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Mordenite/Nafion and Analcime/Nafion Composite Membranes Prepared by Spray Method for Improved Direct Methanol Fuel Cell Performance

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Highlight

- Mordenite and analcime were used as fillers in Nafion composite membranes for DMFC.
- The composite membranes were fabricated by spray method.
- Methanol permeability was reduced up to 2-3 times using the composite membranes.
- Mordenite/Nafion membrane showed 2 times higher DMFC performance than Nafion 117.

Abstract

The aim of this work was to improve proton exchange membranes (PEMs) used in direct methanol fuel cells (DMFCs). A membrane with a high proton conductivity and low methanol permeability was required. Zeolite filler in Nafion (NF matrix) composite membranes were prepared using two types of zeolite, mordenite (MOR) and analcime (ANA). Spray method was used to prepare the composite membranes, and properties of the membranes were investigated: mechanical properties, solubility, water and methanol uptake, ion-exchange capacity (IEC), proton conductivity, methanol permeability, and DMFC performance. It was found that MOR filler showed higher performance than ANA. The MOR/Nafion composite membrane gave better properties than ANA/Nafion composite membrane, including a higher proton conductivity and a methanol permeability that was 2 – 3 times lower. The highest DMFC performance ($10.75 \text{ mW} \cdot \text{cm}^{-2}$) was obtained at 70°C and with 2 M methanol, with a value 1.5 times higher than that of ANA/Nafion composite membrane and two times higher than that of commercial Nafion 117 (NF 117).

Keywords: Composite membrane; direct methanol fuel cell; spray method; mordenite; analcime; methanol permeability.

1. Introduction

Fuel cell technology has been developing rapidly because of a number of advantages that it possesses compared to conventional power sources, such as internal combustion engines or batteries. Fuel cells have higher energy efficiency than diesel or gas engines, and in using

them, there is no pollution caused, as there is in burning fossil fuels, and no toxic by-product. Therefore, use of fuel cell can reduce greenhouse gases [1, 2].

Direct methanol fuel cells (DMFCs) have been an attractive power source for portable electronics applications such as cellular phones, laptop computers, and personal digital assistants [3]. Methanol is used as a fuel source because of its high energy density, low cost, and the fact that it is easily handled and stored. DMFCs work at low and intermediate temperatures and are fed with a dilute solution of methanol [4].

Perfluorosulfonic acid membranes with a hydrophobic backbone and hydrophilic sulfonic acid side chain, such as Nafion, are currently used as proton exchange membranes. This is due to their high proton conductivity, chemical and thermal stability, and mechanical strength [5-8]. Nevertheless, DMFC has some severe problems. One of them is alcohol crossover through the membrane electrolyte resulting in waste of fuel, reduction of methanol-oxygen mixed potential at the cathode, and a serious decrease in fuel cell performance [1, 7, 9].

In order to overcome these problems, a large number of methods have been developed to reduce methanol crossover in DMFC. Optimization has focused on operating parameters such as temperature [9], composition of the cathode feed [1, 2, 10], catalyst loading [3] and membrane thickness [11]. Many researchers have developed new composite membranes and modified the existing materials to alter their transport properties. The modification of Nafion has been studied by employing inorganic filler materials such silica, TiO_2 , and zeolite.

Many researchers have selected inorganic materials to improve the water retention in the membrane and also to decrease the alcohol crossover [12-15]. Zeolite is a well-defined microporous structure of crystalline aluminosilicates containing silicon and oxygen in its framework. It has some characteristics that are suitable for DMFC. The regular porous structure of zeolite can also reduce alcohol permeation. In addition, the high surface acidity of zeolite provides a high proton conductivity.

Some examples of polymer-zeolite composite membranes for fuel cells are Nafion-Fe-silicate-1 membranes [16], Nafion-H-ZSM-5 membranes [14], Nafion-chabazite membranes [17], PVA-mordenite composite membranes [18], Nafion-mordenite hybrid membranes [19], sulfonated poly(ether ether ketone)/Analcime composite membrane [20], and Nafion/Analcime [21].

Among the various kinds of zeolite, mordenite (MOR) and analcime (ANA) have been great candidates for fabricating composite membranes. They are hydrophilic substances with molecular sieve properties [5, 12], preferring to adsorb water to alcohol and providing a good

proton pathway through the membrane while blocking the diffusion path of alcohol inside a Nafion composite membrane. In addition, mordenite and analcime are stable in acid and have high temperature tolerance. In our previous work, Yoonoo and coworkers [5] prepared Nafion/mordenite composite membrane to reduce methanol diffusion across the DMFC. The produced membranes exhibited reductions in methanol permeability of 21.62% and 4.27% at 30 °C and 70 °C, respectively, compared to a recast Nafion membrane. Kongkachuichay and coworkers [21] used Analcime and Faujasite as the zeolite in Nafion/zeolite composite membranes for PEMFCs. The proton conductivity of the Nafion/ANA composite membrane was enhanced 11 times at room temperature and 6.8 times at 80 °C, compared to Nafion membrane. It was reported that this enhancement might come from hydration inside the 3D channels of zeolite, with the hydrated water improving the proton motion or hydronium ion motion via the exchange of protons between hydronium ion and water molecules.

In this study, Nafion composite membranes with two fillers, mordenite and analcime, were fabricated by spray method. The properties of membranes with different fillers were studied and compared. The obtained composite membranes were characterized using SEM and mechanical test, and in term of solubility, water uptake, ion-exchange capacity (IEC), proton conductivity, methanol uptake, and methanol permeability. The DMFC performance test was also performed.

2. Experimental

2.1 Materials

Sodium aluminate (Al_2O_3 50-56 %, Na_2O 40-45 %), 3-mercaptopropyl triethoxysilane (MPTES) and hexamethylenimine (98.0 %) were purchased from Sigma-Aldrich. Sodium silicate (neutral solution QP) was purchased from Panreac. Sodium hydroxide (97.0 %), aluminumtrichloride (95.0%), and hydrogen peroxide (35 wt. %) were purchased from Ajax Finechem. A 20 wt. % Nafion solution was purchased from Ion Power. Sulfuric acid, ethanol, methanol, N, N-dimethylformamide, dichloromethane, ammonium chloride, toluene were purchased from ACI Labscan. De-ionized water was used throughout the study.

2.2 Methods

2.2.1 Synthesis of mordenite and analcime

Two types of zeolite were synthesized in this work: mordenite (MOR) and analcime (ANA). The corresponding synthesis procedures are described below;

2.2.1.1 MOR synthesis

The synthesis method was developed from the method of Corma and coworkers, using hexamethylenimine (HMI) as a template mixed with sodium silicate (Na_2SiO_3) as a silica source, sodium aluminate (NaAlO_2) as an alumina source, and sodium hydroxide (NaOH) as an alkali source [22]. The crystallization occurred in an autoclave operated hydrothermally and under agitation as follows. First, a mixture of 0.92 g NaAlO_2 and 0.60 g NaOH was dissolved in 124.2 ml of H_2O . Then, 7.61 g HMI and 25.639 g Na_2SiO_3 were added to the solution using vigorous stirring for 30 min. After that, the resulting gels were introduced into 60 ml of PTFE-lined stainless-steel autoclaves, rotated at 60 rpm, and heated at 170 °C for 24 h. After quenching the autoclaves in cold water, the solution was centrifuged. A portion of the solids was calcined in air at 580 K for 5 h to obtain MOR-Na.

2.2.1.2 ANA synthesis

The synthesis method was developed from that of Kim et al. using materials similar to the first method but without HMI as the template [23]. The crystallization occurred in an autoclave with hydrothermal system as follows: 4 g of water was mixed with 1.9 g of NaOH and stirred until the solid dissolved. Then, 1.43 g of NaAlO_2 was added into the solution and stirred until it too was dissolved. After that, 64.5 ml of water and 19.94 g of Na_2SiO_3 were added into the solution and stirred for 30 min. The resulting gels were introduced into PTFE-lined stainless-steel autoclaves and heated at 170 °C for 24 h. After quenching the autoclaves in cold water, the solution was filtered and washed until pH was less than 10 and dried at 100 °C to obtain ANA-Na.

2.2.2 Grinding of MOR and ANA

Grinding was used to reduce the particle size and obtain a homogeneous size of particles. The grinding procedure can be described in the following steps. First, 4 g of MOR (or ANA) and 10 ml of 0.5 mm zirconia ball grinding media were added into a container. Then, 15 ml distilled water was added to the container. Grinding speed was fixed by speed control. The sample was ground for 200 min to obtain a homogeneous distribution of particles of the smallest possible size.

2.2.3 Protonating of MOR and ANA

MOR and ANA surfaces were transformed into H^+ form in order to provide ionic paths for H^+ to travel from anode to cathode. To this end, MOR-Na and ANA-Na were treated to change Na^+ to H^+ . The protonating method followed the procedure of Zanjanchi et al. [24]. The protonating procedure can be described as follows. First, 2 g of the MOR-Na (or ANA-Na) powder was stirred in 100 ml of 1 M NH_4Cl solution at room temperature for 24 h. At this stage, Na^+ was replaced by NH_4^+ and MOR-Na (or ANA-Na) became MOR- NH_4 (or ANA- NH_4) [25]. The suspension was subsequently vacuum filtered. Then, the sample was washed with deionized water and dried at 105 °C. MOR- NH_4 (or ANA- NH_4) was then calcined in a furnace at 550 °C for 5 h with a heating rate of 2 °C·min⁻¹. At this point, NH_3 was released from NH_4^+ and left H^+ on the surface. In this stage, MOR- NH_4 was converted to MOR-H (ANA- NH_4 was converted to ANA-H).

2.2.4 Functionalization of zeolites

In order to enhance the properties of the interface between polymer matrix and zeolite fillers, surface modification of zeolite was required by using silane coupling agent. The silane coupling agent used in this work was 3-mercaptopropyltriethoxysilane (MPTES). Zeolites before and after functionalization were investigated to ensure successful modification. The procedure of surface modification by MPTES as in the following steps. Catalyst solution was prepared by dissolving 1g of aluminum (III) chloride in 20 ml of ethanol at 70 °C until completely dissolved. Then 20 ml of toluene was added. A silane solution was prepared by mixing 4 ml of MPTES with 40 ml of toluene and stirred for 30 min. Then, 5 ml of the catalyst solution was mixed with the silane solution, followed by the addition of 2 g of MOR-H (or ANA-H) to the mixture. The resulting solution was refluxed at 110 °C for 24 h under stirring condition. From the solution, the zeolite was separated by using a centrifuge (6000 rpm), and it was then rinsed with ethanol and deionized water to remove the silane residues. The filtrated solid was dried at 105 °C for 24 h. Functionalized zeolite was oxidized by 30 wt. % H_2O_2 under stirring condition for 24 h at room temperature in order to convert the $-SH$ groups into $-SO_3$ groups at the surface of the zeolites. MOR after surface treatment was called MOR-MPTES and ANA after surface treatment was referred to as ANA-MPTES.

2.2.5 Composite membrane preparation

The composite membranes were fabricated by spray method, which was developed based on the spray-coated technique utilized by Sun and coworkers [26]. The spray procedure consisted of the following steps. First, the required spraying gun was connected with a 2 barg nitrogen gas system. Using a temperature controlled, the mold template temperature was set to 100 °C. Membrane solution was prepared by following the procedure from our previous work [27]. The solution was poured into the spray gun container and sprayed on the hot template; the resulting membrane dried immediately after been sprayed. The template was cooled at ambient temperature. Several drops of deionized water were added at the contact point between the membrane and the template to assist in the removing of the membrane. Subsequently, the membrane was removed from the template and then heated to 150°C for 4 h for annealing. The average thickness of the fabricated membranes was measured using a micrometer at nine different points across the membrane.

2.3 MOR and ANA Characterization

The particle size of MOR and ANA were examined by using a Mastersizer 2000 (Malvern Instruments Ltd.). Meanwhile, MOR and ANA crystalline structures were characterized using X-ray diffractometry obtained with a BRUKER Advance A25 equipped with Cu-K α radiation (1.5418 Å). These XRD patterns were obtained at 2 θ between 5° and 40°. Fourier transform infrared spectrophotometry (FTIR, BRUKER TENSOR 27) was used to investigate the functional groups on MOR and ANA before and after surface modification at wave numbers of 400 – 4,000 cm⁻¹. Thermogravimetric analysis (TGA, SDT 2960) was used to determine the quantity of silane coupling agent modified on MOR and ANA. Testing was performed in air with a flow rate of 100 cm³min⁻¹, a heating rate of 10 °C min⁻¹, and a temperature range of 25 – 1,100 °C. Surface area and pore size distribution of MOR and ANA were investigated by N₂ sorption measurement using Autosorb-1. The sample was degassed at 150 °C for 15 h under vacuum before N₂ sorption at 77 K. The morphology of composite membranes were investigated by scanning electron microscope (SEM, FEI QUANTA 450) equipped with Oxford X-Max EDX detector. Using a universal testing machine (Instron 4206), the mechanical properties of membranes were investigated. Each sample was cut into a size of 10 mm×50 mm with a gauge length of 30 mm and tested according to ASTM D882. A total of five specimens were tested for each sample under dry condition at a rate of 5 mm/min.

2.4 Membrane characterization

2.4.1 Solubility

Solubility is an important indicator that reflects the chemical resistance of the membrane. The solubility of membrane was determined by following the procedure of Moore and Martin [28]. First, 50 mg of the membrane was added to 10 ml of 50:50 methanol-water solution and sonicated in an ultrasonic bath for 1 h. The water in the ultrasonic bath was changed every 30 min to retain room temperature. To remove undissolved solid, the solution was filtered through Whatman No.1 filter paper. The obtained solid residue after evaporation at 100 °C was weighed, and the percent soluble was calculated by equation (1):

$$\% \text{ Solubility} = \frac{\text{weight of residue}}{\text{weight of membrane}} \times 100\% \quad (1)$$

2.4.2 Water uptake

Water uptake was used to investigate the behavior of the composite membrane when put in contact with water. It was determined by measuring the weight change between dry and wet membranes. The procedure from Theampetch's work and Kongkachuichay's work [20, 29] was followed. Membrane samples were dried at 80 °C in a vacuum oven for 24 h before the dry weight was measured. Then the dry membranes were kept in a desiccator. The samples were soaked in deionized water at room temperature for 24 h. After removal of the excess moisture by Whatman No. 1 filter paper, the samples were reweighed to obtain the wet weight, and % water uptake was calculated from equation (2)

$$\% \text{ Water uptake} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100\% \quad (2)$$

where wet weight (g) and dry weight (g) are the weights of the fully hydrated and the anhydrous membranes, respectively.

The alcohol uptake was examined using a similar procedure: by soaking the membrane of known weight in methanol of a known concentration for 24 h.

2.4.3 Ion-exchange capacity

Representing the quantity of acid equivalents per gram of polymer [20, 29], ion-exchange capacity is an indirect and reliable approximation of the proton conductivity of the membranes [15]. Here, the ion-exchange capacity of the membrane was determined by an acid-based titration method. The procedure of Theampetch's work [29] was followed. First, 50 mg

samples of treated membrane were immersed in 10 ml of NaCl solution (1 M) for 24 h to replace all H^+ with Na^+ . The solution was titrated with 0.01 M NaOH using phenolphthalein as an indicator to determine the amount of H^+ in the solution. The ion-exchange capacity was calculated using equation (3):

$$IEC = \frac{C_{NaOH} V_{NaOH}}{M_{dry}} \quad (3)$$

where C_{NaOH} is the concentration of NaOH (M), V_{NaOH} is the volume of NaOH used in the titration (ml), and M_{dry} is the weight of the dry membrane (g).

2.4.4 Proton conductivity

The proton conductivity test using two-electrode method is a widely used method for measuring membrane conductivity in the transverse direction. The measurement was done under potentiostatic conditions, that is, a small potential perturbation was applied to the cell. In this work, the proton conductivity was characterized at different temperatures. The electrolyte container was surrounded by a water jacket to ensure a constant temperature during the measurement. Before measurement, the fabricated membrane specimens were treated by boiling in deionized water, then in 5 wt.% of H_2O_2 , subsequently, in 1 M H_2SO_4 solution, and finally in deionized water. Consequently, the membranes were immersed in 1 M H_2SO_4 for at least 24 h before prior to the measurement. Each membrane was measured nine times. The procedure followed was that of Theampetch's work [29]. First, 20 ml of 1 M H_2SO_4 was added into the electrolyte container. The potentiostat analyzer was set at a frequency from 1 mHz to 100 Hz and at an amplitude of 5 mV. It was set up by connecting the counter electrode to the reference electrode and the sample to the working electrode. The membrane was placed between the two electrodes. The data was collected in a Nyquist Z' vs Z'' plot. With all of the above, the proton conductivity (σ) was calculated using equation (4):

$$\sigma = \frac{d}{RA} \quad (4)$$

where d is the membrane thickness (cm), R is the membrane resistance (Ohm), and A is the cross-sectional area of electrode (cm^2). In this experiment, the resistance of each membrane was

measured for three points, with each point being measured and three times making a total of nine measurement for each membrane.

2.4.5 Alcohol permeability

In this work, diffusion technique was used. The feed side contained 1M methanol, and the permeate side contained water. Methanol diffused across the membrane due to the concentration gradient. The methanol concentration caused by the crossover in the permeate side was measured as a function of time. The diffusion cell consisted of a feed compartment and a permeate compartment. On the feed side, a 2000 ml tank of methanol was connected to the diffusion cell by plastic tubing, and the methanol solution was circulated by a centrifugal pump. On the permeate side, a bottle containing 250 ml of deionized water was connected with the cell, and the dilute solution was circulated by a centrifugal pump. Before measurement, the membrane was treated and kept in deionized water for 24 h. The hydrated membrane was inserted in the diffusion cell with sealing gaskets to ensure that there was no leakage. The cell was bolted together and connected to methanol solution tank (2000 ml) and deionized water tank (250 ml). To control the temperature, the feed and permeate were then placed in the water bath. At the beginning of the operation, methanol solution was fed to the feed size for 5 min, then the pump on permeate side was switch on. Consequently, the first 1 ml sample was collected by a pipette from the permeate side. Subsequently, samples were collected and kept in glass vials at 5, 30, 60 and 90 min, then they were analyzed by GC for the methanol content. The rate of methanol permeation (P , cm^2s^{-1}) was calculated using equation (5):

$$P = \frac{KVL}{SC_{A0}} \quad (5)$$

where K is the slope of the curve of the concentration in the permeate compartment vs. time plot ($\text{mol cm}^{-3}\text{s}^{-1}$), V is the volume of the permeate compartment (cm^3), S is the membrane area (cm^2), L is the membrane thickness (cm), and C_{A0} is the initial concentration of methanol in the feed compartment (mol cm^{-3}).

The operation temperature was varied as so to be either 30 °C or 70 °C.

2.4.6 Membrane electrode assembly preparation and DMFC performance test

An assembly of anode, membrane, and cathode was arranged for a hot-pressing process. The assembly was sandwiched between two backing plates called the membrane electrode

assembly (MEA). Deionized water was continuously fed to both sides of the MEA and the cell was kept at 80°C ensuring fully hydrated membrane in the MEA.

For the DMFC performance test, methanol solution was delivered to the anode side of the fuel cell by a peristaltic pump. Air was supplied on the cathode side, the air flow rate being controlled by an air flow meter. The potential and current were monitored by an ammeter and a voltmeter, respectively. An external power supply was used for controlling current flowing through the testing unit, the operative temperature was controlled by a temperature controller conjunction with a thermocouple and electric heaters. The membrane area was 4.5 cm × 4.5 cm. Pt-Ru/Carbon paper electrode (2 mg cm⁻²) was used as the anode, and 60% Pt/Carbon paper electrode (0.5 mg cm⁻²) was used as cathode. An air flowrate of 1 L·min⁻¹ and a methanol solution feed rate of 5 ml·min⁻¹ were also used.

3. Results and discussion

After preparing and characterizing the composite membrane, the results were separated to two sections: characterization of MOR and ANA and characterization of membranes.

3.1 Characterization of MOR and ANA

In this section, synthesized MOR and ANA after MPTES surface modification were characterized in terms of particle size, surface area, pore volume, XRD, FTIR, and TGA.

3.1.1 The particle sizes of MOR and ANA

The particle sizes of the synthesized MOR and ANA before and after grinding were measured by using a Mastersizer 2000 (Malvern Instruments Ltd.). The grinding method is popular and widely used in particle reduction due to its simplicity and efficiency. In the process of wet grinding, particles were ground in slurry form to break apart the genuine particles. Additionally, the wet grinding method can produce submicron-size particles and can protect agglomeration of particles [29]. The smaller the particle as a filler in membrane fabrication, the more uniformly dispersed is the membrane matrix obtained. MOR-s and ANA-s represent MOR and ANA as received from the synthesis and before grinding, while MOR and ANA represent MOR and ANA after grinding. The particle size distribution of MOR before grinding was trimodal with peaks in the ranges of 0.1 – 0.3 μm, 0.4 – 3 μm, and 4 – 30 μm (see Figure 1 (a)). However, it could be observed from Figure 1 (a) that most particles had sizes in the

range of 4 – 30 μm . After grinding, the particle size was in the range of 0.1 – 3 μm as shown in Figure 1 (b). It was found that the size distribution was bimodal in distribution.

For ANA, the particle size was in two ranges of 0.4 – 3 μm and 6 – 80 μm as shown in Figure 1 (c). After grinding, the particle size distribution was reduced to the range of 0.1 – 10 μm as shown in Figure 1 (d). As with the corresponding MOR size distribution, it was also bimodal.

3.1.2 Surface area and pore volume characterization

N_2 sorption was used to determine the surface area, pore volume, and pore size diameter of the synthesized MOR and ANA. Coarse ANA and ground ANA were referred to as ANA-s and ANA. Coarse MOR and ground MOR were represented by MOR-s and MOR. Data for surface area, pore volume, and pore size diameter of samples are summarized in Table 1. Upon grinding, the surface area of ANA increased from 15.70 to 34.20 $\text{m}^2 \text{g}^{-1}$, while that of MOR increased from 137.00 to 175.00 $\text{m}^2 \text{g}^{-1}$. The pore volume increased from 0.017 to 0.095 $\text{cm}^3 \text{g}^{-1}$ and 0.150 to 0.286 $\text{cm}^3 \text{g}^{-1}$ for ANA and MOR, respectively. Data for pore diameter of both ANA and MOR before and after grinding confirmed that all samples were microporous [30].

3.1.3 XRD characterization

In this work, XRD was used to examine the crystallinity of MOR and ANA before and after grinding and after surface modification. XRD results of MOR and ANA are shown in Figure 2. The diffraction patterns corresponded to the reflection of MOR and ANA [31]. It was observed that all diffraction pattern of the samples after grinding, protonating, and MPTES surface modification remained the same. This meant that the crystallinity of MOR and that of ANA were not destroyed. These results were consistent with those of our previous work [27, 29].

3.1.4 SEM characterization

SEM was used to identify the morphology of MOR and ANA in each of the following stages: coarse, ground, protonated, and surface modified with MPTES. Figure 3 and Figure 4 show SEM images of MOR and ANA, respectively. It could be observed that coarse and ground MOR clearly showed differences in particle size. Coarse MOR (Figure 3 (a)) exhibited a

bimodal particle size distribution, which was in agreement with the previous Mastersizer measurement. Ground MOR (Figure 3 (d)) was of an irregular shape and a smaller size. MOR modified by MPTES (Figure 3 (c)) showed agglomeration of particles that may be due to adhesion between primary particles and formation of new aggregated structures [29]. Moreover, both coarse and ground MOR in the protonated stage (Figure 3 (b) and (e)) did not show significantly different shape to those without protonation (Figure 3 (a) and (d)).

Coarse ANA particles were spherical in shape, with facets, and the size obtained was in agreement with the previous Mastersizer measurement. Ground ANA (Figure 4(d)) was of a smaller size than coarse ANA, and the structure was broken as a result of grinding process. ANA particles modified with MPTES were found to have agglomerated. The same reasoning as given for modified MOR can be applied to explain the results.

3.1.5 FTIR characterization

The functional groups of MOR and ANA before and after MPTES surface modification were characterized by FTIR. The surface modification was for improving properties of interfaces between Nafion matrix and the zeolite filler. The FTIR spectra of MOR in coarse condition and ground condition are shown in Figure 5 (a) and (b). The band around 3100 – 3500 and that at 1630 cm^{-1} were the stretching and bending vibrations of the hydroxyl group, respectively [27, 32]. The bands in the range of 920 – 1250 cm^{-1} corresponded to the internal asymmetric stretching of tetrahedral groups, while those in the range of 650 – 720 cm^{-1} corresponded to the internal symmetric stretching. The band in the range of 450 – 500 cm^{-1} was indicative of T-O bonds (T = Si or Al with each metal ion bonded to four oxygen atoms) [27, 30, 32, 33]. The band at 550 – 590 cm^{-1} was associated with the structural order of tetrahedral ring and/or a octahedral ring [32]. After surface treatment with MPTES, the peak around 2884 – 2973 cm^{-1} could be observed, and this peak is associated with the asymmetric stretching of CH_2 from the propyl groups of the grafted silane [27, 34].

The FTIR spectra of ANA in coarse condition and those of that ANA which has already been ground are also shown in Figure 5 (c) and (d). The band at around 937 cm^{-1} corresponded to the internal vibration of tetrahedral TO_4 of ANA. The band at about 1100 cm^{-1} was due to the vibrations of the external linkages between tetrahedral groups. Symmetrical stretching of T-O-T was attributed to the bands at 445, 620, and 737 cm^{-1} [35]. For ANA-s-MPTES and ANA-MPTES, the band around 2884-2973 cm^{-1} was detected as asymmetric stretching of CH_2 from the propyl groups after surface modification with MPTES [27, 36].

For other works that reported the conversion of –SH group to –SO₃H group by oxidation were the works from Ren [37] and Kim [38]. Ren and coworkers (2006) used silane coupling agent to enhance the proton conductivity of composite membrane [37]. They reported the treatment of thiol group (–SH) in mercaptopropyl methyldimethoxysilane using H₂O₂. The –SH group was changed to –SO₃H group after oxidizing with 30 wt.% H₂O₂ solution for 1 h at room temperature. Kim and coworkers (2010) also reported the change of –SH group into –SO₃H group by oxidation with 10 wt.% H₂O₂ [38].

3.1.6 TGA characterization

In order to determine the amount of treated silane on the zeolite surface, TGA was used. TGA curves of both unmodified zeolite and modified zeolite are shown in Figure 6. The weight loss at temperature below 250 °C was due to the loss of water in the interlayer and the weakly adsorbed water [27, 38]. Results temperatures in the range between 250 – 800 °C could be attributed to the loss of the strongly bond water and the dehydroxylation of the external zeolite surface as shown in the equation (6) [8]:

For MPTES modified MOR (MOR-MPTES), the 15% weight loss observed in the temperature range 25 – 250 °C was due to the evaporation of weakly adsorbed water, whereas the additional loss of 9% between 250 °C and 650 °C was due to the decomposition of the organic species attached to MOR surface after modification. The data from TGA was used to calculate % silane treatment. For modified ground MOR (MOR-MPTES), the weight loss due to water evaporation between 25 °C and 250 °C was 10%, as shown in Figure 6, and about 7% weight loss occurred between 250 and 650 °C for the organic species.

For ANA-s-MPTES and ANA-MPTES, that is MPTES-modified coarse ANA and MPTES-modified ground ANA, the loss of adsorbed water in the range of 25 – 250 °C were 10% for the former and 13% for the latter. Corresponding values for the degradation of organic species were 14% and 10%, shown in Figure 6. The minor weight loss observed beyond 800 °C may be due to a high temperature solid-state transformation or because of oxide formation [32]. Data for total weight loss and percentage of silane treatment of all samples are summarized in Table 2.

3.2 Membrane characterization

In this section, the results of membrane characterization of ANA/Nafion composite membrane (ANA/NF), MOR/Nafion composite membrane (MOR/NF), Nafion (NF), and commercial Nafion 117 (NF117) are presented. ANA/NF, MOR/NF, and NF were prepared by spray method. The average thicknesses calculated based on data obtained from nine positions along each membrane are summarized in Table 3.

3.2.1 Morphology of composite membranes

The SEM/EDS images in Figures 7–10 show the morphology and particle dispersion of the composite membranes. The 5 wt.% of ground MOR and ground ANA were used as fillers in composite membranes, which were then referred to as MOR/NF and ANA/NF, respectively. For EDS images, red and blue dots were silicon (Si) and aluminium (Al), respectively, representing zeolite particles (MOR or ANA). Green and white dots were fluorine (F) and sulfur (S) representing Nafion polymer.

In this work, MOR and ANA were added into a Nafion matrix in order to reduce the methanol crossover through the membrane during membrane solution preparation. Spray method was used to prepare the membranes as it was expected to improve the homogeneous dispersion of filler particles in the Nafion matrix and reduce the particle separation from the matrix which was found in the composite membrane fabricated from the solution casting method [5, 27].

3.2.2 Solubility

Solubility is one of the important indicator for proton-conducting membrane properties, and a solubility test is used to reflect chemical resistance of the membrane. Moore and Martin [28] defined a good conducting membrane as one either dry or wet, which is insoluble in a solvent. This means the membrane should have a solubility less than 5% [28]. Looking at the data in Figure 11, it can be seen that all the membrane prepared by spray method exhibit good chemical resistance as all membranes have solubility lower than 5% as Moore and Martin's suggestion [28].

3.2.3 Water uptake

Water uptake is one of the important parameters affecting the performance of PEM. While water molecules in a matrix are used for proton transport, water uptake is required to not be too great because excess water uptake may lead to low mechanical stability and other undesirable mechanical properties [39]. Xu and coworkers reported the water uptake of PEM to be in the range of 2.51 – 67.23 % at 25 °C.

Figure 12 shows that ANA/NF composite membrane could adsorb higher water content than MOR/NF composite membrane. This may be due to the stronger polarity of ANA as it has a lower Si/Al ratio than MOR (2 relative to 10). Thus, more water was absorbed into the ANA/NF composite membrane [21].

3.2.4 Ion-exchange capacity

The ion-exchange capacity (IEC) is an indirect indication of proton conductivity [15]. Figure 13 gives IEC values of the membranes. It can be observed that all composite membranes had higher IEC than NF and commercial membranes, and this fact is due to the presence of $-\text{SO}_3\text{H}$ groups on the zeolite [15].

It was also observed that IEC value of MOR/NF (0.88 Meq g^{-1}), again see Figure 13, was slightly higher than that of ANA/NF (0.82 Meq g^{-1}). This was due to the higher surface area of MOR ($175.00 \text{ m}^2 \text{ g}^{-1}$) relative to ANA ($34.20 \text{ m}^2 \text{ g}^{-1}$).

3.2.5 Proton conductivity

Figure 14 shows proton conductivity of the composite membranes prepared via spray method under testing temperatures of 30, 50, and 70 °C. At 30 °C, ANA/NF and MOR/NF composite membranes showed comparable results: the former giving 0.0494 and the latter giving $0.0501 \text{ S}\cdot\text{cm}^{-1}$. However, ANA/NF exhibited slightly higher proton conductivity than MOR/NF when temperature was raised to 50 °C or 70 °C.

A number of researchers investigated the proton conductivity of membranes and reported that the proton conductivity of composite membranes were improved according to the existing of proton conducting group such as sulfonic acid, phosphoric acid, and imidazole. The presence of the proton conducting group benefited the proton migration through the membrane [40-42].

3.2.6 Methanol uptake

In order to develop a membrane with low methanol permeability, it is necessary to examine methanol uptake in the membrane structure [43]. Figure 15 shows the methanol uptake of the membranes using 1 M and 2 M methanol concentration. For all membranes, it was found that the uptake for the lower methanol concentration was lower than that obtained using the higher concentration.

Comparing the composite membranes to NF and NF117, it was found that the composite membranes had a lower methanol uptake than NF and NF117 at both 1 M and 2 M methanol concentrations. Thus, it can be concluded that the presence of MOR and ANA particles was able to enhance the degree to which the membrane acts as a barrier to methanol molecules. This was attributed to the tortuousness of the voids of added particles resulting in more methanol diffusion path ways through the membrane [15, 44, 45].

ANA/NF had higher methanol uptake than MOR/NF both at low and high methanol concentrations (1 M and 2 M). This may be due to the intrinsic properties of ANA and MOR or may be because ANA has larger pore diameter (15.00 Å) than MOR (5.16 Å). Therefore, more methanol was able to be adsorbed in the voids of ANA/NF than in the MOR/NF composite membrane [46].

3.2.7 Methanol permeability

Methanol permeability of composite membranes prepared by spray method were studied under testing temperatures of 30 °C and 70 °C: see Figure 16. The results of methanol permeability are shown in Figure 16. At 30 °C, the composite membranes exhibited lower methanol permeability than NF and NF117, with the lowest methanol permeability being obtained using MOR/NF composite membrane. This might be due to the homogeneous dispersion of MOR fillers in Nafion matrix that can block the passage of methanol through the Nafion membrane. The fact that NF had a lower methanol permeability than NF117 might be due to the difference in preparation method: prepared solvent, evaporation time, or fabrication apparatus. However, ANA/NF composite membrane exhibited higher methanol permeability than MOR/NF composite membrane both at low and high testing temperature. This might be due to the intrinsic properties of ANA and MOR. Furthermore, ANA has a larger pore diameter (15.00 Å) than MOR (5.16 Å). Thus, more methanol can be adsorbed in the voids of ANA/NF than in than MOR/NF composite membrane, as previously mentioned when discussing methanol uptake [46]. MOR/NF composite membrane showed lower methanol permeability than ANA/NF at both testing temperatures. Thus, it can be concluded that MOR was a suitable filler for use in PEM or DMFC.

3.2.8 Selectivity

Membranes for DMFC application are required to have high proton conductivity and low methanol permeability. In order to compare the applicability of a fabricated PEM, the selectivity is usually evaluated [15]. Figure 17 shows the selectivity of the composite membranes filled with ANA and MOR. It was observed that MOR/NF composite membrane showed the highest selectivity: 36.6×10^3 and $32.7 \times 10^3 \text{ S} \cdot \text{s} \cdot \text{cm}^{-3}$ at 30°C and 70°C , respectively. This was mainly due to the small value of methanol permeability and high value of proton conductivity of this membrane. The results suggested that the MOR/NF composite membrane prepared by spray method should be suitable for DMFC application.

3.2.9 Mechanical properties

The mechanical properties of the PEMs are important for fuel cell applications. Many studies have indicated that mechanical failures of PEM due to the impacts of temperature, humidity, and force during the fuel cell operation can reduce the fuel cell life [47-49]. Tensile properties of all composite membranes are summarized in Table 4. It was found that the tensile strength of NF117 was 26.65 MPa, which was in good agreement with Lin's work [50], and it was found that the composite membranes had slightly lower tensile strength than those of NF and commercial membrane.

It was observed that all composite membranes have tensile strength slightly lower than those of NF and NF117, which may be due to the addition of inorganic particles causing the formation of rigid polymer chains and reduction in elongation [26]. Silane treated on the surface caused higher cross-linking between polymer chains and fillers, increased the stiffness (stiffness being the deformation resistance of the object responding to an applied force) of the membrane, and reduced its tensile strength [48]. ANA/NF had a slightly higher tensile strength (18.29 MPa) than MOR/NF (16.60 MPa): see Table 4. However, MOR/NF had a greater Young's modulus than ANA/NF, NF, and NF117. From this, it can be inferred that MOR/NF had a better resistance to the deformation under applied force than ANA/NF.

3.2.10 DMFC performance

DMFC tests were performed using composite membranes and compared with results for NF and NF117. Operation conditions were as follows: operating temperatures of 30°C , 50°C , and 70°C ; a methanol flow rate of $5 \text{ ml} \cdot \text{min}^{-1}$; and an air flow rate of $1 \text{ L} \cdot \text{min}^{-1}$. The voltage

and power density of the composite membranes were found to be higher than those of NF and NF117. Normally, a low proton conductivity and a high methanol permeability contribute to poor DMFC performance. DMFC performance could thus be enhanced by improving proton conductivity and lower methanol permeability, which are represented in terms of selectivity, as mentioned in section 3.2.8. All composite membranes showed higher selectivity than those of NF and NF117 membranes.

Using a methanol concentration of 1bM (see Figure 18), all membranes showed similar performance, as could be observed from power density values. When increasing the methanol concentration to 2 M and 4 M, the DMFC performance of MOR/NF composite membrane exhibited obviously greater power density than those of ANA/NF composite membrane, NF and NF117, as shown in Figure 19 and Figure 20. The higher DMFC performance of MOR/NF composite membrane was due to lower methanol permeability and higher proton conductivity or higher selectivity, relative to other membranes.

From Figures 18–20 show that when increasing the operation temperature from 30 °C to 50 °C, and then to 70 °C, the DMFC performance improved, can be observed from the higher (increased) power density. This was due to better transportation of proton through the membrane occurring at higher temperature [51]. Moreover, the gas diffusivity and membrane conductivity increase with increased operation temperature. Thus, using a higher temperature, the DMFC performance was enhanced. MOR/NF composite membrane showed higher DMFC performance than the other membranes, especially at 70 °C [51].

MOR/NF composite membranes could resist methanol transport, resulting in lower methanol diffusion with increasing methanol concentration. Therefore, better DMFC performance was achieved when using methanol concentrations. This was consistent with Deluca's report in which the DMFC performance increased with increasing methanol feed concentration when membranes with a higher selectivity were used [52]. The highest power density of MOR/NF composite membrane was achieved at 70 °C and with 2M methanol: 10.75 mW·cm⁻². The result was slightly lower with 4 M methanol, this is, 10.64 mW·cm⁻².

4. Conclusions

In this work, ANA/NF, MOR/NF, NF, and NF117 membranes for use in DMFC were characterized and compared. Spray method was used to prepare the membranes as it was

expected to improve the homogeneous dispersion of filler particles in Nafion matrix and reduce the particle separation from the matrix which can be found in the composite membrane fabricated following a solution-casting method. The composite membranes with MOR filler gave better membrane properties than those using ANA filler. In particular, they had higher proton conductivity and lower methanol permeability, which reflected in the selectivity value. MOR/NF composite membrane had a selectivity about two and three times higher than that of ANA/NF composite membrane at 30 and 70 °C, respectively. As regards use as DMFC, it was found that MOR/NF composite membranes showed the best performance. It was clearly seen that MOR/NF composite membrane showed excellent performance, especially at high temperature and high concentration, relative to the others. The maximum power density ($10.75 \text{ mW} \cdot \text{cm}^{-2}$) was obtained with MOR/NF composite membrane using 2 M methanol and at 70 °C. Furthermore, MOR/NF composite membrane had a power density 2.1, 1.4, and 1.5 times higher than those of NF117, NF, and ANA/NF composite membrane, respectively. Therefore, the composite membrane with MOR filler prepared via spray method was promising for PEM to improve DMFC performance.

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Figure 1 The particle size distributions of (a) MOR-s, (b) MOR, (c) ANA-s, and (d) ANA.

Figure 2 Comparison of XRD diffraction patterns of (a) MOR and (b) ANA at various conditions.

Figure 3 SEM images at 5000x magnification: (a) MOR-s, (b) MOR-s-H, (c) MOR-s-MPTES, (d) MOR, (e) MOR-H and (f) MOR-MPTES.

Figure 4 SEM images at 5000x magnification: (a) ANA-s, (b) ANA-s-H, (c) ANA-s-MPTES, (d) ANA, (e) ANA-H, and (f) ANA-MPTES.

Figure 5 FTIR spectra of MOR and ANA before and after MPTES modification: (a) MOR-s, (b) MOR, (c) ANA-s, and (d) ANA.

Figure 6 TGA diagrams of MOR and ANA before and after MP TES modification: (a) MOR-s, (b) MOR, (c) ANA-s, and (d) ANA.

Figure 7 SEM/EDS images of composite membranes prepared using spray method: (a) cross-section of ANA/NF, (b) Si mapping of ANA/NF, (c) cross-section of MOR/NF, and (d) Si mapping of MOR/NF.

Figure 8 SEM/EDS images of composite membranes prepared using spray method: (a) cross-section of ANA/NF, (b) Al mapping of ANA/NF, (c) cross-section of MOR/NF, and (d) Al mapping of MOR/NF.

Figure 9 SEM/EDS images of composite membranes prepared using spray method: (a) cross-section of ANA/NF, (b) F mapping of ANA/NF, (c) cross-section of MOR/NF, and (d) F mapping of MOR/NF.

Figure 10 SEM/EDS images of composite membrane prepared using spray method: (a) cross-section of ANA/NF, (b) S mapping of ANA/NF, (c) cross-section of MOR/NF, and (d) S mapping of MOR/NF.

Figure 11 Solubility of all membranes prepared from spray method.

Figure 12 Water uptake of all membranes prepared via spray method.

Figure 13 IEC of all membranes.

Figure 14 Proton conductivity of all membranes tested at 30, 50, and 70 °C.

Figure 15 Methanol uptake of all membranes using methanol concentration of 1 M and 2 M.

Figure 16 Methanol permeability of all membranes at testing temperature of 30 °C and 70 °C.

Figure 17 Selectivity of composite membranes prepared by spray method at testing temperature of 30 °C and 70 °C.

Figure 18 Polarization and power density curves highlighting the effect of preparation method of MOR/NF, ANA/NF, NF, NF117 on DMFC performance using 1 M methanol: (a) – (b) 30 °C, (c) – (d) 50 °C, and (e) – (f) 70 °C.

Figure 19 Polarization and power density curves highlighting the effect of preparation method of MOR/NF, ANA/NF, NF, NF117 on DMFC performance using 2 M methanol: (a) – (b) 30 °C, (c) – (d) 50 °C, and (e) – (f) 70 °C.

Figure 20 Polarization and power density curves highlighting the effect of preparation method of MOR/NF, ANA/NF, NF, NF117 on DMFC performance using 4 M methanol: (a) – (b) 30 °C, (c) – (d) 50 °C, and (e) – (f) 70 °C.

Table 1 Summary of sorption analysis.

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (Å)
ANA-s	15.70	0.017	9.61
ANA	34.20	0.095	15.00
MOR-s	137.00	0.150	6.84
MOR	175.00	0.286	5.16

Table 2 Summary of TGA data for unmodified and modified zeolite.

Sample	Weight loss (%) 20 – 250 °C	Weight loss (%) 250 – 650 °C	MPTES (%)
MOR-s-H	12	2	-
MOR-s-MPTES	15	9	7
MOR-H	11	2	-
MOR-MPTES	10	7	5
ANA-s-H	2	6	-
ANA-s-MPTES	10	14	8
ANA-H	11	3	-
ANA-MPTES	13	10	7

Table 3 Average thickness of all composite membranes, NF, and NF117.

Sample	Average thickness (µm)	SD
ANA/NF	160.78	11.19
MOR/NF	172.89	8.37
NF	165.78	16.65
NF117	186.67	3.20

Table 4 Mechanical properties of composite membranes prepared by spray method

Sample	Thickness (mm)	Tensile strength (MPa)	Elongation (%)	Young's Modulus (MPa)
ANA/NF	0.15	18.29 ± 0.54	304.67 ± 22.01	279.17 ± 7.32
MOR/NF	0.18	16.60 ± 0.32	225.00 ± 17.44	311.57 ± 2.94
NF	0.15	21.52 ± 0.83	205.00 ± 25.15	276.81 ± 5.05
NF117	0.18	26.65 ± 1.22	359.33 ± 34.21	236.42 ± 7.66

Table 5 Maximum power densities obtained with the composite membranes prepared by spray method with MOR and ANA filler at various temperatures and methanol concentrations.

Sample	[MeOH] (M)	Max power density (mW·cm ⁻²)		
		30 °C	50 °C	70 °C
ANA/NF	1	4.05	6.13	7.40
MOR/NF		3.55	6.29	7.66
NF		2.59	5.98	7.54
NF117		2.58	4.15	5.83
ANA/NF	2	3.67	5.30	7.15
MOR/NF		5.88	8.91	10.75
NF		3.26	5.33	7.35
NF117		2.56	4.24	5.04
ANA/NF	4	2.86	4.32	5.91
MOR/NF		5.82	9.56	10.64
NF		3.08	4.92	6.01
NF117		2.68	4.15	4.47