CHAPTER VII

Effect of sulfonated graphene oxide on the performance enhancement of acid-base composite membranes for direct methanol fuel cells

7.1 Introduction

Currently, chemically modified graphene is receiving great deal of attention in wide range of application, such as energy related materials, sensors, field-effect transistors and biomedical application [1-6]. The interesting properties of graphene oxide (GO) like high surface area, inherent flexibility, electronic insulating property, thermal and excellent mechanical strength etc., makes it an important material to be used as organic filler for nano-composite membrane [7]. GO can be easily modify because of the oxygen containing functional groups such as carbonyl, hydroxyl and epoxy. For PEM preparation, GO nano-sheets have been usually sulfonated to achieve high proton conductivity. Jung et al., observed the graphene reinforced Nafion composite shows improved water uptake and proton conductivity [8], while Zarrin et al., found that higher water uptake and proton conductivity in a sulfonic acid functionalized GO-Nafion composite membrane than that of powdered GO [9]. Later, in the work done by Gaholt et al., the composite membranes of sulfonated poly (ether sulfone) (SPES) incorporated with sulfonated GO (SGO) resulted in improved electrochemical properties [10].

Polymer blending approach is one of the favored methods to improve the PEM properties, as the required behavior of the two components can be combined in one blend [11]. In our previous chapter, we reported the physico-chemical properties of the SPEES/PEI composite membrane for DMFC application [12]. These composite membranes had excellent methanol barrier properties with reasonable proton conductivity. Increasing the concentration of PEI improves the chemical stability of
highly sulfonated PEES matrix but reduces the proton conductivity. Addition of 15 wt% of PEI into the SPEES matrix shows promising performances such as good oxidative stability and higher membrane selectivity. In this study, SGO was synthesized and SP/SGO-X (Where SP is SPEES/PEI-15 wt% and X=0 to 0.8 wt% of SGO content) composite membranes were prepared with various contents of SGO using solution casting and evaporation method. It is expected in the improvement of proton conductivity when SGO was introduced into the SPEES/PEI-15 composite membranes. The prepared composite membranes were characterized by proton conductivity, methanol permeability, water uptake, IEC, dimensional and oxidative stability.

7.2 Results and Discussion

7.2.1 Characterization of GO and SGO

The FTIR spectrum was employed to confirm the successful oxidation of graphite into GO and sulfonation of GO into SGO. The presence of different
functional groups such as hydroxyl, carboxyl, epoxy etc., on GO was shown in the Figure 7.1(a). It shows C=C stretching at 1623 cm\(^{-1}\) and C-O deformation at 1390 cm\(^{-1}\) [13, 14]. The peak at 1727 cm\(^{-1}\), 1234 cm\(^{-1}\) and 1055 cm\(^{-1}\) confirms the presence of carboxyl, epoxy and alkoxy functional groups [15]. Presence of these peaks confirms the successful oxidation of graphite into GO. Figure 7.1(b) shows the FTIR spectrum of SGO. By comparing Figure 7.1(a) and 7.1(b), two new characteristic peaks at 2920 cm\(^{-1}\) and 1180 cm\(^{-1}\) appear in the SGO spectra which attributed to the absorption of sulfonic acid group [8, 14]. Hydrogen bonded O-H stretching vibration found at 3398 cm\(^{-1}\) for GO and SGO.

7.2.2 Characterization of SP/SGO-X membranes

Blending of PEI was done to improve the properties such as oxidative stability, methanol resistance etc., of the SPEES membrane as well as to reduce the membrane manufacturing cost. Among all, membranes prepared from the cast solution of SPEES/PEI-15% exhibits good oxidative stability with high relative selectivity; therefore SPEES/PEI-15% (SP) dope solution was used for further work.

7.2.3 Ion exchange capacity

The IEC of the PEM provides information on the charge density of the membrane, which is an important factor associated with proton conductivity and transport property of the membrane [16]. Table 7.1 shows the IEC value of the prepared membranes. The IEC capacity of SP membrane was 1.28 meq/g. The IEC of the composite membrane increases with increasing SGO content. This is due to the SGO contains \(-\text{CO}_2\text{H}/-\text{SO}_3\text{H}\) groups, responsible for high mobility for ionizable group. With the increase in SGO content in the composite membrane, the membrane becomes more hydrophilic and augments the suitable ion exchangeable sites.
Table 7.1. IEC, \( \lambda \) value, water uptake and swelling ratio of SP and SP/SGO-X composite membranes

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>IEC, meq/g</th>
<th>( \lambda ) value</th>
<th>Water uptake, %</th>
<th>Swelling ratio, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 °C</td>
<td>80 °C</td>
</tr>
<tr>
<td>SP</td>
<td>1.28</td>
<td>14.3</td>
<td>33.0</td>
<td>46.4</td>
</tr>
<tr>
<td>SP/SGO-0.1</td>
<td>1.30</td>
<td>14.6</td>
<td>34.2</td>
<td>49.2</td>
</tr>
<tr>
<td>SP/SGO-0.2</td>
<td>1.33</td>
<td>15.3</td>
<td>36.7</td>
<td>52.5</td>
</tr>
<tr>
<td>SP/SGO-0.5</td>
<td>1.39</td>
<td>16.1</td>
<td>40.3</td>
<td>54.7</td>
</tr>
<tr>
<td>SP/SGO-0.8</td>
<td>1.45</td>
<td>17.1</td>
<td>44.8</td>
<td>58.3</td>
</tr>
</tbody>
</table>

\( ^a, ^b \) dimensional stability measured at 25 °C and 80 °C respectively

7.2.4 Water uptake, dimensional stability and \( \lambda \) value

The water uptake of the composite membranes plays a crucial role in proton transferring because it provides proton carriers in vehicle type mechanism and forms a hydrogen bond network for Groutthuss type mechanism [17-19]. As shown in Table 7.1 and Figure 7.2 the water uptake of the prepared membranes increases with the increase in SGO content of the membrane. This is due to the hydrophilic groups of SGO, which can interact with water via electrostatic bond or hydrogen bond. The water uptake of the SP/SGO-X membranes was measured at 25 °C and 80 °C as presented in Figure 7.2. The water uptake of the composite membranes increases with increase in temperature. The only possible reason is that polymer chain mobility increases at higher temperatures that cause larger space for water absorption [20]. The SP/SGO-0.8 membrane possessed the highest water uptake of 44.8% at 25 °C and 58.3% at 80 °C owing to its most hydrophilic content. The number of water molecules absorbed per sulfonic acid group (designated as \( \lambda \)) was calculated by using water
uptake and IEC. From Table 7.1, λ value for the SP membrane is found to be 14.3. The λ value increases gradually with increasing in SGO content due to the presence of highly acidic functionalized SGO. The λ value of the composite membrane was in the range of 14.6-17.1. The higher λ value in the composite membranes is responsible for formation of ionic cluster in the membrane.

![Figure 7.2](image.png)

**Figure 7.2** Water uptakes of SP and SP/SGO-X composite membranes

Swelling ratio is also considered as an important parameter for the practical utilization of PEM in DMFCs [21]. As shown in the Table 7.1, swelling ratio of the composite membranes display a similar dependence to that of water uptake. The swelling ratio of the composite membranes was in the range of 18.3 - 22.0% at 80 °C. Enhanced swelling ratio of SP/SGO-X composite membranes was attributed to the high hydrophilic membrane surface, which is due to the high density of carboxylic and sulfonic acid group in SGO [22]. The largest swelling ratio is 22.4% at 80 °C, which is slightly higher than that of Nafion 117 (21.7%) [23]. The experimental results indicate that the SP/SGO-X membranes display comparable swelling property with Nafion 117.
7.2.5 Thermal stability

Figure 7.3  Thermal stability of SP and SP/SGO-X composite membranes

Figure 7.3 shows the TGA curves of SP, SP/SGO-0.2, SP/SGO-0.5 and SP/SGO-0.8 membranes. It is obvious that all the composite membranes exhibited three stages of weight loss in TGA curve. For SP membrane, the initial weight loss below 150 °C was due to the evaporation of absorbed/bound water. The second weight loss started approximately around 274 °C, was caused by the thermal decomposition of sulfonic acid groups. The third weight loss started at about 480 °C was attributed to the thermal decomposition of the polymer backbone. For the SP/SGO-X composite membranes, thermal degradation of SGO occurs in the second and third stages. In the second stage, the incorporated SGO retards the decomposition of SP chains as confirmed by their highest onset temperatures [14]. The composite membranes displayed higher desulfonation and polymer backbone degradation temperature compared to those SP membranes due to the strong interaction between
the SGO and SP polymer which hinders the polymer chain mobility [24, 25]. These results showed that the incorporation of SGO can improve the thermal stability of the composite membranes.

### 7.2.6 Oxidative stability

**Figure 7.4** Oxidative stability of SP and SP/SGO-X composite membranes

Fenton’s test provides an indication of relative durability of membrane from free radical attack under fuel cell operating condition [26]. The retained weight and rupture time of the composite membranes are shown in Table 7.2 and Figure 7.4. It has been observed that SP/SGO-X membranes retained 95.6 % of weight after immersion in Fenton’s solution, while the rupture time of the membrane decreases slightly caused by oxidative attack on the aromatic rings of main chain by HO\(^-\) and HOO\(^-\) radicals. From the results, the impact on the radicals on the SP/SGO-X composite membranes was very low. This may be due to the stable nature of the SGO filler and the presence of oxygen containing functional groups on the SGO surface.
forms a hydrogen bonding network with the SP matrix, which may protect the polar groups of SP matrix from the attack of the radicals [27, 28]. This result demonstrates that the SP/SGO-X membrane has good oxidative stability against Fenton’s test.

**Table 7.2.** Oxidative stability, proton conductivity, methanol permeability and relative selectivity of SP and SP/SGO-X composite membranes

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Oxidative stability, %</th>
<th>Proton conductivity, S/cm</th>
<th>Methanol permeability, cm² s⁻¹</th>
<th>Relative selectivity, S cm⁻³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Retained weight, %</td>
<td>Rupture time, min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP</td>
<td>98.5</td>
<td>304</td>
<td>$5.32 \times 10^{-3}$</td>
<td>$3.26 \times 10^{-7}$</td>
</tr>
<tr>
<td>SP/SGO-0.1</td>
<td>98.2</td>
<td>304</td>
<td>$5.86 \times 10^{-3}$</td>
<td>$3.19 \times 10^{-7}$</td>
</tr>
<tr>
<td>SP/SGO-0.2</td>
<td>97.4</td>
<td>301</td>
<td>$6.41 \times 10^{-3}$</td>
<td>$3.05 \times 10^{-7}$</td>
</tr>
<tr>
<td>SP/SGO-0.5</td>
<td>96.7</td>
<td>299</td>
<td>$7.02 \times 10^{-3}$</td>
<td>$2.89 \times 10^{-7}$</td>
</tr>
<tr>
<td>SP/SGO-0.8</td>
<td>96.3</td>
<td>296</td>
<td>$8.47 \times 10^{-3}$</td>
<td>$2.96 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

**7.2.7 Surface morphology of the membranes**

The morphology of the composite membranes was investigated by SEM and AFM. Figure 7.5 (a-c) shows the SEM micrographs of the composite membranes. The SP membrane exhibited a smooth surface, while the SP/SGO-X membrane showed relatively rough surface and the incorporated SGO was well embedded in the SP matrix [22]. Comparing the AFM images of SP and SP/SGO-X membranes as shown in Figure 7.6 (a-c), the surface morphology of the membranes had occurred change considerably after the addition of SGO particles. The surface roughness values of the prepared membranes are tabulated in Table 7.3. It reveals that the increasing roughness value of the membrane with increasing the amount of SGO. This is due to the fact that the electrostatic attraction between the oxygen containing functional
groups of SGO surface with sulfonic acid group in the SP matrix, which gives good compatibility between SGO with SP matrix [28, 29]. However, the surface roughness of the SP/SGO-X membrane was lower than the pristine SP membrane. The incorporated SGO forms numerous small peaks in the surface.

![Figure 7.5](image) SEM images of SP and SP/SGO-X composite membranes (a) SP, (b) SP/SGO-0.2 and (c) SP/SGO-0.8

![Figure 7.6](image) AFM images of SP and SP/SGO-X composite membranes, (a) SP, (b) SP/SGO-0.2 and (c) SP/SGO-0.8
<table>
<thead>
<tr>
<th>Membrane</th>
<th>$R_m$ (nm)</th>
<th>$R_q$ (nm)</th>
<th>$R_z$ (nm)</th>
<th>Tensile strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>4.66</td>
<td>5.35</td>
<td>20.1</td>
<td>31.3</td>
</tr>
<tr>
<td>SP/SGO-0.2</td>
<td>1.15</td>
<td>1.44</td>
<td>7.33</td>
<td>32.4</td>
</tr>
<tr>
<td>SP/SGO-0.8</td>
<td>1.29</td>
<td>1.58</td>
<td>7.71</td>
<td>36.5</td>
</tr>
</tbody>
</table>

$R_m$ - the mean roughness, $R_q$ - the root mean square of Z data and $R_z$ - mean height of roughness profile.

7.2.8 Proton conductivity

Proton conductivity is a key property of PEM and it is necessary to be high for their effective utilization in fuel cell devices. Initially, all the membrane samples were immersed in DI water for one day and then reached a fully hydrated condition [30]. Table 7.2 shows the proton conductivity values of SP/SGO-X membranes are higher than that of SP membrane. Presence of two different acidic groups (-CO$_2$H, -SO$_3$H) in the membrane bring about more facile proton transport [31]. The SP membrane shows the conductivity of $5.32 \times 10^{-3}$ S/cm, which is raised up to $8.87 \times 10^{-3}$ S/cm for the SP/SGO-0.8 membrane. Since the water uptake of the composite membrane increases, the protons effortlessly passing through the hydrogen bond network of the water molecules. Hydrogen bonding is an important factor for proton mobility in PEMs. Protons are transported in PEM via the formation and breakage of hydrogen bonds between water molecule and functionalities in polymer. As is well known, hydroxyl groups have the potential to produce hydrogen bonds with water molecules and other hydroxyl groups [32, 33]. The hydroxyl groups and epoxy groups in SGO also enhance the proton conductivity of composite membranes through hydrogen bonding.
7.2.9 Methanol permeability and relative selectivity

Methanol permeability through the PEM from anode to cathode would poison the electro-catalyst at the anode and reduce the open circuit potential. Table 7.2 shows the methanol permeability of the prepared membranes measured at room temperature. The thickness of the membranes used were about 110-125 μm for this methanol permeability measurement. As shown in the Table 7.2, the SP membrane (3.26 × 10⁻⁷ cm² s⁻¹) displayed lower methanol permeability than Nafion 117 membrane (3.41 × 10⁻⁶ cm² s⁻¹). Furthermore, the methanol permeability of SP membranes was significantly suppressed from 3.19 × 10⁻⁷ cm² s⁻¹ to 2.89 × 10⁻⁷ cm² s⁻¹ by incorporating the SGO content increasing from 0.1 to 0.5 wt%. The membrane with 0.8 wt% of SGO exhibit slightly higher methanol permeability, although they have high IEC and conductivity. On one hand, the SGO in the membrane act as a methanol barrier by suppressing the polymer chain mobility. So it was decreasing the dimensions of ionic clusters for methanol permeation [34]. On the other hand, more compact microstructures that were formed by the interaction between hydroxyl groups of SGO and -SO₃H group of SP matrix reduces the methanol transport through the membrane.

Table 7.2 shows the relative selectivity of the SP and SP/SGO-X membranes at room temperature. As can be seen, all the SGO incorporated membranes had higher selectivity values than the SP membrane and Nafion 117 membrane. Higher selectivity was observed for the SGO incorporated composite membranes due to their lower methanol permeability and high proton conductivity. Moreover, the relative selectivity of the membranes increased with increasing the SGO content. The highest selectivity value was obtained for SP/SGO-0.8 membrane (2.99 × 10⁴ S cm⁻³ s⁻¹), which
was about 75% higher than that of unmodified membrane and 186% higher than that of Nafion 117 membrane.

### 7.2.10 Mechanical property

Tensile strength of the composite membranes was shown in the Table 7.3. SP membrane and SP/SGO-0.2 and SP-SGO-0.8 were chosen as representatives. SP membrane showed the acceptable tensile strength of 31.3 MPa in its dry state. The results from the table indicate that the addition of SGO into SP polymer matrix can improve the tensile strength of the composite membranes. The SP/SGO composite membranes have higher tensile strength value of 36.5 MPa and lower tensile strength value of 32.4 MPa at 0.8 wt% and 0.2 wt% of SGO content respectively. The maximum tensile strength was attributed to the uniform distribution of SGO in the polymer matrix [35] and the mutual interaction between the sulfonic acid group of SGO and SPEES, imide group of PEI which helped to distribute the stress throughout the membrane.

### 7.3 Conclusions

SP and SP/SGO-X composite membranes were prepared by solution casting method. The essential characteristics such as water uptake, ion exchange capacity, swelling ratio, proton conductivity and methanol permeability of the composite membranes were investigated. The water uptake and IEC of the composite membranes were increases with increasing SGO content. AFM study showed that the addition of SGO in to the SP matrix increases the surface roughness of the membranes. The introduction of SGO (contains hydroxyl and epoxy groups) into the membrane matrix helps to form hydrogen bond and thus increase the proton conductivity. These composite membranes exhibit good dimensional and thermal stability. Methanol permeability decreases gradually from $3.26 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}$ to $2.89 \times$
$10^{-7}$ cm$^2$ s$^{-1}$ with increasing SGO content from 0.1 to 0.5 wt%. Although, proton conductivities of the SP/SGO-X membranes were higher than those of SP membrane, and higher selectivity value was found for only SP/SGO-0.8 membrane. All the results suggest that the SP/SGO-0.8 composite membranes offered the possibility of good performance in DMFCs.
References


