CHAPTER VIII

SUMMARY

Low cost and high performance SPVdF-co-HFP based PEMs were successfully fabricated and characterized,

(i) by blending with organic polymers such as PES, and SPES individually

(ii) by using inorganic additives such as PWA laminated by PPY (surface modification)

(iii) by adding SGO nanosheets.

On the basis of the results obtained for different PEMs, the individual and general summary/conclusions were drawn.

8.1 SPVdF-co-HFP/PES blend PEM

Proton exchange membranes (PEMs) based on blends of poly(ether sulfone) (PES) and sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) (SPVdF-co-HFP) were prepared successfully. Fabricated blend membranes showed favorable PEM characteristics such as reduced methanol permeability, high selectivity and improved mechanical integrity. Additionally, these membranes afford comparable proton conductivity, good oxidative stability, moderate ion exchange capacity and reasonable water uptake. In order to appraise PEM performance, blend membranes were characterized using techniques such as FT-IR spectroscopy, AC impedance spectroscopy, atomic force microscopy and thermogravimetry. Addition
of hydrophobic PES confines the swelling of the PEM and increases the ultimate tensile strength of the membrane. Proton conductivities of the blend membranes are about $10^{-3}$ S/cm. Methanol permeability of $1.22 \times 10^{-7}$ cm$^2$ s$^{-1}$ exhibited by the SPVdF-co- HFP/PES10 blend membrane is much lower than that of Nafion -117. AFM studies divulged that the SPVdF-co-HFP/PES blend membranes have nodule like structure which confirms the presence of hydrophilic domain. The observed results demonstrated that the SPVdF-co-HFP/PES blend membranes have promise for possible usage as a PEM in direct methanol fuel cells (DMFCs).

8.2 SPVdF-co-HFP/SPES blend PEM

Sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) (SPVdF-co-HFP)/ sulfonated poly(ether sulfone) (SPES) blend polymer electrolyte membranes (PEMs) were fabricated effectively as an alternative PEM for direct methanol fuel cell (DMFC) applications. In order to prepare PEMs with improved proton conductivity PVdF-co-HFP and PES were preferred and sulfonated using chlorosulfonic acid and sulfuric acid respectively. The presence of sulfonic acid groups were confirmed by FT-IR spectroscopy. TGA results showed that SPVdF-co-HFP/SPES blend membranes were superior than control one. Atomic force microscopy images of the blend PEMs clearly showed that the surface roughness and nodule size are increased. The influential characteristics of the PEMs, such as, water uptake, swelling ratio, ion-exchange capacity, proton conductivity, methanol crossover, selectivity ratio were characterized with respect to the control membrane. Though, the tensile strength and elongation at break slightly decreases by the addition of hydrophilic SPES, the water uptake and proton conductivity of SPVdF-co-HFP/SPES blend membranes were increased and found to be higher than that of the pure SPVdF-co-HFP. Selectivity ratio of the prepared blend PEMs were in the
range of $1.709 \times 10^4$ to $2.193 \times 10^4$ Scm$^{-3}$s which is much higher than that of Nafion 117 ($0.214 \times 10^4$ Scm$^{-3}$s) membrane.

8.3 SPVdF-co-HFP/PWA/PPY-n composite PEMs

A series of SPVdF-co-HFP/PWA/PPY-n composite membranes were successfully fabricated and studied for its suitability as a proton exchange membrane (PEM) used in DMFCs. In-situ polymerization technique was used for the lamination of polypyrrole (PPY) on the SPVdF-co-HFP/PWA membrane surface to diminish the leaching of phosphotungstic acid (PWA). The electrochemical property, surface morphology, mechanical stability and thermal stability of laminated PEMs were evaluated by ion exchange capacity, water uptake, swelling ratio, proton conductivity, methanol crossover, surface roughness, oxidative stability, tensile strength, and TGA curves. The surface coating of hydrophobic PPY leads to a substantial drop in methanol crossover with workable levels of proton conductivity. The methanol crossover of SPVdF-co-HFP/PWA/PPY-5 hybrid PEM was found to be $1.73 \times 10^{-7}$ cm$^2$ s$^{-1}$ and was much lower than Nafion-117 ($63 \times 10^{-7}$ cm$^2$ s$^{-1}$). The membrane selectivity of SPVdF-co-HFP/PWA/PPY-5 was found to be high ($2.775 \times 10^4$ Scm$^{-3}$s). AFM study indicated that the surface roughness of the composite membrane was gradually decreased by increasing in PPY layer on the surface of the membrane. The FT-IR analysis confirmed the blending of PWA to SPVdF-co-HFP and the coating of PPY on the composite PEM SPVdF-co-HFP/PWA. The ion exchange capacity, the water uptake and the swelling ratio of the laminated membranes decreased regularly by increasing the PPY layer. The tensile strength of SPVdF-co-HFP/PWA/PPY composite membranes also steadily increased with increasing the PPY layer. Thus, all the experimental results revealed that the SPVdF-co-HFP/PWA/PPY-n composite membranes are excellent materials as PEM used for direct methanol fuel cells.
8.4 SPVdF-co-HFP/SGO nanocomposite PEMs

Sulfonated poly(vinylidene fluoride-co-hexafluoropropylene) incorporated with sulfonated graphene oxide (SPVdF-co-HFP/SGO) was represented as a novel proton exchange membrane (PEM) used for DMFCs. SPVdF-co-HFP/SGO nanocomposite proton exchange membrane (PEM) was fabricated using the solution casting method and PEM with high membrane selectivity was obtained. The blending of SPVdF-co-HFP with inorganic SGO nano-filler was confirmed by FTIR and XRD measurement. The uniform distribution of SGO throughout the SPVdF-co-HFP polymer matrix has been studied by FE-SEM and the decrease of surface roughness investigated by AFM studies. The proton conductivity and mechanical stability have been prominently increased by the addition of SGO, due to the formation of extended proton conducting pathways and better interfacial interactions between the SGO additive and SPVdF-co-HFP polymer which leads to the good mechanical integrity of prepared membranes. This improved mechanical stability was identified by computing their tensile strength, Young’s modulus and elongation at yield. The physiochemical properties like ion exchange capacity, water uptake, swelling ratio, proton conductivity and methanol permeability were determined and confirmed that the increase of SGO content with SPVdF-co-HFP increased the proton conductivity with reduced methanol permeability.

From the summary, it is concluded that different types of PEM showed appropriate proton conductivity which is very essential for electrolyte in DMFCs. All the PEMs displayed good thermal stability, excellent mechanical strength and adequate chemical stability. AFM and FE-SEM study revealed that compatibility among the constituents in all the fabricated PEMs are good. From current research work, it may me concluded that SPVdF-co-HFP/SGO-0.7 wt. % membrane is highly suitable for DMFC application.
FUTURE WORK

Based on the results of the present study, the following recommendations are made to the future research on the development of SPVdF-co-HFP PEMs.

- Other organic polymers such as SPEEK, SPEES, SPSf can be blended with SPVdF-co-HFP.

- In chapter VI, we selected polypyrrole (PPY) layer to immobilize phosphotungstic acid particles in SPVdF-co-HFP matrix. Besides PPY, other electronic conducting polymers such as polythiophene, polyaniline, may be utilized in the place of PPY. And these layers on membrane surface can also be studied to examine their effect on the SPVdF-co-HFP/PWA membrane structure and performance.

- Other hetero polyacid such as silico tungstic acid can be added followed by surface modification.

- The functionalized graphene oxide increases proton conductivity of PEM. Some other functionalized graphene such as sulfonated propylsilane GO, sulfonated organosilane functionalized GO and zwitterion-coated GO can be employed to enhance the proton conductivity of PEM.

In the present work, we didn’t emphasis on the performance of fuel cell analysis because fabrication of the membrane itself a broader research and hence we can try out the viability of all the fabricated membranes as a PEM in our future studies.
Research papers published in international journals (Thesis Work)


Research papers communicated in international journals (Thesis Work)

1. **A. Uma Devi, D. Rana, A. Nagendran.** Highly selective and methanol resistant polypyrrole laminated SPVdF-co-HFP/PWA proton exchange membranes for DMFC applications, *Materials Chemistry and Physics* (Elsevier)

2. **A. Uma Devi, Noel Jacob Kaleekal, D. Rana, A. Nagendran.** Tailored SPVdF-co-HFP/SGO nanocomposite alternate proton exchange membranes for Nafion in direct methanol fuel cells, *Journal of Industrial and Engineering Chemistry* (Elsevier)