Conclusion

Conclusions and Suggestions for Further Work

In order to prove that PVDF based polymer electrolyte has formed, it is important to show the occurrence of complexation between the polymer and the salt. The fluorine atom in PVDF which has excess negative charge is therefore expected to interact with the Li^+ cation from the dopant salt in a similar manner the Li^+ cation interacts with the lone pair electron from the heteroatoms in polymers such as polyethylene oxide (PEO) or chitosan.

XPS studies in the present investigation have shown Li-F interaction between the cation of the salt and the fluorine atom of the polymer when the Li 1s core level spectrum contains a Gaussian peak at binding energy between 54 to 56 eV attributed to Li-F interaction in the polymer. This assignment is based on the fact that the binding energy of the electron in Li-F is of almost the same value as in the literature.

The enhancement in ionic conductivity is higher in the case of DMF plasticizer based polymer electrolytes than the other plasticizers used in the present study. This high ionic conductivity in DMF plasticizer based polymer electrolyte may be due to the interaction of the plasticizer with the polymer. This interaction with polymer suppresses the depletion of the plasticizer from the polymer electrolyte and hence the DMF is able to dissociate more salt and thereby increases the number of mobile carriers. Other plasticizers do not interact with the polymer as proven by FTIR. DMF therefore is able to decrease the glass transition temperature of the polymer and increase its segmental motion.

The temperature dependent ionic conductivity studies (log σT versus 1000/T (K^{-1}) for all the high conducting polymer electrolyte follows Arrhenius behaviour. This indicates that the ion transport is similar to that of ionic crystals i.e. via hopping mechanism. The ions hop from one site to another. The activation energy for ion migration is calculated from the temperature dependent studies. The activation energy is found to be lowest for DMF plasticized polymer electrolyte followed by EC and MF. This low activation energy is responsible for the high ionic conduction DMF based polymer electrolytes. The dielectric relaxation studies also show that the dielectric constant increases with plasticizer addition. X-ray diffraction clearly shows that the plasticizer addition disrupts the crystalline nature of the host polymer and converts then into semi-crystalline nature. This reduced crystallinity by the addition of plasticizers will enhance the ionic conductivity to higher values. The ionic conductivity is inversely proportional to the crystallinity of the polymer electrolyte.

FTIR analysis provides evidence of plasticizer-salt interaction. This interaction is mainly between the lithium cation and the oxygen atom of the plasticizer. In the case of DMF interaction is mainly between Li and the oxygen atom in the O=C-N group. The nitrogen atom in the O=C-N group of the DMF plasticizer did not show any interaction with the lithium cation. This has been confirmed by XPS studies. FTIR spectroscopy also shows the evidence of interaction between the DMF plasticizer and the polymer. The other plasticizers EC and MF did not show any interaction with the polymer. The plasticizer-salt interaction reduces possible cross-links between the salt and the polymer thereby softening the polymer backbone and helps to increase segmental motion of the polymer. However, plasticizer-polymer

interaction which holds only in the case of DMF help to reduce plasticizer elimination from the system and enables the plasticizer to dissociate more salt producing more mobile ions when subjected to an electric field. This explains the higher conductivity exhibited by the DMF plasticized polymer electrolyte.

Thermal studies were carried out for unplasticized and plasticized polymer electrolytes to analyse their thermal stability. DSC studies of unplasticized and plasticized polymer electrolyte show that the polymer electrolytes melt in the temperature range between 140^0 C to 160^0 C. The plasticized polymer electrolyte melting point is decreased more in the case of DMF plasticizer based polymer electrolyte compared to EC and MF plasticizer based polymer electrolyte. This decrease in melting point with respect to pure PVDF may be due to the decrease in crystallinity of the system. TGA studies also show that the polymer electrolytes are thermally stable up to 160^0 C. The small mass loss at around 100^0 C may be due to the removal of water molecules. Such stability implies that the battery employing these polymer electrolytes can withstand up to a temperature of more than 100^0 C.

Polymer batteries based on lithium anode and graphite cathode materials are fabricated with all the high ion conducting polymer electrolytes. The galvanostatic charge/discharge characteristics of the above batteries with PVDF based polymer electrolytes gives a rather poor capacity. The poor capacity of the batteries may be due to the comparatively low ionic conductivity of the polymer electrolyte (10^{-4} S/cm) and high interfacial resistance of the batteries due to the formation of passive layers on the electrode/electrolyte interface. However, the internal resistance of the

battery with DMF plasticized electrolyte is lowest when compared to the batteries that makes use of the EC and MF plasticized electrolytes.

Suggestions for Further Work

Since the ionic conductivity of the polymer electrolyte is comparatively low, addition of several plasticizers can help the situation. One of the reasons behind the low ionic conductivity at ambient temperature is the removal of plasticizers from the polymer electrolyte system. Using the copolymers of the polymer host can eliminate the subsequent removal of such plasticizers. Another approach to improve the ionic conductivity is to use plasticizers of low volatility. The ionic conductivity can be improved further by adding dispersive agents such as Al_2O_3 and SiO_2 into the polymer electrolyte.

The battery studies show poor capacity. The capacity may be improved further by substituting graphite with other materials such as $SnSO_4$ or barium metaplumbate which is known to have a higher capacity than carbon and has not been tried yet for such PVDF systems. Further studies are needed to improve the interfacial resistance of the electrode/electrolyte interface and to reduce the self-discharge of the battery.