

## CHAPTER VII

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

Firstly, the sulfonated poly(ether ketone ether sulfone)s (S-PEKESs) derived from bisphenol S were successfully synthesized and chemically characterized by FTIR and  $^1\text{H-NMR}$ , confirming the structures. The thermal properties, DS, IEC, and the water uptake of the synthesized S-PEKESs were compared with those of the commercial S-PEEK 150XF. The data show that the synthesized S-PEKESs have a higher degradation temperature, DS, IEC, and water uptake values than those of the commercial one. DS, IEC, and water uptake of all polymers were also compared with those of Nafion 117. All properties of S-PEKES at the highest sulfonation time are relatively lower than Nafion 117. Furthermore, the dielectric permittivities of synthesized S-PEKES-A (12 h, 48 h, and 84 h) and S-PEKES-B (12 h and 48 h), and commercial S-PEEK 150XF (12 h, 48 h, and 84 h) are independent of frequency and they increase with DS value. The dielectric permittivity of the 84 h S-PEKES-B decreases with increasing frequency due to the high polarity of the sulfonic acid groups. The water uptake, dielectric permittivity, and electrical conductivity values increase monotonically with increasing degree of sulfonation.

The S-PEKESs show a high glass transition temperature and a higher heat resistance in the solid state. The S-PEKES membranes with the highest DS and water uptake (%) values possess comparable proton conductivity values but with lower methanol permeability than those of the Nafion 117 membrane. In particular, its methanol permeability,  $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , is much lower than that of the Nafion 117 membrane,  $1.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , at a room temperature. In addition, the oxidative stabilities and the storage moduli ( $G'$ ) of all the S-PEKES and S-PEEK 150XF membranes are better than those of Nafion 117. These results suggest that the S-PEKES and S-PEEK 150XF membranes are potential candidates for the application in direct methanol fuel cells operating at medium temperatures. The S-PEKES-B membrane shows superior properties than those of the S-PEKES-A and S-PEEK 150XF membranes.

Then, molecular sieve 3A, 4A, and 5A/S-PEKES composite membranes were fabricated. They show high thermal stability, because the degradation temperature starts at above 250 °C indicating that the composite membranes can be safely operated for DMFC at normal condition (Sangeetha *et al.*, 2007) and can be used in PEMFC as well (Guhan *et al.*, 2009). The water uptake (%), IEC, proton conductivity of the molecular sieve composites membranes are found to be higher than that of the pure S-PEKES membrane and they increase with increasing content of molecular sieve. Particularly, the mechanical strength of composite membrane is the property which shows the most significant improvement. Although, the methanol permeability of composite membrane increases from the pristine one, the value is still much lower than that of Nafion 117 membrane. From the overall results, the molecular sieve 3A/S-PEKES composite membrane at 12%v/v is selected to be the PEM candidate for DMFC, due to its higher proton conductivity, lower methanol permeability, and much higher tensile strength, when compared with the two other composite membranes.

Finally, the ZSM-5/S-PEKES composite membranes show high thermal stability, because the degradation temperature starts at above 400 °C indicating that the composite membranes have high thermal stability in the DMFC service temperature and can be used in PEMFC as well. The water uptake (%) of the composite membrane first increases relative to the pristine S-PEKES membrane; the decrease of the water uptake with the increment of Si/Al ratio and amount of zeolite is due to its hydrophobicity. The ZSM-5 zeolite is demonstrated here in increasing the proton conductivity apart from the pristine S-PEKES and Nafion 117 membranes. The effects of the Si/Al ratio and zeolite content on the proton conductivity show the same tendency with the water uptake (%). Moreover, the methanol permeabilities of all composite membranes are much lower than the S-PEKES and Nafion 117 membrane, due to the low diffusion of methanol molecules.

The 2%v/v CBV 2314/S-PEKES composite membrane is selected to be the proton exchange membrane candidate due to its membrane selectivity is the highest among all the membrane systems investigated.

## 7.2 Recommendations

There are several possible modifications to increase the proton conductivity of the membrane including modifying the functional group of the monomer and polymer, polymer blending, grafting, or copolymer with high proton conducting polymer, and incorporating other proton conducting fillers.

The blending of the composites membrane with selected proton conductors such as metal oxides, heteropolyacids, zeolites and a mixture of both can help to improve the proton conductivity of the membrane. Further study should be conducted on the influence of atmospheric conditions and viscosity of the membrane on membrane casting techniques.

The effects of various parameters such as operating temperature, pressure, flow rate of methanol and humidification on the performance of the membrane in the direct methanol fuel cell should be investigated.

Long term performance of the membrane in the fuel cell should be investigated. In order to achieve the actual performance of the proton exchange membrane, all pristine and composite S-PEKES membranes should be fabricated with a catalyst to form the membrane electrode assembly and incorporated into the DMFC single cell system. The important properties such as the power density and the fuel cell voltage could be achieved.