







where  $d$  is gap of electrodes,  $s$  is wide of electrodes,  $L$  is thickness of membrane and  $R$  is membrane resistance derived from the low intersection of the high frequency semicircle on a complex impedance plane with  $\text{Re}(z)$  axis.

### 3. RESULT AND DISCUSSIONS

#### a. Thermal analysis

The thermal stability of a PEMs in DMFC is a key property for its durability fuel cell operation at high temperatures. TGA measurement under  $\text{N}_2$  flow conditions from  $25^\circ\text{C}$  to  $600^\circ\text{C}$  was carried out in order to evaluate the thermal stability of composite membranes and the results are shown in Fig. 1.

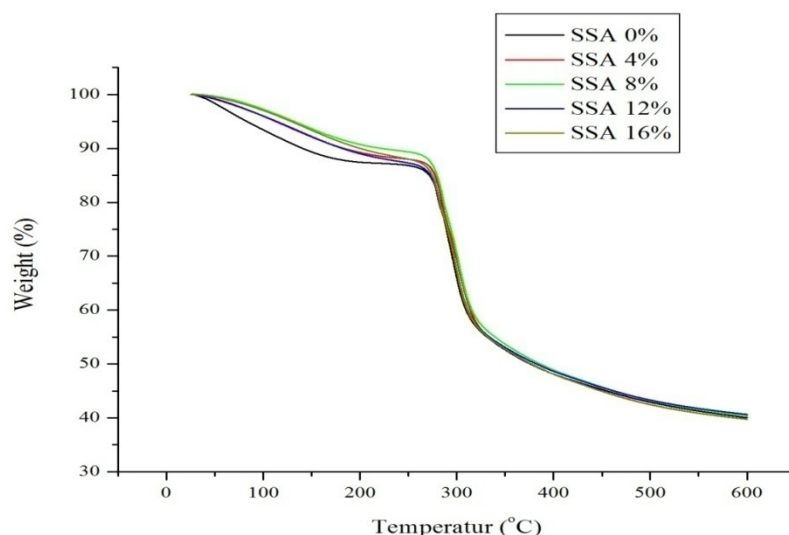


Figure 1. Thermograms of CS/MMT-Sil 10% and CS/MMT-Sil 10%/SSA membranes

TGA curves shown in Fig. 1 indicated that all membranes exhibited three major weight loss stages. The first weight loss region ( $50\text{-}100^\circ\text{C}$ ) was attributed to the loss of adsorbed water molecules in the membranes. The second weight loss ( $210\text{-}300^\circ\text{C}$ ) was corresponded to the degradation of the bond between chitosan-silane and chitosan-SSA in the membranes. The third weight loss ( $310\text{-}450^\circ\text{C}$ ) was attributed to the decomposition of chitosan chains [12]. Through the comparison of the modified and pure composite membranes thermogram, it is understood that thanks to the formation of covalent and ionic interactions, the thermal stability of cross-linked chitosan network of composite membrane has been improved. The cross-linked membranes were stable at the desired operating temperature range of DMFC applications [10].

#### b. Proton Conductivity

Proton conductivity of CS/MMT-Sil 10% and CS/MMT-Sil 10%/SSA membranes was determined by means of the complex impedance method. All impedance were carried out after hydration of the membranes. According to literature, proton conductivity will occur only after membrane is hydrate [13]. The proton conductivity data and graph the the obtained CS/MMT-Sil 10% and CS/MMT-Sil 10%/SSA

membranes were listed also in Table 1 and Figure 2. It is noted that membranes in wet state exhibit proton conductivity between  $1.18 - 2.62 \times 10^{-4}$  at room temperature. As seen, value of conductivity is improved by increasing the SSA content. The presence of  $-\text{SO}_3$  groups leads to the formation of more accessible pathway for protons migration through the membrane. Hence, the observed high proton conductivity could be ascribed to the sulfonate groups as well as the hydroxyl and amine groups present in the ionomers, which give rise to hydrophilic regions in the structure due to their strong affinity toward water molecules [6]. Anyway, it should be noticed that the enhancement of proton conductivity have shown a plateau. This behavior could be interpreted with counter effect of sulfonate groups, which not only cause increasing affixed negatively charged sites for proton transportation, but could also to the restriction of conduction channels due to over-cross-linking of the structure [10].

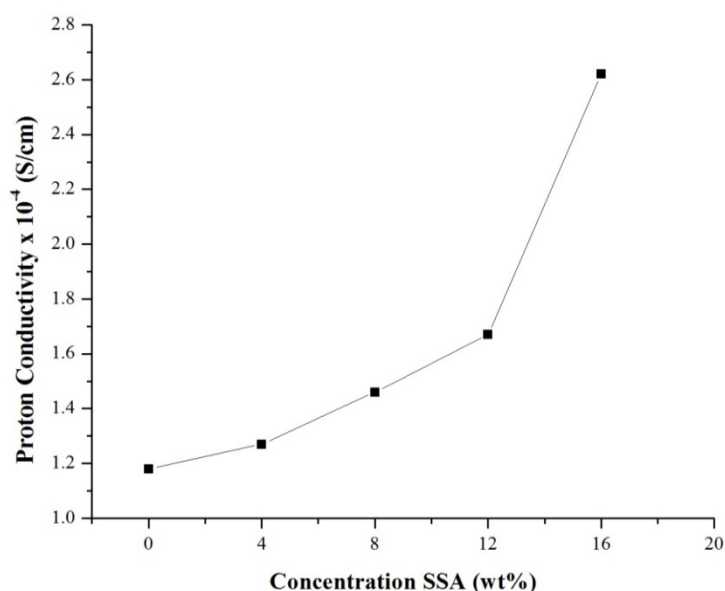


Figure 2. Effect of SSA loading weight on the proton conductivity of cross-linked composite membranes

### c. Methanol permeability

Methanol permeability is an important parameter in DMFC applications. If a membrane have high permeability of methanol, it will degrade the performance of DMFC. The result of the methanol permeability measurements are shown in Table 1 and Figure 3. The notable feature in Table 1 and Fig. 3 is that the methanol permeability of the composite membrane are three and four times lower than corresponding value from Nafion<sup>®</sup> 117 ( $2.00 \times 10^{-6} \text{ cm}^2/\text{s}$ ). It is indicated that sulfosuccinic acid was taken place in membrane to improve the methanol rejecting. The lower methanol permeability was obtained in CS/MMT-Sil 10%/SSA 12% of  $3,96 \times 10^{-7} \text{ cm}^2/\text{s}$ .



Table 1. Proton Conductivity and Methanol Permeability of CS/MMT-Sil 10% and CS/MMT-Sil 10%/SSA

Membrane	$\sigma$ ( $\times 10^{-4}$ S/cm)	P ( $\times 10^{-7}$ cm <sup>2</sup> /s)
CS/MMT-Sil 10%/SSA 0%	1.18	9.88
CS/MMT-Sil 10%/SSA 4%	1.27	7.67
CS/MMT-Sil 10%/SSA 8%	1.46	6.32
CS/MMT-Sil 10%/SSA 12%	1.67	3.96
CS/MMT-Sil 10%/SSA 16%	2.62	5.78

As seen, the methanol permeability of CS/MMT-Sil 10%/SSA 16% increased is due the increasing sulfonate groups, the methanol permeation rate increases, which is associated with the hydrophilic of these polar sites [10].

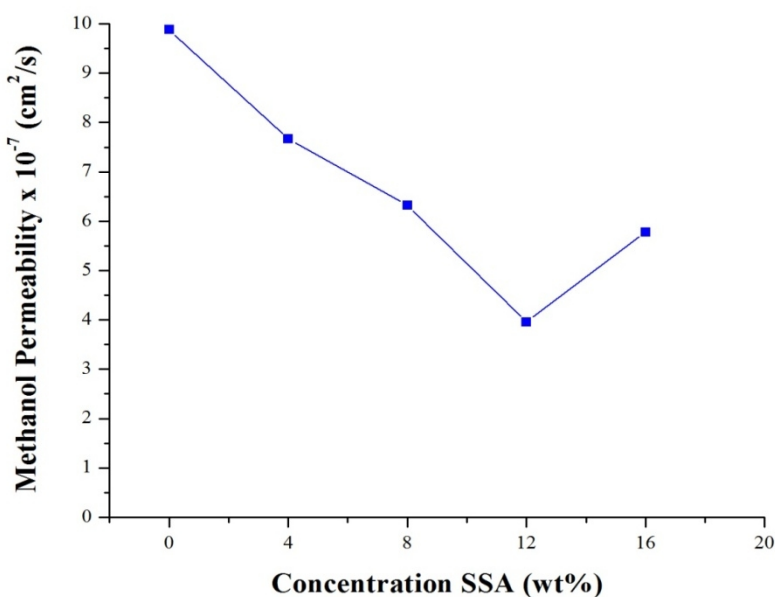


Figure. 3. Methanol permeability of CS/MMT-Sil 10% and CS/MMT-Sil 10%/SSA membranes

#### 4. CONCLUSION

The increase of sulfosuccinic acid concentration from 4 to 16 % (%wt/wt) causing the increase of thermal properties, proton conductivity and decrease methanol permeability. The best composition of membrane was obtained in CS/MMT-Silan/SSA 12% with the highest proton conductivity and lowest methanol permeability. However, the proton conductivity was still an order magnitude lower than Nafion at  $3.84 \times 10^{-1}$  S/cm. This result implies that this complex-composite membrane is a good candidate for DMFC in fuel cell application.

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