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Homogeneous Polymer/filler Composite Membrane by Spraying Method for Enhanced Direct Methanol Fuel Cell Performance

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Abstract

In this work, composite membranes for a direct methanol fuel cell (DMFC) were prepared using a spraying method to improve cell performance especially at a high methanol concentration. Nafion polymer and mordenite as a filler were used for the composite membrane preparation using a spraying method and a conventional solution casting method and the membranes from the two methods were compared. SEM images showed that a more homogeneous composite membrane could be obtained using the spraying method. The effect of mordenite content was also studied. The membranes were consequently characterized and tested in DMFC operation. The results were compared to those prepared using the solution casting method at 30, 50, and 70 °C with methanol concentrations of 2, 4, and 8 M. It was found that the membrane with 5 wt.% mordenite from the spraying method showed a vast improvement in DMFC performance. When the cell was operated at 70 °C, the maximum power density of 5 wt.% mordenite from the spraying method was higher than that of commercial membrane and 5 wt.% from the solution casting method. Power densities from the 5 wt.% sprayed membrane were higher by around 29%, 40%, and 60% at 2, 4, and 8 M methanol concentration, respectively.

Keywords: Direct methanol fuel cell; composite membrane; spraying method; methanol permeability; DMFC performance.

1. Introduction

A fuel cell is an electrochemical device that offers the prospect of a greener future to advance global energy resources with environmental and economic benefits [1]. Fuel cells have been extensively acknowledged as a clean and an efficient technology for generating electricity [2, 3] as they have several advantages in terms of high-energy efficiency, high-energy density, low noise, near-zero pollutants, and short charging time [3-5]. Direct methanol fuel cells (DMFCs) have attracted much interest due to their advantages of inexpensive raw materials, high energy conversion efficiency, and low operating temperature [6-9]. The transportation of methanol fuel is more convenient than that of hydrogen fuel because methanol is in liquid form at room temperature and atmospheric pressure making it having high energy density [3, 7]. The benefit of using liquid energy carrier is enable long operating times without refilling and cheaper

cost compared to pressurized hydrogen gas storage [3, 7]. Furthermore, methanol has a simple molecular structure and its electrochemical activity is relatively high. Thus, DMFCs are promising for proton exchange membrane fuel cell (PEMFC) applications [10]. Polymer electrolyte membrane or proton exchange membranes (PEMs) is a key components used in PEMFC [11] as it plays a vital role in transporting protons and blocking electrons from anode to cathode as well as preventing fuel going through during the fuel cell operation [10, 12]. The limitation of using PEMs in DMFC is that methanol can permeate through the polymer electrolyte membranes from the anode to the cathode and this methanol crossover is possibly the most severe problem in DMFCs [12-15].

The polymer electrolyte membrane has two important functions as a proton conductor and a fuel and gas barrier [12]. Therefore, a good conducting membrane should have key properties of high proton conductivity, low methanol permeability, good chemical resistance, good thermal and mechanical stability [5]. Many types of sulfonated polymers have been used as polymer electrolyte membranes such as Nafion, chitosan, sulfonated poly(arylene ether sulfone), and sulfonate poly(ether ether ketone) [16-20]. Ahmed et al. [10] and Zakil et al. [21] presented overview of membranes for direct methanol fuel cell application. Nafion has been the most widely used as a proton-conducting membrane because of its excellent chemical, mechanical, thermal stability, and high proton conductivity, (0.1 S cm^{-1}) [22]. However, Nafion exhibits high alcohol permeability leading to reduced DMFC performance [23]. Many approaches have been studied to improve the alcohol resistance in a Nafion membrane, such as developing an alternative polymer electrolyte [24, 25] and Nafion membrane modification [26-31].

According to many researchers, membrane modification by incorporating fillers into the Nafion matrix could enhance DMFC performance [15, 32-35]. Zeolites have a highly crystalline structure and are resistant to an organic solvent due to their hydrophilicity. Mordenite (MOR) is one of the zeolites which can withstand an acidic medium and high temperature (above 800°C) [26]. However, the weak interaction between an organic component and the zeolite in the composite membrane causes poor interfacial properties [22, 36, 37]. Many researchers have reported that the incompatibility can attributed to pinholes between the filler and the Nafion matrix [26, 36, 37]. These pinholes facilitate alcohol transport or fuel crossover [32]. The interfacial properties can be improved by grafting a silane coupling agent onto the surface of MOR [38].

There are several methods to fabricate membranes for DMFC such as the sol-gel method, dip coating, and the solution casting method (SCM) [39-41]. The sol-gel method has not been widely used because of its chemical complexity [42]. Thus, SCM with the addition of zeolites has become of interest because of its simplicity. However, the SCM has limitations because it takes time to evaporate the solvents. Therefore, the additive cannot be suspended and this results in deposition at the bottom of the composite membrane [43, 44]. Thus, to overcome this problem, a new method was used to fabricate the composite membrane, which was intended to improve the dispersion of MOR in the polymer matrix.

Xing et al. [45] successfully used a solution-spray process to fabricate Nafion/polytetrafluoroethylene composite membrane. Our previous work reported a preliminary study on applying a spraying method to fabricate Nafion/filler composite membrane [46]. It was found that sprayed membranes can result in a more homogeneous composite membrane compared to that produced using the solution casting method. In this work, the spraying method (SM) was the focus and was used to investigate the composite membrane morphological properties with different filler loadings, as it was expected that a higher filler loading could lead to lower alcohol permeability while the membranes maintained high proton conductivity. Consequently, the performance of DMFCs using sprayed composite membranes may be improved. Therefore, this study investigated a series of membrane characterizations and tests of the membranes in DMFC operation over a range of temperatures from low to high. Furthermore, the DMFC performance test was carried out at a high methanol concentration.

2. Materials and methods

The 20 wt.% Nafion solution was purchased from Ion Power. Mordenite-Na with a Si/Al molar ratio of 5 and an average particle size of 2.7 μm was purchased from Zeolyst International. 3-Mercaptopropyl triethoxysilane (MPTES), sulfuric acid, hydrogen peroxide, ethanol, methanol, N,N-dimethylformamide (DMF), dichloromethane, ammonium chloride, and toluene, were purchased from Sigma-Aldrich. De-ionized water was used throughout the study.

2.1 Mordenite preparation

Mordenite preparation was carried out following the procedure described in Prapainainar et al. [38, 44, 46]. The MOR-Na powder was ground using a zirconia ball mill (0.5 mm diameter)

to reduce the particle size. After grinding, an average particle size of 0.317 μm was obtained. The ground MOR-Na particles were protonated in 1M NH_4Cl at room temperature for 24 h, then washed with deionized water, and dried at 105 $^\circ\text{C}$ for 24 h. Then, it was calcined at 550 $^\circ\text{C}$ for 5 h with a heating rate of 2 $^\circ\text{C}\cdot\text{min}^{-1}$ to produce MOR-H. The MOR-H was surface modified using MPTES. The catalyst solution was prepared by dissolving 1 g of AlCl_3 in 20 cm^3 of ethanol at 70 $^\circ\text{C}$ until the AlCl_3 dissolved and then, 20 cm^3 of toluene was added. Silane solution was prepared by mixing 4 cm^3 of silane with 40 cm^3 of toluene and stirring for 30 min. Then, 5 cm^3 of the catalyst solution was mixed with the silane solution and 2 g of MOR-H. The solution was refluxed at 110 $^\circ\text{C}$ for 24 h with continuous stirring. The product was separated using centrifugation at 6,000 rpm and rinsed with both ethanol and deionized water to remove the silane residues. The filtrated solid was dried at 105 $^\circ\text{C}$ for 24 h. Functionalized MOR was subsequently oxidized by 30 wt.% H_2O_2 under stirring for 24 h at room temperature to convert the $-\text{SH}$ groups into $-\text{SO}_3$ groups.

2.2 Composite membrane preparation

The composite membrane was fabricated using the spraying method (SM) which was developed from the spray-coated technique illustrated by Sun and coworkers [47] and the preparation procedure was previously described in Prapainainar et al. [46]. The apparatus set up is shown in Figure 1 and comprised a spray gun (Badger Model 100-LGF, USA), a template (stainless steel), a heater, a temperature controller, and a nitrogen gas line. Preparation of solution for composite membrane fabrication was adopted from the procedure described by Tricoli and Nannetti [48]. First, the solution was prepared by mixing 7.5 cm^3 of 20 wt. % Nafion solution with 5.1 cm^3 of methanol, 28.9 cm^3 of ethanol, and 20.5 cm^3 of DMF. Then functionalized MOR powders (0.078, 0.165, 0.372, and 0.638 g for a MOR content of 5, 10, 20, and 30 wt.%, respectively) were added to the mixture using ultrasonication and a magnetic stirrer for 15 min each interval for a total period of 2 h. In the spraying procedure; first, the spray gun was connected to a nitrogen gas line at a pressure of 2 bar. Next, the spraying temperature of 100 ± 1 $^\circ\text{C}$ was set for a stainless steel template using a temperature controller. The solution was then poured into the spray gun container and sprayed onto the template at a distance of around 5 cm above the template. The solution evaporated and the composite membrane formed on the template surface. Finally, the composite membrane was heated to 150 $^\circ\text{C}$ for 4 h for annealing.

The membrane was treated in boiled deionized water for 10 min to obtain full hydration. Then, it was heated in 5 wt. % H_2O_2 at 80 °C for 30 min to remove the organic residue and boiled in 1 M H_2SO_4 for 30 min to change the Nafion membrane to an acid form. Finally, the membrane was thoroughly washed three times in boiling deionized water for 10 min. Solution cast composite membranes were prepared following the standard method reported in Yoonoo et al. [43], while Nafion117 commercial membrane was purchased from Ion Power.

Figure 1. Schematic diagram for fabrication of sprayed membranes [49].

2.3 Characterization

The particle size of MOR was determined using a Mastersizer 2000, Malvern Instruments Limited. The MOR crystalline structure was characterized using a BRUKER Advance A25 equipped with Cu-K α radiation (1.5418 Å). The X-ray diffraction, XRD, patterns were obtained at 2θ between 5° to 40°. Fourier-transform infrared spectroscopy, FT-IR, (BRUKER TENSOR 27) was used to investigate functional groups on MOR before and after silane coupling agent functionalization at wave numbers of 400–4000 cm^{-1} . Thermo-Gravimetric Analysis, TGA, (SDT 2960) was used to determine the quantity of silane coupling agent modified on the MOR surface. TGA was performed in air at a flow rate of 100 $\text{cm}^3 \cdot \text{min}^{-1}$ with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$. The temperature range was 25–1100 $^\circ\text{C}$. The morphology of the composite membranes was investigated using an FEI QUANTA 450 scanning electron microscope (SEM) equipped with an Oxford X-Max EDX detector.

2.4 Composite membrane properties

2.4.1 Solubility

The solubility was used to determine the chemical resistance of the membrane following Moore and Martin's procedure [50] by immersing membrane samples in 50:50 ethanol-water solution. A good conducting membrane for both dry and wet film should have a solubility less than 5% in alcohol solution [50]. The procedure of solubility testing is explained in Prapainainar et al. [38, 44, 46].

2.4.2 Water uptake

Water uptake represents membrane behavior when it is in contact with water and it can be measured by the weight difference between the dry membrane and wet membrane as explained in Prapainainar et al. [38, 44, 46].

2.4.3 Mechanical strength of the membrane

Mechanical property is an essential requirement for membrane in high temperature DMFC applications. Several studies indicated that mechanical failures of PEMs were because the effect of thermodynamic, humidity, and force during the DMFC operation leading to decrease of membrane lifespan [45, 51, 52]. Tensile strength of sprayed and solution cast membranes with MOR and without MOR were investigated using a universal testing machine (Instron 4206). The membranes were cut into a length and width of 50 mm×10 mm and tested according to ASTM D882. A total of five specimens with a gauge length fixed at 30 mm were tested at a rate of 5 mm·min⁻¹. The film was then stretched at a cross-head and its tensile strength was estimated from the ratio of maximum load and cross-sectional area of the sample.

2.4.4 Proton conductivity

The measurement of proton conductivity was carried out using the two-electrode method by a potentiostat/galvanostat instruments (Metrohm Autolab) under potentiostatic conditions. The measurement was conducted over a frequency range of 10000–100 Hz and an amplitude at 5 mV to measure the resistance of the membranes and consequently the proton conductivity can be calculated as shown in Prapainainar et al. [38, 44, 46]. Before measurement, specimens were treated in boiling water and acidic solution and then immersed in 1 M H₂SO₄ for 24 h following

the procedure reported in Prapainainar et al. [38, 44, 46]. During the measurement of the membrane resistance, all specimens were measured under a fully hydrated condition by being immersed in a temperature-controlled container with 1 M H₂SO₄ solution. This was to ensure that all the samples were tested under a controlled condition [46].

2.4.5 Methanol permeability

A diffusion technique was used to determine the methanol permeability through the membrane in order to measure the rate of alcohol permeating through the membrane and consequently the methanol permeability can be calculated. Details of the experimental equipment and procedure are described in Prapainainar et al. [38, 44, 46]. The operating temperature was varied from 30 °C to 70 °C. To measure the methanol permeability at different temperatures, both containers and the diffusion cell were immersed in a temperature-controlled water bath. The 10 cm³ sample was collected at the permeated side at different times of 0, 5, 30, 60, and 90 min. Then, the methanol concentration was determined using gas chromatography (GC 8A, SHIMADZU) with a Porapak-Q column.

2.5 DMFC performance testing

In order to test DMFC performance, membrane electrode assemblies (MEAs) were incorporated in the fuel cell with a 4.5×4.5 cm² electrode area. The electrodes were Pt-Ru/Carbon paper electrode (2 mg·cm⁻²) for the anode and 60% Pt/Carbon paper electrode (0.5 mg·cm⁻²) for the cathode (Fuel Cell Store). An assembly of the anode, the membrane, and the cathode were put in order for hot-pressing at 60 kg·cm⁻² and 135 °C for 30 min [46]. MEA performance was evaluated in 2, 4, and 8 M methanol solutions with a feed of 5 cm³·min⁻¹ at the anode and a cathode air feed rate of 1,000 cm³·min⁻¹. The operation temperature was 30, 50, and 70 °C.

3. Results and discussion

3.1. Surface modification or mordenite: FT-IR, TGA analysis and XRD

The functional group of MOR before and after modification was investigated. In this section, FT-IR and TGA were used to ensure a successful functionalization process. Figure 2 (a)

shows the FT-IR spectra of MP TES compared with unmodified MOR and modified MOR, called MOR-H and MOR-MP TES, respectively. Normally, the characteristic peak of MP TES is slightly changed around 2884–2973 cm⁻¹ [38, 44]. Considering the spectra of both MP TES (green) and MOR-MP TES (red), the green spectrum revealed a characteristic peak of the epoxy-group around 2884–2973 cm⁻¹, which was probably a characteristic peak of MP TES. Additionally, there were peaks around 3450 and 1630 cm⁻¹ that represented the stretching and bending vibrations of hydroxyl groups, respectively. On the other hand, the spectrum of the modified MOR did not show the change in characteristic wavenumber around 1000–1300 cm⁻¹, which is the stretching vibration of Si – O and Al – O. This implies that the framework structure of MOR still remained after modification [39, 53]. A summary of FT-IR results from unmodified and modified MOR is shown in Table 1. It was confirmed by the XRD analysis of mordenite before and after functionalization with MP TES (Figure 2 (c)) and the XRD patterns showed identical characteristic peaks corresponding to the reflection of mordenite (IZA code MOR) reported by Robson et al. [54].

TGA was used to determine the differential weight loss of the unmodified and modified MOR to ensure successful functionalization. Therefore, the TGA curves in Figure 2 (b) show the weight loss of MOR-H (blue) and MOR-MP TES (red). The results showed rapid weight loss for MOR-H with only one stage at 10% weight loss below 250 °C, which was attributed to the weakly adsorbed water evaporation loss followed by strongly bound water evaporation [32, 55]. The strongly adsorbed water can be described as a dehydroxylation reaction as shown in reaction (1) [32].

For MOR-MP TES (red), the first reduction stage around 20–250 °C revealed a weight loss of 9% which was associated with a desulfonation process or the elimination of flexible chains of MP TES, while the second reduction stage around 250–600 °C was related to the decomposition of the main-chain of the cross-linked membrane [56]. The weight loss of MOR-MP TES was found after the subtraction of the water content to be around 6 wt.% and the results are shown in Table 2.

Figure 2. Characterizations of mordenite after surface modification with MPTES silane coupling agent: (a) FT-IR spectra of silane-MPTES (green), MOR-H (blue), and MOR-MPTES (red); (b) TGA analysis of MOR-H (blue) and MOR-MPTES (red); (c) XRD patterns of MOR-H (blue) and MOR-MPTES (red).

Table 1 Summary of FT-IR results from unmodified and modified MOR [57]

Characteristic Absorption (cm ⁻¹)	Functional Group
3550-3200	Alcohol/Phenol O-H stretching
2950-2850	Alkyl C-H stretching
~1630	O-H bending
1250-920	The internal asymmetric stretching of tetrahedral group

Table 2 Summary of TGA data unmodified and modified MOR

Sample	Weight loss 20 – 250 °C (%)	Weight loss 250 – 600 °C (%)	Weight loss 600 – 800 °C (%)	MPTES (%)
MOR – H	10	-	-	-
MOR – MP TES	9	6	-	6

3.2. Characterization of the membrane

3.2.1 SEM/EDS images of fabricated membranes

3.2.1.1 Composite membranes from different fabrication methods

In this work, a spraying method for membrane fabrication was chosen to fabricate a homogeneous organic-inorganic composite membrane. The cross-section SEM images comparing membranes prepared using different fabrication methods are shown in Figure 3 with Nafion[®]117 (commercial; COMM), Nafion membrane prepared using the solution casting method (SCM), and Nafion membrane prepared using the spraying method (SM). The SEM image of pristine Nafion polymer clearly shows that membranes with different fabrication method have the same morphology as dense membranes. With sprayed membranes, even though the membranes were formed layer by layer, from the SEM image, the layers cannot be identified in the cross-section of the membrane.

Figure 3. SEM images comparing Nafion membranes fabricated using: (a) commercial, COMM, (b) solution casting method, SCM, and (c) spraying method, SM.

3.2.1.2 Composite membranes from various MOR loadings

The dispersion of MOR particles within the membrane was examined on the cross-sectional SEM images and EDS. For a certain size of MOR particle, the dispersion of MOR in the Nafion matrix changed with content. In this work, the weight content of MOR was varied (0%, 5%, 10%, 20%, and 30%). The cross-section SEM images of the sprayed MOR-Nafion composite membranes showed dispersion of MOR in the composite membranes (Figure 4).

From Figure 4, when 5 wt.% MOR was added using the solution casting method (Figure 4 (a), (b) and (c)), a layer of mordenite formed at the bottom of the membrane as previously reported [43, 44]. With the spraying method, when 5% MOR content was added (Figure 4 (d), (e), and (f)), MOR particles dispersed in the matrix with some aggregations. However, from the EDS mapping, it was clear that they were well-dispersed in each phase. Furthermore, increasing the MOR content to 10 wt.% (Figure 4 (g), (h), and (i)) and 20 wt.% (Figure 4 (j), (k), and (l)), the average MOR particles were mostly separated with some agglomerated particles. Moreover, the EDS results displayed good dispersion of both the MOR and Nafion phase. In contrast, when the MOR content was increased to 30 wt.% (Figure 4 (m), (n), and (o)), the MOR particles in Nafion show better dispersion within the membrane. Hence, it could be concluded that the composite membrane fabricated using the spraying method could provide homogeneous filler dispersion in the Nafion matrix, in contrast to the membranes from the solution casting method reported previously [43, 44].

Figure 4. SEM/EDS images (red color is Silicon, Si, mapping, and green color is Fluorine, F, mapping) of Nafion-MOR composite membranes using the solution casting method: (a) SEM-5 wt.%, (b) Si-5 wt.%, (c) F-5 wt.%, and using the spraying method with different MOR contents: (d) SEM-5 wt.%, (e) Si-5 wt.%, (f) F-5 wt.%, (g) SEM-10 wt.%, (h) Si-10 wt.%, (i) F-10 wt.%, (j) SEM-20 wt.%, (k) Si-20 wt.%, (l) F-20 wt.%, (m) SEM-30 wt.%, (n) Si-30 wt.%, and (o) F-30 wt.%.

Additioanlly, images of superficial area of the sprayed membranes are shown in Figure 5. The membrane without MOR fillers (Figure 5(a)) was translucent and the membranes became opaque as the MOR content increased from 5 wt.% to 30 wt.% (Figure 5(b) – (e)). It is notable that MOR particles were well distributed througout the membrane sheet. It is also worth noting that pristine sprayed membrane was flexible but when incorporating inorganic filler with low MOR content (5 – 10 wt.%) the membrane became harder. However, with high MOR content (20 – 30 wt.%), the sprayed membranes bacame more brittle.

Figure 5. Images of superficial area of membranes (approximately 2 cm × 2 cm): (a) SM, (b) SM 5 wt.% MOR, (c) SM 10 wt.% MOR, (d) SM 20 wt.% MOR, and (e) SM 30 wt.% MOR.

3.2.2 Solubility

This section presents the chemical resistance of the membranes, which was described in terms of the solubility of the Nafion-MOR composite membrane with modified MOR by MPTES. To investigate the effect of MOR loading, composite membranes were prepared containing 5, 10, 20, and 30 wt.% MOR contents. Figure 6 presents the solubility of the composite membranes prepared using the spraying method compared with those of commercial and solution cast membranes. The solubility of all Nafion membranes, COMM, and SCM (including SCM 5 wt.% MOR) had solubility below 5%, which was within the criteria that Moore and Martin suggested for a good conducting membrane [50]. The sprayed membranes with a low mordenite content (0–10 wt.%), had a solubility around 5–10% slightly higher than that of the SCM samples, which could have been due to the incomplete inter-diffusion of polymer chains between particles in the composite membrane. Moreover, it could also have been due to the reduced chemical resistance in the composite membrane [47]. When the MOR content increased to 20 and 30 wt.%, the solubility increases dramatically, which could also have been due to the loss of mordenite particles from the composite membranes as the membranes with high MOR content were very brittle, making composite membranes with high filler contents unsuitable for direct methanol fuel cell application.

Figure 6. Solubility of composite membranes prepared using solution casting method (SCM) and spraying method (SM).

3.2.3 Water uptake

A membrane containing a high water content can lead to high proton conductivity [58] because water in Nafion can effectively reduce the activation energy of proton transfer by providing more pathways for proton hopping (Grotthus mechanism) and diffusion mechanism (vehicular mechanism) [59, 60]. However, a membrane with excess water adsorption could lead to poor mechanical properties and low stability [61], which is critical to DMFC performance [62-64]. For example, a high degree of swelling of a chitosan membrane led to a high degree of alcohol and water permeation [53]. Hence, it has been suggested that suitable water uptake is required in the range 2.51–67.23 % at 25 °C [36].

The results showed that all sprayed membranes had higher water uptake than those of COMM and SCM (SCM and SCM 5 wt.% MOR) as shown in Figure 7. Moreover, increasing the MOR content led to increased water uptake. This agreed well with the results reported by Zhang et al. [15] and Kongkachuichay et al. [65], in which the increase of zeolite content resulted in the increase of water uptake. This could be evidence that MOR, which has structure consisting of 3D connected pores having strong polarity and high water retention capacity [15, 65], facilitated higher water absorption in the composite membrane, and resulted in a continuous increase of the water uptake [15]. The slight increase of water uptake could have also been due to functionalization of MOR with MPTES improving interfacial property of MOR making a better dispersion of mordenite within the polymeric material, and reducing voids [38, 43]. Without functionalization of MOR surface, the composite membranes could have exhibited high porosity, and the large number voids accommodating a significant amount of water [15]. It should be noted that functional group of –SH on external surface of MOR-MPTES particles [38], however, could have no insignificant increase of water uptake [58].

Figure 7. Comparison of %water uptake of composite membranes prepared using solution casting method (SCM) and spraying method (SM).

3.2.4 Mechanical strength

The tensile strength of sprayed and solution cast membranes with MOR and without MOR are summarized in Table 3. The tensile strength of the commercial membrane (COMM) was 27.05 MPa, which was in a good agreement with Lin's work [56]. Considering the effect of preparation method, it can be clearly seen that the tensile strength of the composite membranes prepared by solution casting method (22.23 MPa) were slightly higher than that of spraying method (19.90 MPa). When MOR content increased in SM membranes, the tensile strength decreased, which was consistent with the works from Jin et al. [51] and Shrotri et al. [52]. Nafion/MOR composite membranes, both SM and SCM, showed lower tensile strength than those of pristine Nafion membranes, which could have been due to the preparation method.

For Young's modulus, the results from SCM was lower than those of the SM. It could be implied that the SM membranes were more brittle than the SCM membranes. The brittleness of the membranes related to the mechanism of membrane formation [36]. This could be explained that the particles in a layer-by-layer formed in Nafion/MOR membrane prepared by spraying method were completely packed in the matrix structure once the solvent evaporated during the spraying process [47]. On the other hand, the particles in Nafion/MOR membrane prepared by solution casting was added simultaneously, therefore, all particles had the same length of time to

settle. Additionally, the inorganic particles within Nafion matrix increased the rigid of polymer chains and reduced the elongation [47].

Table 3 Mechanical properties of fabricated composite membranes prepared from SCM and SM

Sample	Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	Young's modulus (MPa)
COMM	0.18	27.05±3.16	355.60±49.72	166.77±7.78
SCM	0.13	22.23±1.52	299.20±64.90	191.21±12.66
SCM 5% wt MOR	0.12	19.60±1.91	229.20±54.03	250.92±9.17
SM	0.16	19.90±3.33	153.70±104.54	279.61±6.95
SM 5% wt MOR	0.18	16.05±0.87	224.60±17.73	250.57±10.64
SM 10% wt MOR	0.18	13.94±2.20	140.20±32.83	303.93±20.52
SM 20% wt MOR	0.20	9.99±1.00	10.80±1.79	340.64±17.51
SM 30% wt MOR	0.21	10.36±1.40	2.80±1.79	501.01±41.47

3.2.5 Proton conductivity

Proton transport through a Nafion membrane occurs mainly through water channels within the matrix [43] associated hydronium ions, which can occur via two proposed mechanisms, namely Grotthuss and vehicular mechanism [59, 60]. In Grotthuss mechanism (the jumping or hopping mechanism), the protons pass down from the –OH groups or the SO_4^{2-} ion groups by jumping from one site to another [53, 66, 67]. For the vehicular mechanism, protons attach themselves to a ‘vehicle’ such as water to form hydronium ions (eg., as H_3O^+) and diffuse along with the vehicles [68].

The proton conductivity measurement technique used in this work was alternate current (AC) impedance spectroscopy. In this section, the proton conductivity of all membranes was measured at 30, 50, and 70 °C. There were five composite membranes with 0, 5, 10, 20, and 30 wt.% of modified MOR filler. The proton conductivity of the sprayed composite membranes was compared to solution cast Nafion membranes and a commercial membrane and the results are shown in Figure 8. Overall, incorporating mordenite filler into the Nafion polymer using the spraying method resulted in a more homogeneous composite membrane, so the membrane could maintain high Nafion proton conductivity. The proton conductivity increases with the zeolite

content due to the increased hydrophilic material content. This could have been that mordenite filler in the composite membrane could maintain high mobility of water leading to high concentration of protons [15]. Furthermore, the proton conduction characteristic of the mordenite could also enhance the conductivity of the Nafion polymer composite membrane [69]. Additionally, the proton conductivity increases also due to the sulfonic groups from MP TES silane [58]. Therefore, the Nafion membrane filled with MOR-MPTES facilitated proton transportation [58].

At every testing temperature, the proton conductivity of the sprayed membranes was higher than that of the commercial one, even at a high mordenite loading of 30 wt.%, as the results show that proton conductivity was higher (around 35–40%) when compared to commercial membrane. In the zeolite composite membranes, the proton can transfer along the additional pathways at the interface of inorganic filler and polymer functioning together with the ionomeric cluster network of the Nafion polymer [70]. When the temperature was increased, proton conductivity increased due to the Arrhenius effect as the proton conductivity is proportional to the temperature [56], as well as the vehicular mechanism of proton transfer is characterized by a higher energy of activation making the proton transfer by diffusion more significant at high temperature [70].

Figure 8. Proton conductivity of composite membranes prepared using solution casting method (SCM) and spraying method (SM) and tested at 30, 50 and 70°C.

3.2.6 Methanol permeability

Methanol permeability through proton conducting membrane occurs due to a diffusion mechanism. Methanol molecules diffuse through the membrane voids and hydrophilic channels [71]. It has been reported that the incorporation of fillers with molecular sieve property and low alcohol permeability in a polymeric membrane can result in a reduction of alcohol permeability [16]. Therefore, the addition of MOR in the Nafion membrane could reduce the methanol permeability across the membrane [43, 44]. The presence of MOR could enhance the barrier properties of the membrane to methanol molecules and provided more tortuous pathways for methanol diffusion through the membrane [16, 72, 73] as methanol travel around and between the methanol-impermeable zeolite particles [72]. Thus, it was expected that increasing the MOR content in the membrane should lead to a significant improvement in the methanol resistance.

This experiment was carried out to investigate the methanol permeability of SM at different MOR contents compared with COMM and SCM (SCM and SCM 5 wt.% MOR). The results showed that increasing the MOR content could reduce the methanol permeability to some extent [40]. When the MOR content increased further, SM showed increased methanol permeability dependent on the amount of MOR loading. This was consistent with the research results reported by Kim et al. and Shroti et al., in which the methanol permeability of composite membrane increased with increasing inorganic filler content [16, 52]. The incorporating of zeolite particles was anticipated for methanol crossover suppression, but the excessive filler content could have led to an inverse effect on the membrane properties [44]. Additionally, the increase of MOR content lead to higher solubility, which has effect on methanol permeability [16]. Methanol permeability also depends on the water uptake as the amount of free water correlates closely with membrane swelling in a methanol aqueous solution [16]. Thus, the methanol resistance of the composite membranes could not reduce the methanol permeability when increasing MOR content. This could imply that finding a suitable content of MOR in composite membrane fabrication is necessary.

As for the effect of temperature, at all testing temperatures, the methanol permeability of SM showed the same trend (Figure 9) as the methanol permeability increased at higher temperature. This could be the result of the increase of the anions fixed groups in membrane when increasing temperature leading to the methanol permeability increase [71, 74].

Figure 9. Methanol permeability of composite membranes prepared using solution casting method (SCM) and spraying method (SM), tested at 30 °C and 70°C.

3.2.7 DMFC performance

In this section, the sprayed membranes with different MOR contents (0, 5, 10, 20 and 30 wt.%) were used for making membrane electrode assemblies (MEAs) and tested in a DMFC testing unit. The comparison of their DMFC performance with MEAs using a commercial membrane (COMM), solution cast membranes with 5 wt.% MOR, and sprayed membrane at different MOR contents are discussed. The composite membranes were tested in the DMFC at 30, 50 and 70 °C. The concentrations of methanol solution in the experiment were 2, 4, and 8. Polarization and power density curves are shown in Figure 10, Figure 11, and Figure 12. The maximum power density of the prepared membranes is summarized in Table 4, Table 5, and Table 6.

Figure 10 shows the polarization curves and power density at 30, 50, and 70 °C at a 2 M concentration of methanol solution. Figure 10 (a) and (b) are the results from 30 °C, with all the MEAs producing maximum power density between 1 mW·cm⁻² and 6 mW·cm⁻² with a composite membrane from the spraying method. SM 5 wt.% MOR membrane gave the highest power density at around three times higher than that from a commercial one. Composite membrane using the solution casting method also had a higher maximum power density than commercial membranes by around 2.5 times, which was in good agreement with results previously published

[43, 44]. SM 10 wt.% MOR had a power density around two times higher than that from Nafion117. However, when the MOR content was increased to 20 and 30 wt.%, the cell performance dropped resulting in a maximum power density lower than that from 5 and 10 wt.%. The membrane with 30 wt.% performed worse than the commercial one. This can be attributed to the higher methanol permeability and ohmic resistance of the MEA and may have been because the membranes were quite brittle and fragile when a high content of MOR was added, leading to poor contact between the membrane and the electrodes.

At 50 °C in Figure 10 (c) and (d), overall, it was as expected, namely that when the cell temperature increased, the cell performance increased. SM 5 wt.% MOR still had a power density around 2.25 times higher than that from the commercial one. At 70 °C in Figure 10 (f) and (g), apart from 20 wt.% MOR and 30 wt.% MOR, the other membranes had higher power density than from at 50 °C, with SM 5 wt.% having the highest power density at around 11 mW·cm⁻² followed by SCM 5 wt.% MOR also at around 11 mW·cm⁻².

The results from using the membranes with 4 M methanol solution are shown in Figure 11 and showed that overall, the sprayed membrane with 5 wt.% MOR had the highest power density at around 6, 10 and 11 mW·cm⁻² at 30, 50, and 70 °C, respectively. These results were around 2 to 2.4 times higher than for the commercial membrane and around 1.2 times higher than from SCM 5 wt.% MOR at the same operating temperature. However, with a higher mordenite content in the sprayed membranes, at 10 wt.% MOR, the power density at every temperature with 4 M was not much improved from the commercial one and additionally, at 20 wt.% and 30 wt.% MOR, the membrane performance was even worse.

With the 8 M methanol solution (Figure 12), 5 wt.% MOR membrane using the spraying method had the highest power density at around 7, 9, and 8 mW·cm⁻² at 30, 50, and 70 °C, respectively, around 2–2.3 times higher than for the commercial membrane. For the membranes with a high mordenite content, 10 wt.% had a very similar power density to that of the commercial membrane but 20 wt.% and 30 wt.% MOR performed poorly.

The improvement in the power density of the sprayed membranes may be the result of many factors, such as, a suitable operating temperature and methanol solution for the different membranes. Nafion mordenite composite membranes have shown superior performance to Nafion117 with a mordenite content around 5 wt.% as previously reported [43, 44, 46]. In this work, sprayed membrane had better performance than solution cast membrane at 5 wt.%, which

may have been due to the better mordenite distribution in the composite membrane as shown by the SEM and EDS images. This work showed that increasing the mordenite content to higher than 5 wt.% did not improve the cell performance, even though the membrane was prepared using the spraying method, for which the suitable mordenite content was 5 wt.% or the same as for use in the solution casting method [44].

Prior to this study, it was expected that with the spraying method, it may have been possible to increase the mordenite content and still maintain DMFC performance. This, however, was not the case as the results from 10 wt.% MOR were very similar to that of the commercially available product. The cell performance results from 20 wt.% and 30 wt.% were quite poor even though proton conductivity can be maintained at a higher value than 5 wt.% MOR though the methanol permeability increased. Apart from higher methanol permeability, the lower power density can also be attributed to fabricated membranes being very brittle and fragile leading to poor interfacial resistance between the membrane and the electrode for membrane electrode assemblies made from those membranes.

It is worth noting that the maximum power density in this work may be low when compared with results from other publications. There may be a number of reasons for this, for example, a low catalyst content in the electrodes and the setup of the DMFC testing units. However, in this work, commercial Nafion117 was used as a benchmark and it can be seen that the power density from composite membranes increased compared to the commercial Nafion117 and the sprayed and solution cast Nafion membranes without fillers that were tested using the same fuel cell setup.

Figure 10. Polarization and power density curves, respectively, of membranes with 2 M methanol concentration at various temperatures: (a) and (b) at 30 °C, (c) and (d) at 50 °C and (e) and (f) 70 °C.

Figure 11. Polarization and power density curves, respectively, of membranes with 4 M methanol concentration at various temperatures: (a) and (b) at 30 °C, (c) and (d) at 50 °C and (e) and (f) 70 °C.

Figure 12. Polarization and power density curves, respectively, of membranes with 8 M methanol concentration at various temperatures: (a) and (b) at 30 °C, (c) and (d) at 50 °C and (e) and (f) 70 °C.

Table 4. Maximum power densities obtained with composite membranes prepared using solution casting method (SCM) and spraying methods (SM) compared to commercial membrane (COMM) at 30 °C and various methanol concentrations.

Cell temperature at 30 °C			
Membrane sample	Methanol concentration		
	2 M	4 M	8 M
COMM	2.53	2.83	3.38
SCM	3.32	3.08	NA
SCM 5wt.% MOR	5.07	4.44	NA
SM	4.89	4.71	5.22
SM 5wt.% MOR	5.93	5.82	7.12
SM 10wt.% MOR	3.83	4.21	4.06
SM 20wt.% MOR	2.55	2.96	2.55
SM 30wt.% MOR	0.67	0.33	NA

Table 5. Maximum power densities obtained with composite membranes prepared using solution casting method (SCM) and spraying methods (SM) compared to commercial membrane (COMM) at 50 °C and various methanol concentrations.

Cell temperature at 50 °C			
Membrane sample	Methanol concentration		
	2 M	4 M	8 M
COMM	3.85	3.90	4.67
SCM	5.33	4.92	NA
SCM 5wt.% MOR	8.04	6.44	NA
SM	6.68	6.68	7.16
SM 5wt.% MOR	9.18	9.56	9.18
SM 10wt.% MOR	4.91	5.09	5.08
SM 20wt.% MOR	2.11	2.57	1.88
SM 30wt.% MOR	0.51	0.33	NA

Table 6. Maximum power densities obtained with composite membranes prepared using solution casting method (SCM) and spraying methods (SM) compared to commercial membrane (COMM) at 70 °C and various methanol concentrations.

Membrane sample	Cell temperature at 70 °C		
	Methanol concentration		
	2 M	4 M	8 M
COMM	3.73	4.44	3.38
SCM	7.35	6.01	NA
SCM 5wt.% MOR	9.09	7.70	NA
SM	7.62	7.20	7.60
SM 5wt.% MOR	10.80	10.70	7.94
SM 10wt.% MOR	5.48	4.71	4.77
SM 20wt.% MOR	1.68	1.55	0.99
SM 30wt.% MOR	0.30	0.18	NA

4. Conclusions

This work used a spraying method to prepare composite membranes as proton exchange membranes in DMFC. The spraying method improved the homogeneous dispersion of particles in the Nafion matrix and improved the filler distribution compared to the solution casting method as shown by SEM and EDX images. Sprayed composite membranes showed improvement in methanol permeability while maintaining proton conductivity with a mordenite content not higher than 5 wt.%. When the mordenite contents were increased to 20% and 30%, even though proton conductivity was maintained, methanol permeability was sacrificed. Consequently, 5 wt.% mordenite content with a sprayed membrane gave the best DMFC performance, while increasing the mordenite content only worsened the DMFC results, which could be contributed to higher methanol permeability and poor interfacial adhesion between the membranes and electrodes.

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References

- [1] Kakati N, Maiti J, Das G, Lee SH, Yoon YS. An approach of balancing the ionic conductivity and mechanical properties of PVA based nanocomposite membrane for DMFC by various crosslinking agents with ionic liquid. *International Journal of Hydrogen Energy*. 2015;40:7114-23.
- [2] Nacef M, Affoune AM. Comparison between direct small molecular weight alcohols fuel cells' and hydrogen fuel cell's parameters at low and high temperature. Thermodynamic study. *International Journal of Hydrogen Energy*. 2011;36:4208-19.
- [3] Kjeang E, Goldak J, Golriz MR, Gu J, James D, Kordesch K. Modeling methanol crossover by diffusion and electro-osmosis in a flowing electrolyte direct methanol fuel cell. *Fuel Cells*. 2005;5:486-98.
- [4] Kang K, Park S, Cho SO, Choi K, Ju H. Development of lightweight 200-W direct methanol fuel cell system for unmanned aerial vehicle applications and flight demonstration. *Fuel Cells*. 2014;14:694-700.
- [5] Abdul Rasheed RK, Liao Q, Caizhi Z, Chan SH. A review on modelling of high temperature proton exchange membrane fuel cells (HT-PEMFCs). *International Journal of Hydrogen Energy*. 2017;42:3142-65.
- [6] Li X. *Principles of Fuel Cells*. Washington: Taylor & Francis Inc; 2005.
- [7] Müller M, Kimiaie N, Glösen A. Direct methanol fuel cell systems for backup power – Influence of the standby procedure on the lifetime. *International Journal of Hydrogen Energy*. 2014;39:21739-45.

840 [8] Furukawa K, Makino K, Okajima K, Minakuchi H, Okano Y, Sudoh M. Intelligent structure
841 design of membrane cathode assembly for direct methanol fuel cell. *International Journal of*
842 *Energy Research*. 2005;29:1073-82.

843 [9] Cai W, Fan K, Li J, Ma L, Xu G, Xu S, et al. A bi-functional polymeric nano-sieve Nafion
844 composite membrane: Improved performance for direct methanol fuel cell applications.
845 *International Journal of Hydrogen Energy*. 2016;41:17102-11.

846 [10] Ahmad H, Kamarudin SK, Hasran UA, Daud WRW. Overview of hybrid membranes for
847 direct-methanol fuel-cell applications. *International Journal of Hydrogen Energy*. 2010;35:2160-
848 75.

849 [11] Wan H, Yao Y, Liu J, You Y, Li X, Shao K, et al. Engineering mesoporosity promoting
850 high-performance polymer electrolyte fuel cells. *International Journal of Hydrogen Energy*.
851 2017;42:21294-304.

852 [12] Li C, Yang Z, Liu X, Zhang Y, Dong J, Zhang Q, et al. Enhanced performance of sulfonated
853 poly (ether ether ketone) membranes by blending fully aromatic polyamide for practical
854 application in direct methanol fuel cells (DMFCs). *International Journal of Hydrogen Energy*.
855 2017;42:28567-77.

856 [13] Jung S. High-performance direct methanol fuel cell with optimized membrane electrode
857 assembly: A theoretical approach. *International Journal of Hydrogen Energy*. 2016;41:9022-34.

858 [14] Colpan CO, Ouellette D, Glösen A, Müller M, Stolten D. Reduction of methanol crossover
859 in a flowing electrolyte-direct methanol fuel cell. *International Journal of Hydrogen Energy*.
860 2017;42:21530-45.

861 [15] Zhang Z, Désilets F, Felice V, Mecheri B, Licoccia S, Tavares AC. On the proton
862 conductivity of Nafion–Faujasite composite membranes for low temperature direct methanol fuel
863 cells. *Journal of Power Sources*. 2011;196:9176-87.

864 [16] Kim D-J, Hwang H-Y, Jung S-b, Nam S-Y. Sulfonated poly(arylene ether
865 sulfone)/Laponite-SO₃H composite membrane for direct methanol fuel cell. *Journal of Industrial*
866 *and Engineering Chemistry*. 2012;18:556-62.

867 [17] Li C, Sun G, Ren S, Liu J, Wang Q, Wu Z, et al. Casting Nafion–sulfonated organosilica
868 nano-composite membranes used in direct methanol fuel cells. *Journal of Membrane Science*.
869 2006;272:50-7.

870 [18] Wang J, Zheng X, Wu H, Zheng B, Jiang Z, Hao X, et al. Effect of zeolites on
871 chitosan/zeolite hybrid membranes for direct methanol fuel cell. *Journal of Power Sources*.
872 2008;178:9-19.

873 [19] Luo Q, Zhang H, Chen J, You D, Sun C, Zhang Y. Preparation and characterization of
874 Nafion/SPEEK layered composite membrane and its application in vanadium redox flow battery.
875 *Journal of Membrane Science*. 2008;325:553-8.

876 [20] Li C, Xiao L, Jiang Z, Tian X, Luo L, Liu W, et al. Sulfonic acid functionalized graphene
877 oxide paper sandwiched in sulfonated poly(ether ether ketone): A proton exchange membrane
878 with high performance for semi-passive direct methanol fuel cells. *International Journal of*
879 *Hydrogen Energy*. 2017;42:16731-40.

880 [21] Zakil FA, Kamarudin SK, Basri S. Modified Nafion membranes for direct alcohol fuel cells:
881 An overview. *Renewable and Sustainable Energy Reviews*. 2016;65:841-52.

882 [22] Yen C-Y, Lee C-H, Lin Y-F, Lin H-L, Hsiao Y-H, Liao S-H, et al. Sol-gel derived
883 sulfonated-silica/Nafion® composite membrane for direct methanol fuel cell. *Journal of Power*
884 *Sources*. 2007;173:36-44.

885 [23] Claude Lamy AL, V. LeRhun, Fabien Delime, Christophe Coutanceau, Jean-Michel L.
886 Recent advances in the development of direct alcohol fuel cell (DAFC). *Journal of Power*
887 *Sources*. 2002;105:283-96.

888 [24] Kim DJ, Lee HJ, Nam SY. Sulfonated poly(arylene ether sulfone) membranes blended with
889 hydrophobic polymers for direct methanol fuel cell applications. *International Journal of*
890 *Hydrogen Energy*. 2014;39:17524-32.

891 [25] Zhong S, Cui X, Gao Y, Liu W, Dou S. Fabrication and properties of poly(vinyl alcohol)-
892 based polymer electrolyte membranes for direct methanol fuel cell applications. *International*
893 *Journal of Hydrogen Energy*. 2014;39:17857-64.

894 [26] Larminie J. *Fuel cell systems explained*. 2nd ed.. ed. New York: New York : J. Wiley; 2003.

895 [27] Bagotskiĭ VS. *Fuel cells : problems and solutions*. 2nd ed.. ed. Hoboken, N.J.: Hoboken,
896 N.J. : Wiley; 2012.

897 [28] Escudero-Cid R, Montiel M, Sotomayor L, Loureiro B, Fatás E, Ocón P. Evaluation of
898 polyaniline-Nafion® composite membranes for direct methanol fuel cells durability tests.
899 *International Journal of Hydrogen Energy*. 2015;40:8182-92.

- [29] Parthiban V, Akula S, Sahu AK. Surfactant templated nanoporous carbon-Nafion hybrid membranes for direct methanol fuel cells with reduced methanol crossover. *Journal of Membrane Science*. 2017;541:127-36.
- [30] Sha Wang L, Nan Lai A, Xiao Lin C, Gen Zhang Q, Mei Zhu A, Lin Liu Q. Orderly sandwich-shaped graphene oxide/Nafion composite membranes for direct methanol fuel cells. *Journal of Membrane Science*. 2015;492:58-66.
- [31] Zheng J, He Q, Liu C, Yuan T, Zhang S, Yang H. Nafion-microporous organic polymer networks composite membranes. *Journal of Membrane Science*. 2015;476:571-9.
- [32] Li X, Roberts EPL, Holmes SM, Zholobenko V. Functionalized zeolite A-nafion composite membranes for direct methanol fuel cells. *Solid State Ionics*. 2007;178:1248-55.
- [33] Cui Y, Baker AP, Xu X, Xiang Y, Wang L, Lavorgna M, et al. Enhancement of Nafion based membranes for direct methanol fuel cell applications through the inclusion of ammonium-X zeolite fillers. *Journal of Power Sources*. 2015;294:369-76.
- [34] Rambabu G, Nagaraju N, Bhat SD. Functionalized fullerene embedded in Nafion matrix: A modified composite membrane electrolyte for direct methanol fuel cells. *Chemical Engineering Journal*. 2016;306:43-52.
- [35] Yildirim MH, Curdòs AR, Motuzas J, Julbe A, Stamatialis DF, Wessling M. Nafion®/H-ZSM-5 composite membranes with superior performance for direct methanol fuel cells. *Journal of Membrane Science*. 2009;338:75-83.
- [36] Xu J, Ni H, Wang S, Wang Z, Zhang H. Direct polymerization of a novel sulfonated poly(arylene ether ketone sulfone)/sulfonated poly(vinylalcohol) crosslinked membrane for direct methanol fuel cell applications. *Journal of Membrane Science*. 2015;492:505-17.
- [37] Hoogers G. *Fuel cell technology handbook*. Boca Raton, Fla.: Boca Raton, Fla. : CRC Press; 2003.
- [38] Prapainainar C, Kanjanapaisit S, Kongkachuichay P, Holmes SM, Prapainainar P. Surface modification of mordenite in Nafion composite membrane for direct ethanol fuel cell and its characterizations: Effect of types of silane coupling agent. *Journal of Environmental Chemical Engineering*. 2016;4:2637-46.
- [39] Wang Y, Jiang Z, Li H, Yang D. Chitosan membranes filled by GPTMS-modified zeolite beta particles with low methanol permeability for DMFC. *Chemical Engineering and Processing: Process Intensification*. 2010;49:278-85.

931 [40] Yoonoo C. Development of Nafion-Mordenite Composite Membranes for Direct Methanol
 932 Fuel Cell Application. Manchester, UK: The University of Manchester 2010.

933 [41] Peron J, Mani A, Zhao X, Edwards D, Adachi M, Soboleva T, et al. Properties of Nafion®
 934 NR-211 membranes for PEMFCs. *Journal of Membrane Science*. 2010;356:44-51.

935 [42] Jung H-Y, Kim JW. Role of the glass transition temperature of Nafion 117 membrane in the
 936 preparation of the membrane electrode assembly in a direct methanol fuel cell (DMFC).
 937 *International Journal of Hydrogen Energy*. 2012;37:12580-5.

938 [43] Yoonoo C, Dawson CP, Roberts EPL, Holmes SM. Nafion®/mordenite composite
 939 membranes for improved direct methanol fuel cell performance. *Journal of Membrane Science*.
 940 2011;369:367-74.

941 [44] Prapainainar P, Theampetch A, Kongkachuichay P, Laosiripojana N, Holmes SM,
 942 Prapainainar C. Effect of solution casting temperature on properties of nafion composite
 943 membrane with surface modified mordenite for direct methanol fuel cell. *Surface and Coatings*
 944 *Technology*. 2015;271:63-73.

945 [45] Xing D, He G, Hou Z, Ming P, Song S. Properties and morphology of
 946 Nafion/polytetrafluoroethylene composite membrane fabricated by a solution-spray process.
 947 *International Journal of Hydrogen Energy*. 2013;38:8400-8.

948 [46] Prapainainar P, Du Z, Kongkachuichay P, Holmes SM, Prapainainar C. Mordenite/Nafion
 949 and analcime/Nafion composite membranes prepared by spray method for improved direct
 950 methanol fuel cell performance. *Applied Surface Science*. 2017;421:24-41.

951 [47] Sun Y-M, Huang W-F, Chang C-C. Spray-coated and solution-cast ethylcellulose
 952 pseudolatex membranes. *Journal of Membrane Science*. 1999;157:159-70.

953 [48] Tricoli V, Nannetti F. Zeolite–Nafion composites as ion conducting membrane materials.
 954 *Electrochimica Acta*. 2003;48:2625-33.

955 [49] Du Z. Improvement of Nafion Composite Membrane for Direct Methanol Fuel Cell: Effect
 956 of Analcime and Mordenite Addition and Fabrication Method. Bangkok: Kasetsart University;
 957 2016.

958 [50] Moore RB, Martin CR. Chemical and morphological properties of solution-cast
 959 perfluorosulfonate ionomers. *Macromolecules*. 1988;21:1334-9.

960 [51] Jin Y, Qiao S, Zhang L, Xu ZP, Smart S, Costa JCDd, et al. Novel Nafion composite
 961 membranes with mesoporous silica nanospheres as inorganic fillers. *Journal of Power Sources*.
 962 2008;185:664-9.

963 [52] Shrotri N, Barbora L, Verma A. Neodymium triflate modified nafion composite membrane
 964 for reduced alcohol permeability in direct alcohol fuel cell. *International Journal of Hydrogen*
 965 *Energy*. 2011;36:14907-13.

966 [53] Wu H, Zheng B, Zheng X, Wang J, Yuan W, Jiang Z. Surface-modified Y zeolite-filled
 967 chitosan membrane for direct methanol fuel cell. *Journal of Power Sources*. 2007;173:842-52.

968 [54] Robson H. Chapter 68 - MOR Mordenite Si(90), Al(10). *Verified Syntheses of Zeolitic*
 969 *Materials*. Amsterdam: Elsevier Science; 2001. p. 212-3.

970 [55] Byun SC, Jeong YJ, Park JW, Kim SD, Ha HY, Kim WJ. Effect of solvent and crystal size
 971 on the selectivity of ZSM-5/Nafion composite membranes fabricated by solution-casting method.
 972 *Solid State Ionics*. 2006;177:3233-43.

973 [56] Lin H, Zhao C, Jiang Y, Ma W, Na H. Novel hybrid polymer electrolyte membranes with
 974 high proton conductivity prepared by a silane-crosslinking technique for direct methanol fuel
 975 cells. *Journal of Power Sources*. 2011;196:1744-9.

976 [57] Larkin PJ. Chapter 6 - IR and Raman Spectra–Structure Correlations: Characteristic Group
 977 Frequencies. *Infrared and Raman Spectroscopy (Second Edition)*: Elsevier; 2018. p. 85-134.

978 [58] Nur H, Lee Kee G, Hamdan H, Indra Mahlia TM, Efendi J, Cornelis Metselaar HS.
 979 Organosulfonic acid functionalized zeolite ZSM-5 as temperature tolerant proton conducting
 980 material. *International Journal of Hydrogen Energy*. 2012;37:12513-21.

981 [59] Kreuer K-D, Paddison SJ, Spohr E, Schuster M. Transport in proton conductors for fuel-cell
 982 applications: simulations, elementary reactions, and phenomenology. *Chemical Reviews*.
 983 2004;104:4637-78.

984 [60] Tai CC, Chen CL, Liu CW. Computer simulation to investigate proton transport and
 985 conductivity in perfluorosulfonate ionomeric membrane. *International Journal of Hydrogen*
 986 *Energy*. 2017;42:3981-6.

987 [61] Morris DR, Sun X. Water-sorption and transport properties of Nafion 117 H. *Journal of*
 988 *Applied Polymer Science*. 1993;50:1445-52.

989 [62] Kim DS, Park HB, Rhim JW, Moo Lee Y. Preparation and characterization of crosslinked
 990 PVA/SiO₂ hybrid membranes containing sulfonic acid groups for direct methanol fuel cell
 991 applications. *Journal of Membrane Science*. 2004;240:37-48.

992 [63] Li L, Zhang J, Wang Y. Sulfonated poly(ether ether ketone) membranes for direct methanol
 993 fuel cell. *Journal of Membrane Science*. 2003;226:159-67.

994 [64] Wei Z, Su K, Sui S, He A, Du S. High performance polymer electrolyte membrane fuel cells
 995 (PEMFCs) with gradient Pt nanowire cathodes prepared by decal transfer method. *International*
 996 *Journal of Hydrogen Energy*. 2015;40:3068-74.

997 [65] Kongkachuichay P, Pimprom S. Nafion/Analcime and Nafion/Faujasite composite
 998 membranes for polymer electrolyte membrane fuel cells. *Chemical Engineering Research and*
 999 *Design*. 2010;88:496-500.

1000 [66] López-Chávez E, Martínez-Magadán JM, Oviedo-Roa R, Guzmán J, Ramírez-Salgado J,
 1001 Marín-Cruz J. Molecular modeling and simulation of ion-conductivity in chitosan membranes.
 1002 *Polymer*. 2005;46:7519-27.

1003 [67] Agmon N. The Grotthuss mechanism. *Chemical Physics Letters*. 1995;244:456-62.

1004 [68] Kreuer K-D. Proton Conductivity: Materials and Applications. *Chemistry of Materials*.
 1005 1996;8:610-41.

1006 [69] Baglio V, Arico AS, Blasi AD, Antonucci PL, Nannetti F, Tricoli V, et al. Zeolite-based
 1007 composite membranes for high temperature direct methanol fuel cells. *Journal of Applied*
 1008 *Electrochemistry*. 2005;35:207-12.

1009 [70] Lavorgna M, Sansone L, Scherillo G, Gu R, Baker AP. Transport Properties of Zeolite Na-
 1010 X–Nafion Membranes: Effect of Zeolite Loadings and Particle Size. *Fuel Cells*. 2011;11:801-13.

1011 [71] Bakangura E, Wu L, Ge L, Yang Z, Xu T. Mixed matrix proton exchange membranes for
 1012 fuel cells: State of the art and perspectives. *Progress in Polymer Science*. 2016;57:103-52.

1013 [72] Libby B, Smyrl WH, Cussler EL. Polymer-zeolite composite membranes for direct
 1014 methanol fuel cells. *AIChE Journal*. 2004;49:991-1001.

1015 [73] Arbizzani C, Donnadio A, Pica M, Sganappa M, Varzi A, Casciola M, et al. Methanol
 1016 permeability and performance of Nafion–zirconium phosphate composite membranes in active
 1017 and passive direct methanol fuel cells. *Journal of Power Sources*. 2010;195:7751-6.

1018 [74] Lufrano F, Baglio V, Staiti P, Antonucci V, Arico AS. Performance analysis of polymer
1019 electrolyte membranes for direct methanol fuel cells. Journal of Power Sources. 2013;243:519-
1020 34.
1021
1022