Sulfonated PEI membrane with GPTMS-TiO$_2$ as a filler for potential direct methanol fuel cell (DMFC) applications

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Abstract

This study addresses the effect of 3-Glycidyloxy propyl trimethoxysilane (GPTMS)-modified titanium dioxide (TiO$_2$) which composited sulfonated polyetherimide (SPEI) as a proton exchanger on direct methanol fuel cell (DMFC). The membrane fabrication was mainly based on phase-inversion method after GPTMS-TiO$_2$ and SPEI were prepared separately. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electronic microscopy (SEM), ion exchange capacity (IEC), proton conductivity, water uptake, methanol permeability, and mechanical properties were utilized to characterize and measure their physical and thermal stability. As the result, high water uptake and IEC performance were achieved using the fabricated membrane. Lower methanol permeability was observed compared to Nafion 117 membranes. The membrane performance showed improvement using 20 wt% SPEI and 5wt% TiO$_2$-5 wt% GPTMS with an optimum result of 3 times lower in terms of methanol uptake and methanol permeability with proton conductivity of 21 mS cm$^{-1}$ than the remaining membranes and Nafion. Thus, the obtained results of SPEI/TiO$_2$-GPTMS can be promoted as a novel polymeric membrane for DMFC.

Keywords: Sulfonated polyetherimide, titanium dioxide, blend membrane, direct methanol fuel cell, glycidyloxypropyltrimethoxysilane

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INTRODUCTION

A fuel cell as an electrochemical device has been developed to convert chemicals into electrical energy which based on the redox reactions (Ma et al., 2013). A composite polymeric membrane as a favourable proton exchanger has been widely used as the electrolyte for direct methanol fuel cells (DMFC). DMFC is capable of producing high energy with a simple design, easy handling, light in weight, environmentally-friendly and easy to move. Therefore, DMFC is commonly developed as a safe source of clean energy to be applied compared to the remaining fuel cells (Heo et al., 2012; Tohidian et al., 2013; Ting et al., 2014).

Such polymer electrolyte membranes (PEM) were mainly used in the middle between cathode and anode side. The mostly developed commercial membrane with the same function is a perflurosulfonic acid membrane (Nafion$^5$) due to high chemical stability and proton conductivity (Lu et al., 2013). However, the membrane has several drawbacks, such as expensive, high methanol movement, low thermal stability (up to 100 °C), and dehydrated quickly with decreasing proton conductivity over 100 °C (Wang et al., 2010; Lufrano et al., 2013). In order to solve this problem, a novel electrolyte membrane material with a higher performance compared to the commercial material is promoted in this study.

The composite membrane consists of combined organic and inorganic materials which improved the comprehensive properties of a matrix as reported in the previous study (Yang, 2009). PEI is a polymer composed of phenyl groups, ether linkages with an imide group bonded angularly between aromatic rings in the backbone and branched chain then generate strong hydrogen bonding. The strength of the bond produces high chemical and mechanical stability, solvent and heat resistance, as well as good film-forming properties. In terms of cost effectiveness, PEI (USD 255.4 / kg) is much cheaper than Nafion 117 (USD 363.7 / 100 ml). Moreover, sulphonated PEI modification was able to increase proton conductivity up to 0.0014 S / cm at 25 °C and an ion exchange capacity at 0.553 meq / g as reported by Rajagopalan et al. and Guhathakurta et al. Thus, it can be expected to have good prospects as a base material of polymer matrix membrane for DMFC application. In addition, the mechanical and chemical stability can be further improved using filler addition such Nafion or polymers-TiO$_2$ composite membranes which have attracted the attention of many researchers (Baglio et al., 2005; Chen et al., 2007; Hammami et al., 2005; Hammami et al., 2012).

Titanium dioxide (TiO$_2$) is a good candidate for the hydrophilic filler because it provides suitable hydration of the membrane under fuel cell operation conditions (Hammami et al., 2012). Nafion with blended TiO$_2$ by sol-gel method to form a composite membrane showed an improved cell performance at 130 °C. In addition, GPTMS has been...
used to improve the interconnection between organic and inorganic material, due to its coupling agent characteristic (Wang et al., 2010). Therefore, the present investigation was performed to study the effect of sulfonated polyetherimide with TiO2 modification using GPTMS as a filler to enhance the performance of a novel composite electrolyte membranes which has not been reported yet.

**EXPERIMENTAL**

**Materials**

Commercially available polyetherimide (PEI) (Sigma-Aldrich) was used as SPEI membrane material as well as chlorosulfonic acid (p.a 97%, Sigma-Aldrich) and 1,2-dichloroethane (p.a 99%, Sigma-Aldrich). N,N-dimethyl-acetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were supplied by Sigma-Aldrich and used as a solvent to prepare the polymeric solution. Isopropanol (Sigma-Aldrich) as a precipitating agent. The Nafion® 117 membranes was purchased from DuPont Co. TiO2 (Mw= 79.87 g/mol, 21nm particle size) by Sigma-Aldrich. Toluene, chloride acid, sulfuric acid, and GPTMS were also purchased from Sigma Aldrich. Demineralized water was used to reduce the acidity.

**Preparation of Sulfonated polyetherimide (SPEI)**

Firstly, 10 g PEI was dissolved in 60 °C of 50 mL dichloroethane for 5 h. Next, the solution was stirred at room temperature for 1 h. Then, a mixture of 2.06 mL chlorosulfonic acid:35 mL dichloroethane was dropped gradually into the polymer solution under stirring for 45 min. The product was filtered and washed with isopropanol three times to remove the excess of acidity, and dried at 50 °C of 10 ℃ for 24 h with a weighted ratio of 2:1:20, respectively. Then, the resulting product was washed using ethanol in three times and immersed in a 0.1 M HCl for 12 h. After that, the solution was cooled down to room temperature before being cast on glass plates. The resulted membrane was then dried at room temperature for 12 h before being immersed in deionized water, and dried at 100 °C (Wang, 2010).

**Fabrication of SPEI/GPTMS-TiO2 membranes**

The GPTMS addition in a different mass composition of 3, 5, and 7 wt% was prepared to modify in composite membrane. The SPEI polymers were dissolved in NMP, put on the GPTMS-TiO2, and stirred at 60 °C for 12 h. After that, the solution was cooled down to room temperature before being cast on glass plates. The resulted membrane was then dried at room temperature for 12 h before being immersed in sulfuric acid for 12 h.

**Characterization of SPEI/ GPTMS-TiO2 membranes**

The fabricated membranes were dried at 80 °C for 1 h before examining the functional groups by using FT-IR measurement which was conducted in the range of 4000-400 cm⁻¹. The morphological study on the membrane surface and cross-section of SPEI/GPTMS-TiO2 were analyzed using a Zeiss field emission scanning electron microscope (SEM). The membrane was frozen and cut apart after being immersed in liquid nitrogen to obtain a cross-section membrane sample analysis. The membrane performance was then evaluated using contact angle (CA) Optima Surface Analysis System OCA (AST Products Inc., Billerica, MA). The membrane sample with dimension 5 cm × 1.5 cm was placed on a glass plate and fixed with a tape. A drop of distilled water was dropped onto the sample surface using a microsyringe (Hamilton Company, Reno, NV). The CA was measured within 30 s period after the water was dropped. The CA value was presented as an average value from 10 different spots on the membrane sample.

The mechanical strength properties of the SPEI/GPTMS-TiO2 membrane were measured by the tensile machine (Instron 5567, TA Instruments Co.) at room temperature. The sample was taken at a rate of 5.0 mm min⁻¹ which taken five times to obtain an average value. Thermal stability of the SPEI/ GPTMS-TiO2 membrane was characterized using TGA. Dry sample was ground into fine powder and the sample was placed in a platinum pan. The sample powder was prepared in the pin stub holder and coated with gold with carried out temperature between 30-900 °C using heating rate of 10 °C min⁻¹ under air atmosphere.

**Water uptake and swelling ratio**

The SPEI/GPTMS-TiO2 membrane was dried at 80 °C under vacuum for 24 h. The weight and dimension of the membrane were measured before being immersed in deionized water for 24 h at room temperature. The membrane was then weighed to determine its weight in the wet condition. The dimension of the wet membrane was also recorded. Prior to the measurement, the moisture on the surface of the membrane was blotted dry using absorbent paper. The water uptake and swelling ratio of the membrane were determined using the following equations:

\[
\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \tag{1}
\]

where \(W_{\text{wet}}\) and \(W_{\text{dry}}\) are the weight of the membrane in wet and dry state, respectively (Purwanto et al., 2016).

\[
\text{Swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \tag{2}
\]

where \(L_{\text{wet}}\) and \(L_{\text{dry}}\) are the length of the membrane in wet and dry condition, respectively (Liu et al., 2014).

**Ion exchange capacity (IEC)**

The IEC of the SPEI/GPTMS-TiO2 membrane was obtained using titration method. The membrane was dried at 50 °C for 24 h, and weighed. Then the membrane was soaked in 50 mL of 1 M NaCl solution to exchange the H⁺ ions in the membrane matrix with Na⁺. The solution was titrated with 0.01 M NaOH. 1 wt% phenolphthalein in ethanol solution was used as an indicator. The IEC of the membrane was calculated using the following equation:

\[
\text{IEC (mmol/g)} = \frac{M_{\text{NaOH}} \times 1000 \times V_{\text{NaOH}}}{w_{\text{d}}} \tag{3}
\]

where \(V_{\text{NaOH}}\) is the NaOH consumed solution, \(M_{\text{NaOH}}\) is the concentration of NaOH, and \(w_{\text{d}}\) is the weight of the dry membrane (Purwanto et al., 2016).

**Methanol permeability and proton conductivity**

Methanol permeability was determined using a two-compartment diffusion cell. Compartment A was filled with 1 M methanol solution and compartment B was filled with deionized water. The membrane was placed between compartment A and B. Samples from compartment B were taken out every 30 minutes for 6 hours to determine the methanol concentration using high-performance liquid chromatography (HPLC). The methanol permeability values were determined by using equation (4).

\[
P = \frac{\Delta C_{A}}{\Delta t} = \frac{I_{V} R}{A C_{A}} \tag{4}
\]

Based on Equation 4, \(P\) is methanol permeability of the membrane (cm².s⁻¹), \(\Delta C_{A}/\Delta t\) is the slope variation of methanol concentration in compartment B as a function of time (mol L⁻¹.s⁻¹), \(L\) is the thickness of the membrane (cm), \(V_{0}\) is the volume of the water at compartment A (cm³), \(A\) is the membrane surface area (cm²), and \(C_{A}\) is the concentration of methanol in the cell A (mol L⁻¹) (Purwanto et al., 2016).

The proton conductivity of the SPEI/ GPTMS-TiO2 membrane was measured using electrochemical impedance spectroscopy (EIS) over a frequency range of 1-10⁶ Hz. The proton conductivity values were calculated using equation (5):

\[
\sigma = \frac{L}{R \times A} \tag{5}
\]
where \( \sigma \) is the proton conductivity of the membrane \((S \text{ cm}^{-1})\), \( L \) is the membrane \((\text{cm})\), \( A \) is the membrane surface area \((\text{cm}^2)\), and \( R \) is the membrane resistance \((\Omega)\) (Purwanto et al., 2016).

RESULTS AND DISCUSSION

Morphological analysis

Figure 1 shows the SEM image of different morphological structure of PEI-based polymeric membrane. According to the previous work by Muliawati et al. (2017a), Figure 1a shows SPEI-based membrane with dense structure and some defects at the surface while Figure 1b illustrates the remains of TiO\(_2\) agglomeration (spherical bulk) on the surface, indicating low TiO\(_2\) particle distribution and interconnection bonding between TiO\(_2\) as inorganic material with SPEI as organic compound. In this work, the tight bonding between TiO\(_2\) and SPEI was successfully modified by GPTMS addition as shown in Figure 1c. The red arrow shows the GPTMS as connecting fiber which leads to the interconnection of those SPEI and TiO\(_2\). This means that the interconnection can improve the mechanical and proton conductivity properties as referred to Wang et al. (2010) using Chitosan/GPTMS-zeolite \(\beta\) membrane.

FT-IR measurement

To gather more information about the presence of SPEI/GPTMS-TiO\(_2\) interconnections, the membranes were characterized by FT-IR as shown in Figure 2. Figure 2a shows SPEI membrane spectra while Figure 2b shows SPEI spectra after GPTMS-TiO\(_2\) addition at various ratio i.e. 3%-5%, 5%-5%, and 7%-5%. The results showed that the broadening absorption peak on both spectra at around 3600 cm\(^{-1}\) assigned a vibration of –OH from the interaction between –SO\(_3\)H and H\(_2\)O molecules (Rajagopalan et al., 2010; Liu et al., 2014; Muliawati et al., 2017a)). The absorption spectra at around 3000-2800 cm\(^{-1}\) reveal to Csp3-H span and the methylene absorption band at 1400 cm\(^{-1}\) as well as –CN absorption band at 1460 cm\(^{-1}\). In addition, the S = O absorption from -SO\(_3\)H functional group was shown at around 1279 and 1071 cm\(^{-1}\). Furthermore, on the SPEI/GPTMS-TiO\(_2\) spectra showed a sharp peak at around 400-700 and 995 cm\(^{-1}\) (Ti-O,Ti-O-Ti and Ti-O-Si) which indicated the presence of GPTMS and TiO\(_2\). This FTIR result indicates that the modification of GPTMS-TiO\(_2\) has been successfully interconnected in SPEI as accordance to the SEM result.

Mechanical and thermal stability properties

PEM with good mechanical properties is required to improve the performance in terms of the membrane flexibility for DMFC application. As can be seen in Figure 3, the mechanical properties of the SPEI / GPTMS-TiO\(_2\) membrane shows higher tensile strength as compared to the SPEI membrane. The tensile strength of the SPEI membrane showed higher value than 3% GPTMS-5% TiO\(_2\) addition because 3% GPTMS was not enough to be used to form SPEI and TiO\(_2\) interconnection. The less crosslinking formation reduced the molecular flexibility and became less elongated before the membrane was damaged. While the increasing GPTMS addition from 3% to 7% showed increasing tensile strength from 15.8 to 22.0 MPa.

Moreover, the resulting mechanical properties measurement also showed that the increasing filler addition increased the mechanical properties up to 3% addition of GPTMS then significantly constant at 5% and 7% GPTMS addition of 21.1 and 22 MPa, respectively. This is due to GPTMS-TiO\(_2\) perfectly interact with SPEI monomer to form macromolecules of SPEI/GPTMS-TiO\(_2\) at 3% GPTMS composition. It indicated that the crosslinking between filler and polymer was perfectly connected to form the SPEI/GPTMS-TiO\(_2\) interconnection. The illustration of the interaction between GPTMS-TiO\(_2\) and SPEI monomer is clearly revealed in Figure 4 which also shows the probability of proton transport mechanism. The proton from methanol and/or water passes the membrane through the –OH and –SO\(_3\)H groups then the proton initiated the electric current production on DMFC application as reported by Purwanto et al. (2016).
In addition, TGA was also applied to measure the membrane thermal stability and a cross-linking formation, respectively. It can be seen in Figure 5, the TGA measurement of SPEI/5%GPTMS-5%TiO₂ shows a difference in temperature weight loss compared to the SPEI membrane. However, the stability of the two membranes was still above 80 °C, indicating that the membrane thermal stability was good enough for the desired DMFC application conditions. The weight lost at around 100 °C and 250 °C in SPEI/GPTMS-TiO₂ membrane indicate the decomposition of hydroxyde and sulfonic acid groups in the polymer chain (Rajagopalan et al., 2010). The few percentage of weight lost at above 100 °C described the sufficient thermal stability of the membrane for required DMFC application conditions.

Performance Test of SPEI/GPTMS-TiO₂ membrane

The membrane has been measured the membrane capacity, methanol permeability, and proton conductivity as reported in Table 1 and Table 2, respectively. The SPEI/GPTMS-TiO₂ membrane with 5 wt% GPTMS showed the highest performance as it possessed the desired properties to be applied for DMFC application where the parameters were the water uptake, methanol uptake, membrane swelling ratio, ion exchange capacity (IEC), water contact angle, proton conductivity, and methanol permeability measurement. Water and methanol uptakes attributes to the ion and methanol diffusion through the electrolyte membrane. The swelling ratio indicates the stability of the membrane in an aqueous solution (Wang et al., 2009) and ion exchange capacity (IEC) is defined as fixed group millionaires of exchange per gram of polymer, usually corresponding to the number of sites for proton transfer (Yang, 2009). The contact angle reveals the hydrophilic or hydrophobic degree of a material. The conductivity of protons is one of the most important factors for proton membranes used in fuel cells. In general, proton transport in a hydrated polymer matrix is described by two main mechanisms: proton hopping or the Grothaus mechanism using a "diffusion mechanism" using water (-OH groups) as proton transport or "vehicular mechanism" (Purwanto et al., 2016). Methanol permeability is measured to evaluate the membrane ability to prevent the methanol crossover or methanol rate through the membrane structure (Liu et al., 2014). All of these parameters are interlinked for good performance in DMFC applications.

Well-performing membranes generally have high proton conductivity with high water uptake, low methanol absorption and permeability of methanol, high ionic exchange capacity (IEC), low membrane swelling ratio, lower contact angle (membrane more likely to be hydrophilic), as well as can be operated at high temperatures (> 80 °C). Water uptake contributes substantially to the formation of hydrophilic properties in membranes capable of facilitating proton transport even under low humidity conditions (Shu et al., 2008). The water absorption rate in the polymer can be increased by increasing the ionic group content (-OH and -SO₃H) in the polymer chain, but too much water uptake leads to an increase in swelling of the membrane, resulting in loss of mechanical stability in the membrane (brittle) and methanol permeability become high (Shu et al., 2008).

IEC values depend on the number of sulfonic acid groups in the chemical structure of the polymer membrane and may affect the water absorption and the conduction properties of protons on the polymer membrane (Liu et al., 2014). The value of IEC is increased when the polymer composition loading is increased (Purwanto et al., 2016). Therefore, all parameters must be optimized for further enhancing the performance of fuel cell operations.
**Table 1** The membrane properties.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water uptake (%w/w)</th>
<th>Methanol uptake (%w/w)</th>
<th>Swelling ratio (%)</th>
<th>IEC (mmol/g)</th>
<th>Contact Angle (°)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% SPEI</td>
<td>6.1</td>
<td>5</td>
<td>4</td>
<td>0.4</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>20% SPEI – 3% TiO2</td>
<td>23.5</td>
<td>18</td>
<td>14.7</td>
<td>1.24</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>20% SPEI – 5% TiO2</td>
<td>49.3</td>
<td>30</td>
<td>12</td>
<td>1.9</td>
<td>68.97</td>
<td></td>
</tr>
<tr>
<td>20% SPEI – 7% TiO2</td>
<td>47.2</td>
<td>29</td>
<td>10</td>
<td>2.1</td>
<td>66.36</td>
<td></td>
</tr>
<tr>
<td>20% SPEI – 3% GPTMS – 5% TiO2</td>
<td>39</td>
<td>28</td>
<td>9</td>
<td>2.0</td>
<td>66.23</td>
<td></td>
</tr>
<tr>
<td>20% SPEI – 5% GPTMS – 5% TiO2</td>
<td>54</td>
<td>33</td>
<td>11</td>
<td>2.4</td>
<td>71.11</td>
<td>This work</td>
</tr>
<tr>
<td>20% SPEI – 7% GPTMS – 5% TiO2</td>
<td>53</td>
<td>32</td>
<td>11.5</td>
<td>2.5</td>
<td>68.66</td>
<td>This work</td>
</tr>
<tr>
<td>20% SPEI – 7%GPTMS – 5% TiO2</td>
<td>52</td>
<td>30.9</td>
<td>12</td>
<td>2.6</td>
<td>63.81</td>
<td>This work</td>
</tr>
<tr>
<td>Nafion® 117</td>
<td>19.3</td>
<td>41</td>
<td>16.4</td>
<td>0.98</td>
<td>80</td>
<td>(Liu et al., 2014)</td>
</tr>
</tbody>
</table>

**CONCLUSION**

It can be concluded that the SPEI/GPTMS-TiO2 membrane with 20wt% SPEI and 5wt% GPTMS-TiO2, 5wt% composition showed high performance which can be applied on direct methanol fuel cell membrane due to the low methanol permeability compared to commercial membrane Nafion. Additionally, it also has a high-temperature stability at above 100 °C. Although proton conductivity was quite low, it can be modified with other polymers or fillers to improve its properties. Given the presence of -OH and -SO3H functional groups on the SPEI/GPTMS-TiO2 membrane, this resulted in the possibility of proton transport through the membrane.

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