CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The present work demonstrated the organic-inorganic composite membrane preparations for the use in proton exchange membrane fuel cells (PEMFCs) via either (i) a homogeneous composite system of Nafion® and inorganic fillers functionalized with Nafion®-like polymer chain or (ii) a nanocomposite system of sulfonated polyether ether ketone and montmorillonite treated with sulfonic acid. In the case of (i) (Chapter III and IV), (3 aminoproply)triethoxysilane (γ-APS) and carbodiimide coupling agent were used as a coupling agent to functionalize the fillers, either silica particle (Si) or montmorillonite (MMT) clay layers with Krytox 157 FSL to obtain Krytox-Si and Krytox-MMT, respectively. Under the concept of "like dissolves like" of Krytox 157 FSL, a fluorocarbon chain with the similar structure as Nafion, was applied. The Nafion®-based composite membranes with Krytox-Si and with Krytox-MMT were achieved by solution casting of the hybrid solution of Nafion® with Krytox-Si and Krytox-MMT. The composite membranes, Krytox-Si-Nafion®, showed the good distribution of the inorganic content all over the membranes as observed by SEM and AFM. The nanocomposite, Krytox-MMT-Nafion®, showed exfoliated layer as observed by XRD. The water uptake and degradation temperature of both membranes increased with the silica or MMT loading content.

Krytox-Si-Nafion® showed proton conductivity of 10^{-3} S/cm at the temperature up to 130 °C when the Krytox-Si loading content reached 5 wt. %. All other properties of this composite membrane were also evaluated and compared to Nafion® membrane and the other hydrocarbon polymer membranes, i.e., sulfonated (poly(oxa-*p*-phenylene-3,3-phthalido-*p*-phenylene-oxy-phenylene) (SPWC) obtained from the sulfonation process of PWC with sulphuric acid (Chapter IV). The proton conductivity and water uptake of SPWC increased with an increase in sufuric acid concentration, used for sulfonation, was increased. Both Krytox-Si-Nafion® and SPWC membranes revealed a significant reduction in hydrogen and oxygen permeability through the membrane as compared to that of Nafion® 117 membrane.

The methanol crossover of SPWC membranes reduced when the sulphuric acid concentration was decreased while that of Krytox-Si-Nafion® composite membrane was decreased with Krytox-Si loading content.

For Nafion®-based composite membranes with Krytox-MMT (Chapter V), their properties were evaluated in view of DMFC application. The composite membranes revealed more than 50 % reduction in methanol crossover as compared to the recast Nafion® membrane at 25 and 60 °C for 5 wt. % Krytox-MMT loading content. The proton conductivity of the composite membrane decreased with Krytox-MMT content. Krytox-MMT-Nafion® composite membrane showed the significant membrane selectivity as compared to that of the recast Nafion® membrane.

In the case of the sulfonated MMT/sulfonated polyether ether ketone (SMMT/SPEEK) composite membrane (Chapter VI) for DMFC systems, γ-APS was functionalized onto the MMT layers to obtain the silylated MMT. This silated silicate layer was further modified with 4-sulfophthalic acid by using the carbodiimide conjugating agent to obtained sulfonic acid functionalized MMT and blended with SPEEK polymer solution for composite membrane preparation via solution casting process. The inorganic aggregation over the SPEEK polymer matrix was increased with SMMT loading content as observed by SEM and AFM. The stability in water and in methanol aqueous solution as well as the mechanical strength increased with the SMMT loading content whereas thermal stability did not exist significantly. More than 50 % reduction in methanol crossover was obtained from 5 wt% SMMT/SPEEK composite membrane. The comparative studies of the SPEEK-based composite membrane with SMMT and the one with MMT revealed the proton conductivity improvement by sulfonation. The DMFC single cell performance and the membrane selectivity of all SMMT/SPEEK composite membranes showed the significant results as compared to the unmodified SPEEK and Nafion® 117 membrane.