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Author: Chaiwat Prapainainar Sawanya Kanjanapaisit Paisan Kongkachuichay Stuart M. Holmes Paweena Prapainainar

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**Surface Modification of Mordenite in Nafion Composite Membrane for Direct Ethanol
Fuel Cell and Its Characterizations: Effect of Types of Silane Coupling Agent**

Chaiwat Prapainainar^{a,b}, Sawanya Kanjanapaisit^c, Paisan Kongkachuichay^{c,d}, Stuart M.
Holmes^e, Paweena Prapainainar^{*c,d}

^aDepartment of Chemical Engineering, King Mongkut's University of Technology North
Bangkok, Bangkok 10800, Thailand

^bResearch and Development Center for Chemical Engineering Unit Operation and Catalyst
Design, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

^cNational Center of Excellence for Petroleum, Petrochemicals and Advance Material,
Department of Chemical Engineering, Kasetsart University, Bangkok 10900, Thailand

^dCenter for Advanced Studies in Nanotechnology, Applications in Chemical Food and
Agricultural Industries, Kasetsart University, Bangkok 10900, Thailand

^eSchool of Chemical Engineering and Analytical Science, The University of Manchester,
Manchester M13 9PL, UK

Email; chaiwat.r@eng.kmutnb.ac.th, pearry.sawanya@gmail.com, fengpsk@ku.ac.th,
stuart.holmes@manchester.ac.uk, fengpwn@ku.ac.th

*Corresponding author at: Department of Chemical Engineering, Faculty of Engineering,
Kasetsart University, Bangkok 10900, Thailand.

Tel.: +66 27970999 Ext.1249; Fax: +66 25614621.

E-mail address: fengpwn@ku.ac.th (P. Prapainainar).

Highlight

- Silane treated mordenite composite membrane was used for DEFC.
- Four types of silane coupling agents were treated on MOR surface.
- Sulfhydryl group in MPTES provided sulfonic group for enhance proton conductivity.
- MOR-MPTES/Nafion membrane had the highest selectivity at all temperature.

Abstract

Mordenite (MOR) has been used to solve the alcohol crossover in direct ethanol fuel cells. However, the lack of compatibility has been a problem. This paper shows the compatibility improvement of MOR in a Nafion composite membrane for use in a fuel cell using four types of silane coupling agents: gamma-glycidoxypyriltrimethoxysilane (GMPTS), (3-mercaptopropyl) trimethoxysilane (MPTS), (3-Mercaptopropyl) triethoxysilane (MPTES) and (3-Mercaptopropyl) methyl-dimethoxysilane (MPDMS). The coupling agents were used to treat the MOR surface before mixing with Nafion. Each type of silane was treated carefully and differently, depending on its structure. Their characterizations were also described. The results showed that better compatibility and a noticeable reduction in ethanol permeability were achieved when using all silane-treated MOR in the composite. It was found that the Nafion/MOR-MPTES membrane had the highest proton conductivity at all temperature ranges from 30-70°C. This was due to the fact that the sulfhydryl (—SH) functional group in MPTES provided the sulfonic group in its structure after the oxidation in the surface treatment process. These sulfonic groups at the MOR surface facilitated proton transport and improved the selectivity of the membrane.

Keywords: Mordenite/Nafion composite membrane; Silane surface treatment; Ethanol permeability; Compatibility; Direct ethanol fuel cell.

1. Introduction

At present, the use of hydrogen and methanol as fuels in the fuel cell is common and has been commercially applied widely. Direct ethanol fuel cells have been under focus due to low emission levels produced and low cost of fuel. Compared with methanol, ethanol has a higher energy density and specific energy [1, 2]. Methanol is mainly obtained from petrochemical processes. Therefore, ethanol is considered a good choice for use in fuel cell development as it can be produced from renewable sources. The performance of a fuel cell depends mainly on the type of catalysts and the membrane used. A significant problem with membranes in a fuel cell is the crossover of alcohol through the membrane from the anode to the cathode. Nafion is a common polymer membrane used as a proton exchange membrane in fuel cells, due to its high proton conductivity and good mechanical properties. The structure of Nafion consists of two parts: a hydrophilic part which is a sulfonic acid group, and a hydrophobic part which is polytetrafluoroethylene (PTFE) [3]. It has been found that the selectivity, proton conductivity and methanol permeability ratio of Nafion are higher compared to other polymers such as chitosan and SPEEK membranes. However, the main problem of Nafion as a membrane in direct alcohol fuel cells is the permeation of alcohol from the anode side to the cathode side, which is known as crossover. The permeated alcohol can react with O₂ and generate carbon dioxide at the cathode. As a result, the performance of the fuel cell is decreased [4]. In the report of Wang et al. [5], the selectivity values of chitosan and a Nafion[®] 117 membrane were 1.49×10^4 and 1.71×10^4 Ss/cm³, respectively. In the report of Maab and Nunes [6], the permeability of ethanol for Nafion 117 was 5 times higher than a plain SPEEK membrane. However, it was found that the power density of a fuel cell using a Nafion[®] 117 membrane was higher than that of a SPEEK membrane. It has been a good choice for selection as a matrix polymer for polymer exchange membrane fuel cells (PEMFC), especially if the ethanol crossover is improved.

Nafion polymer can be incorporated with filler, forming a composite membrane to improve its membrane properties [7-9]. Amiinu et al. [10] reported that doping Imidazole functionalized meoporous silica into Nafion showed an increase in proton conductivity to $1.06 \times 10^{-2} \text{ Scm}^{-1}$ at 130°C . The presence of silica-imidazole within the matrix functioned as a transporting medium to facilitate proton conductivity. Kim et al. [11] enhanced the Nafion membrane by coating it with a delaminated AMH-3 (Microporous layered silicate)/Nafion nanocomposite layer, which resulted in a low methanol permeability and maintained a high proton conductivity. The methanol permeability of the nanocomposite layer was 1.6 times lower than Nafion 115 due to the smaller opening pore size of the filler particles in the nanocomposite layer than methanol molecules. Thus, they played a role as a barrier and blocked the methanol molecules by a tortuous pathway effect. These results were consistent with Kumar's work [12] that lower methanol permeability was achieved from Nafion coated and laminated with sulfonated polyvinylidene fluoride (PVDF). Barbora et al. [13] studied neodymium oxide modified Nafion membrane for direct alcohol fuel cells. The pure Nafion and 5%wt composite membrane showed that the permeability of ethanol ($1.22 \times 10^{-7} \text{ cm}^2/\text{s}$ and $0.85 \times 10^{-7} \text{ cm}^2/\text{s}$, respectively) was less than that of methanol ($1.38 \times 10^{-7} \text{ cm}^2/\text{s}$ and $0.95 \times 10^{-7} \text{ cm}^2/\text{s}$, respectively) due to the larger molecule of ethanol. It was also found that the tensile strength of the composite membranes were higher than that of the pure recast Nafion membrane. Yen et al. [14] prepared sulfonated-silica/Nafion composite membranes, which have a higher selectivity than those of pristine Nafion. Adding silica-SH and silica-SO₃H to the membrane decreased the methanol permeability by approximately 30% and 15%, respectively. Another way to reduce alcohol crossover is by using a zeolite such as NaA-zeolite incorporated with Nafion which has been reported to successfully reduce alcohol crossover [15, 16]. The study found that the methanol permeability of the Nafion composite membrane, incorporated with zeolite-NaA which was treated by APTS silane was up to 55.96% lower than that of a Nafion[®] 117 membrane. However, it was found that zeolite-NaA

was not stable when used in a direct methanol fuel cell (DMFC) for long periods [17]. Various types of zeolite were incorporated with polymers, such as a zeolite beta-filled chitosan membrane. It was found that using zeolite beta can decrease the methanol permeability when compared with a pure chitosan membrane [5]. Yilser et al. [18] prepared the Nafion/zeolite composite membrane with different zeolite loading for a low humidity proton exchange membrane fuel cell (PEMFC). The results showed that water uptake and proton conductivity were enhanced due to the water retention properties of the zeolite and interaction between the Nafion and zeolite particles. PEMFC tests showed the 10 wt.% zeolite loading in the composite membrane was more stable and better than the Nafion membrane.

Cui et al. [19] synthesized Nafion-based membrane containing 5 wt.% and 10 wt.% of nano ammonium-X ($\text{NH}_4\text{-X}$) and submicron $\text{NH}_4\text{-X}$ zeolite. The results showed that the water uptake, ion exchange capacity, and proton conductivity of the submicron 5 wt.% $\text{NH}_4\text{-X}$ zeolite/Nafion composite membrane were higher than the Nafion membrane and the selectivity was more than twice of that of the Nafion membrane. The power density was 62.2 mWcm^{-2} at 60°C , which was 3 times higher than that of the Nafion membrane. Moreover, the report of Kongkachuichay and Pimprom [20] showed that when incorporating analcime and faujasite as fillers with Nafion in PEMFC, the H_2 permeation of both types of Nafion/zeolite composite membranes was lower than that of the Nafion[®] 117 membrane. Nevertheless, mordenite (MOR) was suitable for use in a direct alcohol fuel cell [21]. MOR has 12-membered and 8-membered rings, resulting in 6.7×7.0 and 2.9×5.7 Angstrom channels, respectively. The molecular size of water and ethanol is 2.6 Angstrom [22] and 5.2 Angstrom [23], respectively. Therefore, it can be seen that the ethanol molecule is smaller than the channels of the MOR. This can lead to better adsorption of water than ethanol. In summary, MOR as a type of zeolite has advantages of stability, high proton transport and higher water absorption than methanol or ethanol [24-26]. It can also be used in other applications [27]. It was found that there were some pinholes caused by poor compatibility between the Nafion

polymer and the zeolite crystals which has been a problem reported in several studies [28-32]. Kwak et al. [33] synthesized MOR/Nafion composite membrane for high-temperature operation of PEMFC using various weight percentages of MOR. It was found that a higher MOR content led to lower tensile strength of the composite membranes (45 MPa for Nafion and 33 MPa for 5%wt MOR/Nafion). The strength was as low as 12 MPa for 20%wt MOR/Nafion membrane. This was due to poor compatibility between Nafion and MOR particles. The reduction in alcohol crossover and the higher compatibility can be achieved by improving the interfacial properties between the inorganic and organic parts in the composite membrane. In our previous work, Yoonoo et al. [21], 3-aminopropyl-triethoxysilane (APTS) and gamma-glycidoxypropyltrimethoxysilane (GMPTS) were used for MOR surface modification to increase the compatibility. It was found that GMPTS showed the best performance in DMFC, when 5 wt. % of ground and coarse (non-ground) MOR in Nafion were used. The proton conductivity of Nafion/MOR-GMPTS was slightly lower, but its methanol permeability was much lower than that of the recast Nafion membrane. Nafion/MOR-GMPTS also showed better performance in DMFC. The power density of the Nafion/MOR-GMPTS membrane was 1.11 times that of the recast Nafion membrane. A silane coupling agent was also used to modify zeolite surface for membranes used in gas separation [29, 34]. Li et al. [29] reported that the permeability and selectivity of membranes made from silane modified zeolite were higher than those of membrane made from unmodified zeolite because the degree of partial pore blockage was decreased. Zhao et al. [35] reported the improvement of the adhesion strength of nanoparticles modified by grafting a silane coupling agent onto a TiO₂ nanoparticles surface. Wang et al. [36] used γ -mercaptopropyltrimethoxysilane with sulfhydryl ($-SH$) functional groups modified on the zeolite powders to improve the surface/channel of the zeolite substrates.

In this study, the focused was on reducing the permeation of ethanol and increasing the compatibility of the membrane that has been a crucial problem in DEFC. The main

objective was the synthesis of Nafion/silanated-mordenite composite membranes to reduce ethanol permeability together with increasing the compatibility of the filler and the matrix for DEFC. MOR was used as inorganic filler and four types of silane were used as coupling agents to increase the compatibility. Further investigation of the effect of coupling agents in this study used gamma-glycidoxypolytrimethoxysilane (GMPTS), (3-mercaptopropyl) trimethoxy silane (MPTS), (3-mercaptopropyl) triethoxysilane (MPTES) and (3-Mercaptopropyl) methy-dimethoxysilane (MPDMS) to modify the surface of MOR before composite membrane fabrication. MPTS, MPTES, and MPDMS, which contain a sulhydryl group that can convert to a sulfonic group, have not yet been used to improve the MOR surface, were used in this study to compare with GMPTS, as had been used in our previous studies [21]. These mercapto silanes should benefit from an increase in the sulfuric group ($-\text{SO}_3$). Therefore, these silanes were applied in this study. 5 wt. % MOR was incorporated with Nafion composite membrane synthesis for use in the direct ethanol fuel cell (DEFC). The chemical and physical properties of the composite membranes were characterized and their ethanol permeability and proton conductivity were systematically investigated.

2. Methodology

2.1 Materials

Nafion solution was purchased from Ion Power. MOR-Na with a Si/Al molar ratio of 13 was purchased from Zeolyst International. Gamma-glycidoxypolytrimethoxysilane (GMPTS), (3-Mercaptopropyl) trimethoxysilane (MPTS), (3-Mercaptopropyl) triethoxysilane (MPTES) and (3-Mercapto propyl) methy-dimethoxysilane (MPDMS) were purchased from Sigma-Aldrich. Sulfuric acid, hydrogen peroxide, ethanol, methanol, N,N-dimethylformamide, dichloromethane, ammoniumchloride, toluene and aluminumtrichloride were used. De-ionized water was used throughout the study.

2.2 Preparation of mordenite

Mordenite-Na was ground in a ball mill and was then protonated to obtain MOR-H in 1 M sulfuric acid for 24 h, dried in an oven before being calcined at 550 °C [21, 37]. Functionalization of MOR-H by GMPTS silane was carried out according to the procedure described in the literature [21]. Briefly, 4 g MOR-H was added to the mixture of 4 ml GMPTS and 120 ml dichloromethane. The mixture was stirred for 24 h, centrifuged, rinsed in dichloromethane and re-dispersed in an ultrasonic bath. Finally it was dried at 100 °C for 24 h to obtain MOR-GMPTS. For MPTS, 4 g MOR-H was mixed in the solution of 8 ml MPTS in 80 ml toluene and the reaction was carried out at the reflux temperature of toluene at 110 °C for 24 h. After washing with ethanol and de-ionized water to remove the silane residues, it was oxidized in a 30 wt.% hydrogen peroxide solution at room temperature for 24 h to convert the –SH groups into –SO₃H groups and form MOR-MPTS [38]. The reactions of MPTES and MPDMS used the same method as that of MPTS but included adding a catalyst into the mixture. The catalyst solutions were prepared by dissolving 1 g AlCl₃ in the mixture of 20 ml ethanol and 20 ml toluene. They were mixed under stirring at 70 °C for 1 h. After that, 4 ml MPTES and 40 ml toluene were mixed under stirring at room temperature for 30 min. Subsequently, 5 ml catalyst solution, 44 ml silane solution and 2 g MOR-H were mixed and refluxed under stirring at 110 °C for 24 h. MOR was washed with ethanol and de-ionized water and further oxidized in 30 wt.% hydrogen peroxide solution under ambient conditions and then separated using a centrifuge. The final drying stage occurred at 100 °C for 24 h to obtain MOR-MPTES. For the MPDMS treatment, the same procedure was used as for MPTES except that MPDMS was used instead of MPTES and denoted as MOR-MPDMS.

2.3 Preparation of Nafion/MOR composite membrane and pretreatment

Nafion/MOR composite membranes were cast following the standard solution casting method as reported in Yoonoo et al. [21]. First, 7.5 ml of 20 wt.% Nafion solution was mixed with 34 ml of alcohol (15:85 volume ratio of ethanol/methanol) and 20.5 ml of N,N-dimethylformamide (DMF). Then 0.078 g of treated MOR was added into the mixture and

suspended using an ultrasonic bath and magnetic stirrer for 2 h to ensure good suspension of the MOR powder in the Nafion solution. After that, the suspension was poured onto a Petri dish and dried in a vacuum oven at 80 °C for 20 h, followed by further heat treatment at 150 °C for 4 h. The cast membrane was then cooled down to room temperature and was then treated by soaking in boiling de-ionized water for 10 min, ensuring full hydration. Membranes were then boiled in 5 vol.% hydrogen peroxide in water at 80 °C for 30 min to remove the organic residues, followed by rinsing twice with deionized water and boiling in 1 M sulfuric acid for 30 min. Next, they were rinsed and boiled in de-ionized water 3 times each for 10 min. Finally the membranes were stored in de-ionized water before use.

2.4 Characterizations

The crystalline structures of MOR before and after grinding and after each silane treatment were examined using X-ray diffractometry (XRD) on a BRUKER D8 Advance A25 equipped with Cu-K α X-ray radiation ($\lambda = 1.5418 \text{ \AA}$) to confirm their structures. The result of the MOR surface treatment by silane were observed using Fourier transform infrared spectrophotometry (FTIR, Perkin Elmer System 2000) in the range 4000-400 cm^{-1} . The quantity of silane grafted on the MOR surface was determined by thermo gravimetric analysis (TGA) with air flowing at a heating rate of 5 °C/min from 25 °C to 1,100 °C.

The morphologies of the membranes were observed with scanning electron microscopy (SEM, Philips: XL30 & EDAX). The dispersion of MOR in the Nafion matrix was investigated by applying the elemental mapping using the EDS mode equipped with SEM undertaking at the cross section of the membranes.

2.5 Water uptake and ethanol solution uptake

Water and ethanol uptake is an approach which can be used to study the behavior of the composite membrane when it comes into contact with water and ethanol. The water uptake of membranes was determined by measuring the weight different between the dry and fully hydrated membranes. The membranes were soaked in de-ionized water for 24 h at room

temperature, the excess water adsorbed by filter paper and subsequently the membranes were weighed to obtain W_{wet} , were then dried under vacuum at 80 °C for 2 h and re-weighed to obtain W_{dry} . To test for ethanol solution uptake, they were immersed in a 12 M ethanol solution and tested in the same procedure as for water uptake. The uptake was calculated from Eq.(1) [39]:

$$uptake (\%) = \left(\frac{W_{wet} - W_{dry}}{W_{dry}} \right) \times 100\% \quad (1)$$

2.6 Ion Exchange Capacity (IEC)

Ion-exchange capacity (IEC) of the membranes can be used as an approximation of the proton conductivity [40], indicating quantity of acid equivalents per gram of polymer membrane [20, 41]. The IEC values of the composite membranes were determined with the titration method. The composite membranes in H^+ were converted to Na^+ by immersing in a 0.1 M NaCl solution for 24 h. After that, the remaining solution was titrated with 0.02 M NaOH using phenolphthalein as an indicator. The IEC was calculated from Eq.(2) [42].

$$IEC = \frac{V_{eq} \times C_{NaOH}}{m_d} \quad (2)$$

where V_{eq} is the volume of NaOH solution (ml), C_{NaOH} is the concentration of NaOH solution (mol/l) and m_d is the weight of the dry membrane (g).

2.7 Proton conductivity

AC impedance spectroscopy (Autolab) was used to measure the membrane resistance using the two-probe method over a frequency range of 10,000-100 Hz with an oscillating voltage of 10 mV. The proton conductivity (σ , S/cm) of membranes was then calculated using Eq. (3) [20]. Prior to the measurement, the membranes were immersed in 1 M sulfuric acid for 24 h. During the measurement, membrane samples were placed between two platinum electrodes and resistance was measured at three points in each membrane.

$$\sigma = \frac{d}{R_m A} \quad (3)$$

where d is the thickness of the membrane (cm), A is the sample area of the membrane (cm^2) and R_m is the membrane resistance (Ω).

2.8 Ethanol permeability

The ethanol permeability of the membranes was determined using the two compartments diffusion cell technique, as described in the literature [21]. The cell consists of two compartments: feed and permeate, separated by the membrane sample. The feed and permeate compartments were filled with a solution of ethanol and de-ionized water, respectively. The ethanol concentration difference between the feed and permeate caused ethanol permeation across the membrane. The ethanol concentration in the feed was assumed to remain unchanged during the experiment. Finally, the ethanol concentration on the permeate side was measured as a function of time and determined by using gas chromatography (GC 8A SHIMADZU) with a Porapak-Q column. The ethanol permeability (P , cm^2/s) was calculated using Eq.(4) [43].

$$P = \frac{kVL}{SC_{A0}} \quad (4)$$

where k is the slope of the plot of the concentration in the permeate compartment versus time ($\text{mol}/\text{cm}^3\text{s}$), V is the volume of the permeate compartment (cm^3), S and L are the membrane area (cm^2) and thickness (cm). C_{A0} is the initial concentration of ethanol in a feed compartment (mol/cm^3). Each sample was measured three times. The ethanol concentration was varied at 1, 2 and 4 M and the temperature was varied at 30 °C, 50 °C and 70 °C.

3. Results and discussion

3.1 Characterization of MOR before and after modification

MOR powder purchased from Zeolyst was ground resulting in an average particle size of 3.5 μm . To ensure that the crystallinity of MOR was not changed due to grinding, protonating and the silane treatment, the particles were examined using XRD. The XRD

fingerprints of each treatment and each type of MOR are shown in Fig.1. It can be seen that the surface-modified MOR shows identical characteristic peaks to the pristine MOR. This meant the crystalline structures of the modified MOR were unchanged when compared with the pristine MOR.

Compatibility between the polymer and the surface of the inorganic filler is a key issue in determining the final membrane properties and performance. Therefore, good adhesion between the inorganic filler and matrix is crucial in composite applications. The adhesion can be improved by surface modification. TGA was used to confirm the success of the surface modification of MOR using silanes. Consequently, FT-IR was used to find the functional group of silane attached on the surface of MOR. The functional group of silane and their structures are shown in Fig. 2.

The FT-IR results in Fig.3 show the FT-IR spectra of MOR-H, MOR-GMPTS, MOR-MPTS, MOR-MPTES and MOR-MPDMS samples. Regarding MOR-GMPTS, it was found that the spectrum at 912 cm^{-1} was assigned to the epoxy characteristic band [44]. It was stated in the literature that after heating, hydrolysis-condensation and oxidation treatments, the epoxy peak was no longer present in the spectrum [45, 46]. At 1086 cm^{-1} , it was assigned to the Si-O-C chains in the silane [47]. Moreover, there was a band at $2940\text{-}2960\text{ cm}^{-1}$ assigned to the CH_2 group. The important evidence to confirm the success of the silane treatment was revealed by the decrease in -OH groups at 1630 and 3430 cm^{-1} , as can be clearly seen in Fig. 3(a) [48].

Considering the spectra of MOR-MPTS compared with MOR-H in Fig. 3(b), the intensity of the bands at 1630 and 3430 cm^{-1} decreased after silane modification. This was due to the OH group of MOR reacting with the alkoxy group of silane. Therefore, the number of OH groups decreased. At 2565 cm^{-1} , the spectra were assigned to the sulfhydryl (SH) characteristic bands in the MPTS spectra. However, the sulfhydryl peak was no longer present

in the spectrum, which indicated that the sulfhydryl group of MPTS was converted to a sulfonic acid group (HSO_3^-). Similar behavior for FT-IR of the MPTS-treated zeolite data was reported elsewhere [44]. Nevertheless, the peak of the sulfonic acid group that appeared at $1,000\text{--}1,200\text{ cm}^{-1}$ did not appear in the MOR-MPTS spectra because they were overlapped by the peak of TO_4 (Si, Al tetrahedral units) [5, 38]. This was also the case for the spectra of MPDES and MPDMS. However, the peaks of MOR-GMPTS, MOR-MPTS, MOR-MPDES and MOR-MPDMS at around 3430 and 1630 cm^{-1} (which were assigned to the stretching of --OH and bending vibrations of H--O--H bonds on the surface of MOR, respectively) were found clearly with decreased intensities [48]. The FT-IR results definitely confirmed the success of the silane treatment. However, to determine the amount of silane treated on the MOR surface, TGA was used to obtain further details.

The TGA curves are shown in Fig. 4. From the results, the weight loss of samples can be divided into two intervals separated at 400°C . At $25\text{--}400^\circ\text{C}$, for all types of MOR, the reduction of weight was from water evaporation of only the weakly adsorbed water [15, 48]. Above 400°C , for unmodified MOR, a 0.67% loss was assigned to the strongly bound water and dehydroxylation of the external zeolite surface, according to Eq. (5) [15]. The weight loss of MOR was negligible.

In the case of modified-MOR, between 400 and $1,100^\circ\text{C}$, around $4.5\text{--}10\%$ weight losses were found. Compared with unmodified MOR, these differences could be explained by the surface modification on the MOR surface. As the strongly adsorbed water molecules were bound to the sodium cation within the zeolite windows, the internal pore structure was not affected by the silane. Therefore, the amount of water loss at higher temperatures remained approximately the same for all samples. The weight loss between 400 and $1,100^\circ\text{C}$ for modified-MOR should be attributed to the decomposition of organic substances which were silanes that had been grafted on the surface of MOR [15]. This indicated that the silanes

successfully bonded at the surface of MOR. The amount of grafted silane on the MOR surface was calculated. It was around 3.5%, 4%, 6%, and 8.9% for surfaces treated with MPDMS, MPTS, GMPTS, and MPTES, respectively. This result supported the FT-IR results that silane was successfully grafted onto the MOR surface.

3.2 Characterization of the Nafion composite membranes

Fig.5 shows SEM images (first image on the left) and EDXS mapping images (2nd image on the left: Si-element mapping, 3rd image on the left: Al-element mapping, 4th image on the left: S-element mapping, and the right image: F-element mapping) of the recast Nafion, Nafion/MOR-H, Nafion/MOR-GMPTS, Nafion/MOR-MPTS, Nafion/MOR-MPTES and Nafion/MOR-MPDMS composite membranes. The red color in EDX images represents Si and Al in the MOR structure, while black and green colors represent S and F in the Nafion structure, respectively. All membranes had a thickness of 125-130 μm . Fig. 5(a) shows the cross section of a recast Nafion membrane, which has a homogenous layer. The dispersion of an MOR-H particle which had not been functionalized by silanes is shown in Fig. 5(b). It was found that there were some pin holes (as depicted using arrows) leading to low compatibility between Nafion and MOR particles. The cross sectional layer for all types of membranes that contained silane-treated MOR consisted of two layers with a Nafion-rich layer on top and an MOR-rich layer on the bottom, as shown in Fig. 5 (c-f). Moreover, it was found that some small particles of MOR were dispersed in the Nafion layer, which could be observed using the Al and Si mapping from EDS. The separation of MOR particles might be due to the fact that the sizes of the particles were rather large. This was a limitation of the grinding [5, 14, 15, 38, 49]. Grinding in a fluid energy mill which is commonly used in the pharmaceutical and cosmetic industries may provide very fine-size products. It can be clearly observed that the smaller particles were able to disperse in the Nafion matrix layers. Therefore, more homogeneous dispersion may be improved by using a reduced size of MOR particles.

The tensile strength of the MPTES-MOR/Nafion and recast Nafion were determined using universal tensile testing. The data are provided in the supplementary data. Tensile strength of recast Nafion was 17.68 ± 0.61 MPa while that of MPTES-MOR/Nafion was 14.40 ± 0.46 MPa. It was found that the strength of the composite was slightly lower than that of recast Nafion. This might be due to two layers of MOR and Nafion that were formed. This was consistent to those found by Kwak et al. was less than that of pure Nafion, revealing poor compatibility of the composite due to no surface treatment of MOR was performed [33]. The size of particle filler was found to have an effect on the strength of polymer composite. It was reported that polymer composite with smaller particle size exhibit slightly higher tensile strength than that with larger particle size [50-52]. Therefore, reducing the size of MOR was an essential step in membrane composite fabrication.

3.3 Water and ethanol uptake

Water and ethanol uptake of membranes was carried out in order to study the effect of adsorption on the membrane properties. Since water is a major factor that causes the mechanical motion of proton transport within the membrane, it influences performance inside the fuel cell. Fig. 6 shows the water and ethanol uptake of all composite membranes. It was found that the water uptake of most composite membranes was lower than that of recast Nafion. This may be due to two reasons: that MOR was more hydrophobic than Nafion and

that the addition of zeolite resulted in a decrease in the ability to adsorb water molecules [5, 14]. The water uptake for all types of membranes was much higher than their ethanol uptake. This indicated that composite membranes adsorb water molecules in preference to ethanol molecules [38]. This property was an advantage for membrane use in DEFC as H_3O^+ transfers more easily than ethanol.

3.4 Ion-exchange capacity

Ion exchange capacity (IEC) is an indirect and reliable approximation of proton conductivity. It represents the number of moles of sulfuric acid per 1 g of dry membrane. Hydrogen (H^+) ions in the membranes were exchanged with sodium ions from the NaCl solution. The IEC values of all membranes are shown in Fig. 7. It can be clearly seen that commercial Nafion and recast Nafion had the highest IEC values. In contrast, Nafion/MOR-H displayed the lowest IEC values. These results corresponded with reports from Wang et al. [5] and Lin et al. [45]. Moreover, in our previous study [21], all mercapto silanes with a sulhydryl group ($-\text{SH}$) were not used. GMPTS-treated MOR was found as better than MOR-H. A later study discovered that using mercapto-silanes could be of benefit by having a sulfuric acid group in the composite membrane. When compared with silane modified-MOR membranes, it was found that Nafion/MOR-MPTS and Nafion/MOR-MPTES had higher IEC values than Nafion/MOR-GMPTS, because MPTS and MPTES contained the $-\text{HSO}_3$ group which was converted from the $-\text{SH}$ group after oxidization with hydrogen peroxide. Therefore, the hydrogen ion in the $-\text{HSO}_3$ group contained in the composite membrane can also exchange with the Na ion, leading to increased IEC value [5, 45].

3.5 Proton conductivity

The proton conductivity results of all membranes at various temperatures of 30, 50 and 70 °C are shown in Fig.8. In general, proton transport in Nafion can occur via two

mechanisms. The first mechanism is by a Grotthus or jump mechanism[38]. The protons pass down from the –OH groups or the SO_4^{2-} ion groups to each other by jumping. The proton produced by oxidation of ethanol on the anode side adheres to water molecules, resulting in a provisional hydronium ion being formed, and a different proton from the same hydronium ion hops onto the other water molecules. The second mechanism is called a vehicle mechanism [5]. The proton transfers in the form of a complex species, like H_3O^+ , by combining with the solvent molecules such as water. Therefore, the vehicle mechanism is highly dependent on the amount of water or ethanol molecules in the membrane [53, 54]. It was found from the experiment that Nafion/MOR-MPTES composite membranes had the highest proton conductivity for all conditions which were 0.078 ± 0.011 , 0.082 ± 0.004 and 0.089 ± 0.004 S/cm at 30, 50 and 70 °C, respectively. This may be due to the $-\text{HSO}_3$ group in MPTES being a good proton-passing medium [14]. Furthermore, MPTES had an ethoxy group which reacted more easily with MOR than the methoxy group in other silanes. Moreover, catalyst use in MPTES helped to facilitate the reaction of silane and MOR[38, 45]. When considering the effect of temperature, it was found that increasing the temperature resulted in higher proton conductivity and higher ethanol crossover. This was related to the Arrhenius effect, as shown in Eq. (6)[45].

$$\sigma = \sigma_0 \exp - \frac{E_a}{RT} \quad (6)$$

where σ is the proton conductivity (S/cm), σ_0 is a pre-exponential factor, R is the gas constant (8.314 kJ/molK), T is the absolute temperature (K), and E_a is the activation energy (kJ/mol). It can be seen that the proton conductivity is proportional to the temperature. When temperature of the system is raised, the proton conductivity increases. Moreover, in the fuel cell stack where the catalyst and water are present, the dissociation reaction of ethanol to free protons (H^+) has a higher rate constant (k) at a higher temperature. Eq. (7) shows the dissociation reaction of ethanol on the anode side in a fuel cell [55] and Eq. (8) shows the

relationship of the rate constant (k) with temperature [56]. This result was consistent with the report of Lin et al.[45].

$$k = k_0 \exp -\frac{E}{RT} \quad (8)$$

where k is the rate constant, k_0 is the frequency or pre-exponential factor, R is the gas constant (8.314 J/molK), T is the absolute temperature (K) and E is the activation energy (kJ/mol).

3.6 Ethanol permeability

Ethanol permeability testing in a diffusion cell was carried out systematically to evaluate the performance of the composite membranes. The low permeability of ethanol indicated that the membrane has a good ability to inhibit the permeation of ethanol. The high ethanol permeability resulted in the poor performance of the fuel cell. The ethanol permeability of all membranes is shown in Fig. 9 – 11. It can be observed that Nafion membranes had a high ethanol permeability compared with the other composite membranes and Nafion/MOR-MPTES had the lowest permeability. At 1 M ethanol concentration, the ethanol permeability of recast Nafion was higher than Nafion/MOR-MPTES by 24.16% at 30 °C, 24.98% at 50 °C and 34.79% at 70 °C. At 2 M ethanol concentration, the ethanol permeability of recast Nafion was higher than Nafion/MOR-MPTES by 24.86% at 50 °C and 17.41% at 70 °C. These values of ethanol permeability were comparable to the study of Barbora et al. [13] which Nd_2O_3 was used with the Nafion membrane for DEFC. Furthermore, at 4 M ethanol concentration, the ethanol permeability of recast Nafion was higher than Nafion/MOR-MPTES by 59.82% at 50 °C and 31.95% at 70 °C. These results indicated that the MOR-MPTES incorporated into Nafion was able to reduce the ethanol-crossover from the feed side to the permeate side in the diffusion cell, because the dispersion of zeolite particles

increased the distance and the tortuosity for ethanol molecules to transfer across the membrane in the cell. Moreover, the incorporation of MOR in the polymer compressed the volume between the polymer chains. It also reduced the swelling and reduced the adsorption of ethanol in the membranes [38], leading to the decrease in permeability.

The effect of MOR surface modification on the suppression of the ethanol crossover property was studied by varying the types of silane. It was clearly found that the silane chain grafted on MOR particles enhanced the compatibility between MOR and Nafion in all composite membranes. Considering the types of organic groups in silanes, silane containing sulfonic acid ($-\text{HSO}_3$) in MPTS was compared with silane containing the epoxy group ($-\text{C}-\text{C}-$) in GMPTS. It was found that the Nafion/MOR-MPTS membrane had lower ethanol permeability when compared with the Nafion/MOR-GMPTS membrane. This was due to the sulhydryl group ($-\text{SH}$) in MPTS being converted to a sulfonic acid group while GMPTS had no $-\text{HSO}_3$ group. This group on the treated MOR surface was the same as the $-\text{HSO}_3$ group in the Nafion solution. Therefore, the reaction of treated MOR with Nafion occurred easily. Moreover, the $-\text{HSO}_3$ group helped to facilitate the proton conducting ability. This was in agreement with the report of Lin et al. [45]. Considering the number of alkoxy groups of silanes, the MPDMS structure with two chains of the methoxy group was compared with MPTS with three chains of the methoxy group to react with MOR. It was found that the Nafion/MOR-MPDMS membrane had higher ethanol permeability when compared with the Nafion/MOR-MPTS membrane. This may be because MPDMS had weaker interaction with the zeolite than did MPTS, as MPDMS has two chains while MPTS has three chains to react with the zeolite surface. Considering the types of alkoxy group in all mercapto silanes that were used, MPTES had an ethoxy group while MPTS had a methoxy group to react with the $-\text{OH}$ group on the surface of MOR. It was found that the Nafion/MOR-MPTES membrane had lower ethanol permeability when compared with the Nafion/MOR-MPTS membrane. This may be due to the need to use a catalyst in the reaction of silane containing the ethoxy group

[57]. Therefore, in the MP TES treatment, the AlCl_3 catalyst was used, which meant that MP TES was easier to hydrolyze than MPTS, which contains a methoxy group. This resulted in superior performance in the case of MP TES compared with MPTS.

The temperature of the ethanol feed solution was an important factor that affected the ethanol permeability. It resulted in an increase of the ethanol diffusion rate and proton conductivity, due to the decreased resistance of the membranes. For all ethanol concentrations and for all the membranes, an increase in the temperature increased the permeability. These results agreed with the reports of Mukoma et al. [43] and Yoonoo et al. [21]. The increased temperature caused the mechanical strength of the membranes to decrease, which led to the degradation of the membranes.

4. Conclusions

MOR/Nafion composite membranes were synthesized to reduce the ethanol crossover in DEFC. Four types of silanes, having different functional groups of epoxy (GMPTS) and sulhydryl (MPTS, MP TES, and MPDMS), were selected to treat on the MOR surface to improve the compatibility of MOR in the composite membrane for DEFC. They successfully modified the surface of MOR, as confirmed by the FT-IR and TGA results. These silanes improved the compatibility between the organic and the inorganic parts as well as the interfacial properties, leading to the obvious reduction of the ethanol permeability of the membranes. This was indicated by much lower ethanol permeability and higher selectivity of those composite membranes compared to the recast Nafion membrane. The Nafion/MOR-MP TES composite membranes showed excellent proton conductivity relative to all other membranes under all conditions and had the lowest ethanol permeability under almost all conditions. This was due to several reasons; (1) the sulhydryl group ($-\text{SH}$) in MP TES was converted to a sulfonic acid group ($-\text{SO}_3$) to facilitate the proton transfer while there was none in GMPTS, (2) three chains of the ethoxy group in MP TES form strong bond, while there are

two chains in the MPDMS structure leading to weak interaction with the MOR surface (3) ethoxy group in MPTES and was easier to hydrolyze than the methoxy group in MPTS. This resulted in the Nafion/MOR-MPTES composite membranes having the highest selectivity of about 5.42×10^4 Ss/cm³ at 30 °C in a 1 M ethanol concentration. In conclusion, this paper provides the method and explanation for developing a suitable composite membrane for direct ethanol fuel cells. It also shows the results and explanation of the effect of a functional group of silanes on the ethanol permeability and compatibility in the composite membranes for DEFC.

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Fig. 1. XRD patterns of as-purchased MOR and MOR after the treatment steps of grinding, protonating, and functionalization.

Fig. 2. Structures of silanes (a) GMPTS (b) MPTS (c) MP TES and (d) MPDMS.

Fig. 3. FT-IR results of MOR-H compared with (a) MOR-GMPTS and (b) MOR-MPTS, MOR-MPTES and MOR-MPDMS.

Fig. 4. The TGA results of MOR before and after treatment by different types of silanes.

Fig. 5. SEM images (first image on the left) and EDS mapping (2nd: Si-element mapping, 3rd: Al-element mapping, 4th: S-element mapping, and last images: F-element mapping) of (a) recast Nafion membrane, (b) Nafion/MOR membrane, (c) Nafion/MOR-GMPTS membrane, (d) Nafion/MOR-MPTS membrane, (e) Nafion/MOR-MPTES membrane and (f) Nafion/MOR-MPDMS membrane.

Fig. 6. Water and ethanol uptake of composite membranes.

Fig. 7. Ion exchange capacity composite membranes.

Fig. 8. Proton conductivity of each membrane at 30 °C, 50 °C and 70 °C.

Fig. 9. Ethanol permeability of all types of membranes at 30 °C, 50 °C and 70 °C at 1 M ethanol concentration.

Fig. 10. Ethanol permeability of all types of membranes at 30 °C, 50 °C and 70 °C at 2 M ethanol concentration.

Fig. 11. Ethanol permeability of all types of membranes at 30 °C, 50 °C and 70 °C at 4 M ethanol concentration.