surface where fiber-like structure appeared on the membrane surface, and the diameter is about 1 μm. This might be due to the appearance of aggregated imogolite nanotubes that are visible on the membrane surface.

The hydration of the membrane is closely related to membrane conductivity. The proton conductivity of the membrane depends mainly on the amount and the water uptake behavior of the membrane [23]. The water uptake and membrane swelling become essential parameters that need to be determined in which this property directly affects almost entire membrane properties [24]. The SPPSU-Im nanocomposite membrane's water uptake at different temperatures was illustrated in Fig. 3 (a). When the imogolite was incorporated into the SPPSU membrane, the membrane water uptake was significantly increased. Furthermore, the increasing temperature also has increased the water uptake for the SPPSU-Im nanocomposite membrane. It might be due to the natural properties of imogolite nanotubes that are highly hydrophilic internal pores and can control water retention [25]. However, the water uptake is reducing as the imogolite loading increased to 2 wt%. This suggesting that high concentrations of imogolite causing an aggregation that governs the macroscopic performance of the SPPSU polymer membrane. The aggregation between imogolite in the SPPSU polymer matrix has also suppressed the membrane swelling. This is shown in Fig. 3(b), where the membrane swelling in the thickness direction for SPPSU-Im2 is lower than SPPSU-Im0.5 and SPPSU-Im1. SPPSU-Im1 nanocomposite membrane exhibit larger membrane swelling in the thickness direction as compared to the others. Higher membrane swelling in the thickness direction is favorable in the proton exchange membrane to ensure a better contact with the electrodes in fuel cell configurations. This good contact will reduce the development of a gap between electrodes and membrane, contributing to lower cell resistance. This phenomenon will enhance membrane cell performance.

The hydration of the membrane is closely related to membrane conductivity. The proton conductivity of the membrane depends mainly on the amount and water uptake behavior of the membrane. IEC values and water content of SPPSU-Im nanocomposites membrane are depicted in Fig. 3(c). IEC values of SPPU-Im nanocomposite membranes are found to be in the range 1.55–1.75 meq/g, which is lower than the pristine SPPSU membrane. It has been reported that high IEC values of PEM-based hydrocarbon polymer tend to cause swelling that contributes to deterioration in the membrane mechanical strength [26]. Thus, it would be better to acquired lower IEC values to have stable mechanical properties. The decrease in IEC values suggests a reduction in an available number of exchangeable –SO_3Na groups in the SPPSU polymer subjected to crosslink with imogolite structure [27]. SPPSU polymer can be expected to be crosslinked with imogolite through the sulphonic acid moiety that can interact with Al-OH groups on the imogolite surface. It is noteworthy that hydrated imogolite nanotubes have a very high surface area for water sorption [28]. Therefore, the presence of imogolite in the SPPSU matrix has improved the water content compared to the SPPSU membrane.

The degradation phenomenon of the proton exchange membrane in the fuel cell system is thought to be caused by the H or HO/HO_2 radicals

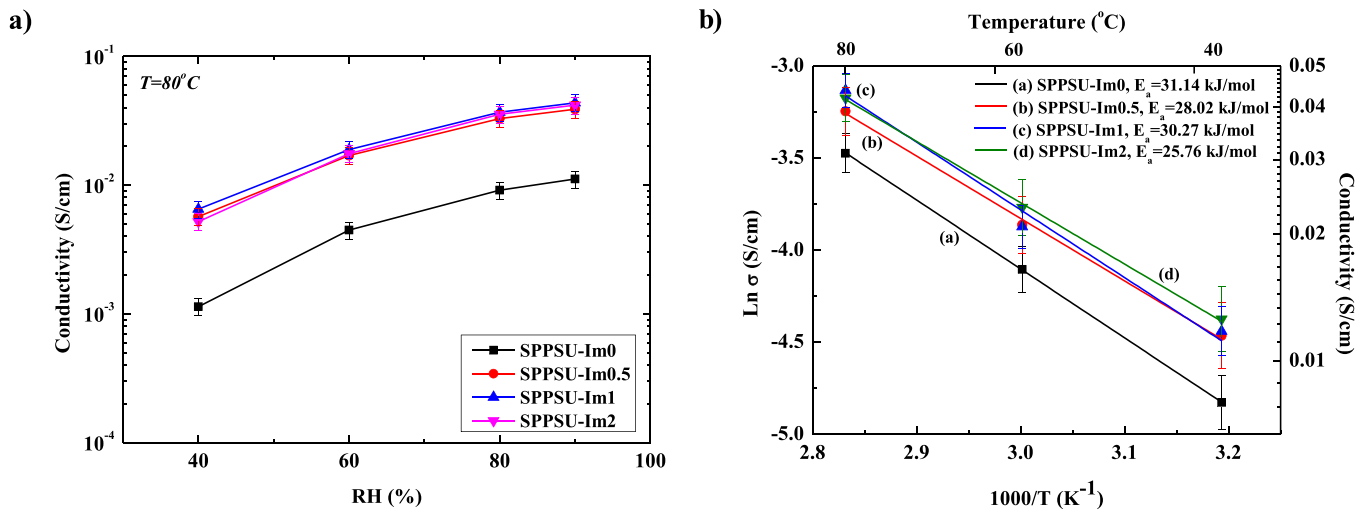

Fig. 5. (a) Proton conductivity values at 80 °C under different RH (%) conditions and (b) Arrhenius plot under 90% RH at different temperature for the SPPSU, SPPSU-Im0, SPPSU-Im1 and SPPSU-Im2 nanocomposite membranes.

that occur at both electrodes. The membrane degradation during single-cell operation is considered to result from the formation of HO/HO_2 radicals [29]. Therefore, the stability of the developed PEM materials in harsh oxidation conditions was investigated. In this study, the SPPSU and SPPSU-1% Im nanocomposite membrane were immersed in 5 wt% H_2O_2 solution containing 3 ppm Fe (II) at room temperature. Fig. 3(d) shows the membrane conditions after prolonged immersing in Fenton's reagent for 14 days at room temperature (RT). From the images, it can be seen that the SPPSU membrane is fully dissolved in the reagent. SPPSU-Im showing excellent chemical stability compared to the pristine SPPSU membrane. This might be due to the active functional group of imogolite that will force the nanotubes to hold together into bundles via hydrogen bonding and van der Waal forces, which increase the chemical resistance of the nanocomposite membrane [17]. From physical observations, the membrane is still in shape. However, the membrane is broken when rubbed by hand after washing with distilled water. It indicates that the fillers enhance the chemical resistance to hydroxyl radicals and the composite membranes were stable enough for PEMFC applications [30].

Inorganic clays are often used as an additive in a polymer to improve the mechanical and physicochemical properties of the polymer. The composite membrane was further characterized in terms of mechanical properties. The mechanical properties of the composite membrane were illustrated in Fig. 4. SPPSU-Im0 membrane displays a typical good mechanical stability with a tensile strength of 47.8 MPa at the elongation at a break of 74.1%. By contrast, incorporation of imogolite nanotube in the SPPSU polymer matrix resulting in reducing the membrane hardness. For instance, SPPSU-Im0.5 results in about 23.4 MPa of tensile strength with 69.8% of elongation at break. However, increasing the imogolite wt% loading, the membrane tensile strength was also increased. Incorporating 1 wt% loading has increased the tensile strength up to 39.7 MPa with 103.3% of elongation at break, showing the most flexible membrane compared to others. The difference in mechanical properties might be ascribed to the interference effect of the imogolite nanotubes on the chain packing motion of SPPSU [31]. Meanwhile, 2 wt% imogolite loading shows the brittle membrane characters as the membrane results in only 27.4% elongation at break. This might be due to a higher concentration of imogolite that will force the nanotubes to hold together into bundles via hydrogen bonding and van der Waal forces, leading to aggregation [32]. It is well known that the inorganic clays are rigid. When the inorganic clays are dispersed into the organic parts, the rigidity of resulted materials will be improved [33]. The SPPSU-Im2 shows a brittle characteristic that has restricted the applications of the membranes in the fuel cell system.

The properties of SPPSU-Im as a proton exchange membrane were characterized in terms of its ability to transport proton. The proton conductivity values of the SPPSU-Im composite membrane were illustrated in Fig. 5(a) as functions of relative humidity at 80 °C. The proton conductivity of the nanocomposite membrane is highly dependent on the % RH conditions [34]. Incorporation of the imogolite nanotubes into SPPSU polymer exhibits significant improvements in the proton conductivity values. At 40% RH, SPPSU-Im nanocomposite membrane resulting in six times higher proton conductivity at 80 °C compared to SPPSU membrane. The high proton conductivity might be caused by the imogolite characteristics that can retain water molecules due to hydrogen bonding with the hydrophilic groups of the nanocomposite membrane [35]. Unfortunately, by having different wt% loading of imogolite, proton conductivity of the nanocomposite membrane did not show a significant difference. It might be due to the unwell dispersed of the imogolite nanotubes inside the SPPSU polymer matrix that will limit the mobile ion available for proton conduction [36].

The activation energy of the proton exchange membrane was calculated from the Arrhenius plot and can provide valuable information regarding the possible proton conduction mechanism. Fig. 5(b) displays the Arrhenius plots for the SSPU-Im nanocomposite membrane at 40 °C, 60 °C, and 80 °C under fully hydrated conditions. For all composite membranes are showing a thermally activated Arrhenius-type behavior within the investigated temperature. The calculated activation energy was lies in the range of 14.0–40.0 kJ/mol. The conducting mechanism in the SPPSU membrane and nanocomposite membrane is not precise, but the Grotthuss mechanism and vehicle conducting mechanism can also be applied. The calculated activation energy of the SPPSU-Im nanocomposite membranes is lower compared to the SPPSU membrane. The incorporation of imogolite nanotubes in the SPPSU matrix has lowering the activation energy of the SPPSU membrane. The difference in activation energy may be attributed to the differences in the internal structure features of nanocomposite membranes, which can affect the proton transportation within the membrane [37,38]. Higher water content with the incorporation of Imogolite nanotubes in the SPPSU matrix also enhancing proton conductivity while lowering the activation energy of the nanocomposite membrane [39].

Based on the obtained results, SPPSU-Im1 exhibited significant improvement properties compared to pristine SPPSU-Im0.5 and SPPSU-Im2 nanocomposite membranes. Therefore, the performance of SPPSU-Im1 was furthers tested under single cell test performance as a function of cell voltage and power densities as a function of current density at 80 °C under fully hydrated conditions. The I-V polarization curves of SPPSU-Im1 were compared with the pristine SPPSU membrane and

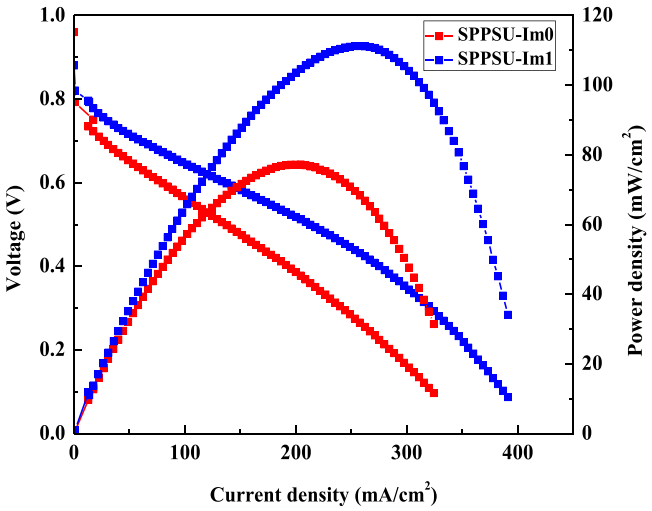

Fig. 6. Polarization curves of power density and potential voltage against current density for SPSU-Im0 and SPPSU-Im1 nanocomposite membrane at 80 °C under fully hydrated conditions.

depicted in Fig. 6. Incorporating imogolite in the SPPSU polymer matrix has improved the membrane properties and the PEMFC performance of the pristine SPPSU membrane. The potential cell voltage of the SPPSU nanocomposite membranes was higher compared to the pristine SPPSU membrane at all current density. For example, the collected voltage potential of the SPPSU membrane at 200 mA/cm^2 is 0.39 V. In contrast, for the SPPSU-Im1, the cell voltage increased up to 0.52 V. The internal ohmic losses dominate the reduction in potential voltage through the fuel cell, which includes electronic and ionic resistance. However, ionic resistance becomes the dominants due to more difficult ionic transportation compared to electronic charge transport. Ionic resistance comes from the resistance of proton transportation through the polymer electrolyte membrane. As the membrane resistance is high, the potential voltage was also reduced. Ionic resistance is closely related to the proton conductivity in which ionic resistance increased when the proton conductivity is reduced [40]. Thus, these behaviors are consistent with the lower proton conductivity values of the SPPSU-Im0 membrane measured at 80 °C and high % RH conditions than SPPSU-Im1, as reported in Fig. 5. Besides, larger membrane swelling of SPPSU-Im1 compared to the SPPSU-Im0 in the thickness direction is also the reason for better cell performance. At 80 °C under fully hydrated conditions, the maximum power density of the SPPSU-Im0 membrane was 77.2 mW/cm^2 and increase up to 111.2 mW/cm^2 as 1 wt% of Im was incorporated into the SPPSU matrix.

4. Conclusions

In this study, imogolite reinforced SPPSU polymer membrane using various loading of imogolite is discussed. The fascinating physicochemical properties of the imogolite are expected to have potential nanotechnological applications in the SPPSU membrane. 0.5 wt%, 1 wt %, and 2 wt% loadings of imogolite are incorporate into the highly sulfonated SPPSU polymer matrix and subjected to thermal crosslinking technique. The membrane hardness was reducing but increasing upon the higher loading of the imogolite nanotubes. The incorporation of imogolite nanotubes was significantly improved the water uptake of the nanocomposite membranes. Hence, the integration of Imogolite nanotubes in the SPPSU matrix also enhancing proton conductivity while lowering the activation energy of the nanocomposite membrane. SPPSU-Im1 results in significantly improved properties compared to pristine SPPSU, SPPSU-Im0.5, and SPPSU-Im2 nanocomposite membranes. The MEA using SPPSU-Im1 nanocomposite membrane shows excellent electrochemical properties under operating conditions of 80 °C and fully hydrated conditions, which is better than the pristine SPPSU membrane. Therefore, the imogolite reinforced SPPSU polymer matrix shows an improvement on the SPPSU polymer matrix as PEM in fuel cell applications.

CRediT authorship contribution statement

Nor Azureen Mohamad Nor: Writing - original draft, Conseptualization, Methodology, Investigation. **Kenji Tamura**: Conseptualization, Methodology. **Juhana Jaafar***: Writing - review & editing, Supervision, Project administration, Funding acquisition. **Je-Deok Kim***: Writing - review & editing, Supervision, Validation. **Ahmad Fauzi Ismail**: Resources, Funding acquisition. **Mohd Hafiz Dzarfan Othman**: Writing - review & editing. **Mukhlis A. Rahman**: Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors would like to express gratitude to the Ministry of Higher Education (MOHE), Universiti Teknologi Malaysia (UTM) and Research Management Centre (RMC), UTM for supporting the research management activities. The authors would also like to acknowledge support by the International Cooperative Graduate School (ICGS) Fellowship under the "Universiti Teknologi Malaysia-NIMS Cooperative Graduate School Program" to conduct research in National Institute of Materials Science (NIMS), Tsukuba, Japan.

Funding

This work was supported by Ministry of Higher Education (MOHE) under project grant MRUN (R.J130000.7851.4L880) and Universiti Teknologi Malaysia (UTMPR:Q.J130000.2851.00L22, UTM-TDR:Q.J130000.3551.06G88). This work also was supported by the MEXT Program for the Development of Environmental Technology using Nanotechnology.

References

[1] R. Espiritu, M. Mamlouk, K. Scott, Study on the effect of the degree of grafting on the performance of polyethylene-based anion exchange membrane for fuel cell application, Int. J. Hydrog. Energy 41 (2) (2016) 1120–1133.
[2] M. Rahsepar, M. Pakshir, P. Nikolaev, Y. Piao, H. Kim, A combined physicochemical and electrocatalytic study of microwave synthesized tungsten mono-carbide nanoparticles on multiwalled carbon nanotubes as a co-catalyst for a proton-exchange membrane fuel cell, Int. J. Hydrog. Energy 39 (28) (2014) 15706–15717.
[3] P.E. Dodds, L. Staffell, A.D. Hawkes, F. Li, P. Grunewald, W. McDowall, P. Ekins, Hydrogen and fuel cell technologies for heating: a review, Int. J. Hydrog. Energy 40 (5) (2015) 2065–2083.
[4] Y. Devrim, H. Devrim, I. Eroglu, Polybenzimidazole/SiO_2 hybrid membranes for high temperature proton exchange membrane fuel cells, Int. J. Hydrog. Energy 41 (2016) 10044–10052.
[5] A. Muthumeenal, A.J. Rethinam, A. Nagendran, Sulfonated polyethersulfone based composite membranes containing heteropolyacids laminated with polypyrrole for electrochemical energy, Solid State Ion. 296 (2016) 106–113.
[6] J.D. Kim, L.J. Ghil, Annealing effect of highly sulfonated polyphneylsulfone polymer, Inter. J. Hydrog. Energy 41 (2016) 11794–11800.
[7] N. Urena, M.T. Perez-Prior, C. del Rio, A. Varez, J.Y. Sanchez, C. Iojoiu, B. Levenfield, Multiblock copolymers of sulfonated PSU/PPSU Poly(ether sulfone)s as solid electrolytes for proton exchange membrane fuel cells, Electrochim. Acta 302 (2019) 428–440, 428-220.
[8] D. An, B. Wu, G. Zhang, W. Zhang, Y. Wang, Gradiently crosslinked polymer electrolyte membranes in fuel cells, J. Power Source 301 (2016) 204–209.
[9] H. Hou, R. Polini, M.L. Di Vona, X. Liu, E. Sgreccia, J.F. Chailan, P. Knauth, Thermal crosslinked and nanodiamond reinforced SPEEK composite membrane for PEMFC, Int. J. Hydrog. Energy 38 (2013) 3346–3351.

[10] H. Lee, J. Han, K. Kim, J. Kim, E. Kim, H. Shin, J.C. Lee, Highly sulfoanted polymer-grafted graphene oxide composite membranes for proton exchange membrane fuel cells, J. Ind. Eng. Chem. 74 (2019) 223–232.
[11] J. Jaafar, A.F. Ismail, T. Matsuura, K. Nagai, Performance of SPEEK based polymer-nanoclay inorganic membrane for DMFC, J. Membr. Sci. 382 (2011) 202–211.
[12] M.M.H. Sadrabadi, S.R. Ghaffarian, P. Renaud, Nafion/benzotriazole functionalized montmorillonite nanocomposites: novel high-performance proton exchange membranes, RSC Adv. 42 (3) (2013) 19357–19365.
[13] K. Charradi, Z. Ahmed, P. Aranda, R. Chtourou, Silica/montmorillonite nanoarchitectures and layered double hydroxide-SPEEK based composite membranes for fuel cell applications, Appl. Clay Sci. 174 (2019) 77–85.
[14] D. Plackett, A. Siu, Q. Li, C. Pan, J.O. Jensen, S.F. Nielsen, A.A. Permyakove, N. J. Bjessum, High-temperature proton exchange membranes based on polybenzimidazole and clay composites for fuel cells, J. Membr. Sci. 383 (1–2) (2011) 78–87.
[15] A.K. Mishra, T. Kuila, N.H. Kim, J.H. Lee, Effect of peptizer on the properties of nafion-laponite clay nanocomposite membranes for polymer electrolyte membranes fuel cells, J. Membr. Sci. 389 (2012) 316–323.
[16] C. Beauger, G. Laine, A. Burr, A. Taguet, B. Otazaghine, A. Rigacci, Nafion®-sepiolite composite membranes for improved proton exchange membrane fuel cell performance, J. Membr. Sci. 130 (2013) 167–179.
[17] E. Paineau, Imogolite nanotubes: a flexible nanoplatform with multipurpose applications, Appl. Sci. 8 (20) (2018) 1–21.
[18] N.A.M. Nor, H. Nakao, J. Jaafar, J.D. Kim, Crosslinked carbon nanodots with highly sulfonated polyphenylsulfone as proton exchange membrane for applications, Int. J. Hydrog. Energy 45 (16) (2020) 9979–9988.
[19] W. Ma, W.O. Yah, H. Otsuka, A. Takahara, Surface functionalization of aluminosilicate nanotubes with organic molecules, Beilstein J. Nanotechnol. 3 (2012) 82–100.
[20] K. Yamamoto, H. Otsuka, S.I. Wada, D. Sohn, A. Takahara, Preparation and properties of [poly (methyl methacrylate)/imogolite] hybrid via surface modification using phosphoric acid ester, Polymer 46 (26) (2005) 12386–12392.
[21] K. Yamamoto, H. Otsuka, A. Takahara, Preparation of novel polymer hybrids from imogolite nanofiber, Polym. J. 39 (1) (2007) 1–15.
[22] L. Guimarães, A.N. Enyashin, J. Frenzel, T. Helne, H.A. Duarte, G. Seifert, Imogolite nanotubes: stability, electronic, and mechanical properties, ACS Nano 1 (2007) 362–368.
[23] P. Knauth, M.L. Di Vona, Hydration and proton conductivity of ionomers: the model case of sulfonated aromatic polymers, Front. Energy Res. 2 (50) (2014) 1–6.
[24] P. Salarizadeh, M. Javanbakht, S. Pourmahdian, Enhancing the performance of speek polymer electrolyte membranes using functionalized TiO_2 nanoparticles with proton hopping sites, RSC Adv. 7 (2017) 8303–8313.
[25] A.F. Martinez, L.J. Michot, Chapter 9-physicochemical properties of imogolite, Dev. Clay Sci. 7 (2016) 202–222.
[26] J.D. Kim, A. Ohira, H. Nakao, Chemically crosslinked sulfonated polyphenylsulfone (CSPPSU) membranes for PEM fuel cells, Membranes 10 (2020) 1–14.
[27] S.B. Brijmohan, S. Swier, R.A. Weiss, M.T. Shaw, Synthesis and characterization of cross-linked sulfonated polystyrene nanoparticles, Ind. Eng. Chem. Res. 44 (2005) 8039–8045.
[28] S. Meenakshi, A.K. Sahu, S.D. Bhat, P. Sridhar, S. Pitchumani, A.K. Shukla, Mesostructured-aluminosilicate-nafion hybrid membranes for direct methanol fuel cells, Electrochim. Acta 89 (2013) 35–44.
[29] D. Xing, J. Kerres, Improved performance of sulfonated polyarylene ethers for proton exchange membrane fuel cells, Polym. Adv. Technol. 17 (2006) 591–597.
[30] S. Neelakandan, P. Kanagraj, R.M. Sabarathinam, A. Muthumeenal, A. Nagendran, SPEES/PEI-based highly selective polymer electrolyte membranes for DMFC application, J. Solid State Electrochem. 19 (6) (2015) 1–10.
[31] H. Zhang, C. Ma, J. Wang, X. Wang, H. Bai, J. Liu, Enhancement of proton conductivity of polymer electrolyte membrane enabled by sulfoanted nanotubes, Int. J. Hydrog. Energy 39 (2) (2014) 974–986.
[32] W.O. Yah, K. Yamamoto, N. Jiravanichanun, H. Otsuka, A. Takahara, Imogolite reinforced nanocomposites: multifaceted green materials, Materials 3 (3) (2010) 1709–1745.
[33] T. Fu, Z. Cui, S. Zhong, Y. Shi, C. Zhao, G. Zhang, K. Shao, H. Na, W. Xing, Sulfonated poly(ether ether ketone)/clay-SO_3H hybrid proton exchange membranes for direct methanol fuel cells, J. Power Sources 185 (1) (2008) 32–39.
[34] Y. Zheng, U. Ash, R.P. Pandey, A.G. Ozioko, J. Ponce-Gonzalez, M. Handl, T. Weissbach, J.R. Varcoe, S. Holdcraft, M.W. Liberatore, R. Hiesgen, D.R. Dekel, Water uptake study of anion exchange membranes, Macromolecules 51 (2018) 3264–3278.
[35] H. Illbeygi, A.F. Ismail, A. Mayahi, M.M. Nasef, J. Jaafar, E. Jalalvandi, Transport properties and direct methanol fuel cell performance of sulfonated poly(ether ether ketone)/cloisite/triaminopyrimidine nanocomposite polymer electrolyte membrane at moderate temperature, Sep. Purif. Technol. 118 (2013) 567–575.
[36] H. Illbeygi, A. Mayahi, A.F. Ismail, M.M. Nasef, J. Jaafar, M. Ghasemi, T. Matsuura, S.M.J. Zaidi, Transport properties of SPEEK nanocomposite proton conducting membranes: optimization of additives content by responsive surface methodology, J. Taiwan Inst. Chem. Eng. 45 (5) (2014) 2265–2279.
[37] Y. Zhang, B. Yue, H. Shuaiyuan, L. Yan, Synergetic proton conducting effect in acid–base composite of phosphonic acid functionalized polystyrene and triazolyl functionalized polystyrene, RSC Adv. 4 (64) (2014) 33702–33712.
[38] D.K. Paul, R. McCreery, K. Karan, Proton transport property in supported nafion nanothin films by electrochemical impedance spectroscopy, J. Electrochem. Soc. 161 (14) (2014) F1395–F1402.
[39] S. Zhai, W. Dai, J. Lin, S. He, B. Zhang, L. Chen, Enhanced proton conductivity in sulfonated poly (ether ether ketone) membranes by incorporating sodium dodecyl benzene sulfonate, Polymers 11 (203) (2019) 1–11.
[40] S.M.R. Niya, M. Hoorfar, Process modelling of the ohmic loss in proton exchange membrane fuel cells, Electrochim. Acta 120 (2014) 193–203.