CHAPTER 7

Conclusions

The present chapter gives the conclusions from the results of all GPE systems which are obtained from the different characterization analysis viz. structural, thermal, mechanical, and electrochemical.The temperature and composition dependence of DC and AC conductivity, dielectric, and modulus studies are summarized.

In the present thesis, electrochemical properties of polymer blend gel electrolytes have been investigated. Results are summarized of work done carried out to synthesis and characterization of Li-ion conducting nanocomposite gel polymer blend electrolyte for the battery applications. Gel polymer electrolyte systems with different concentrations of $LiClO_4$ salt, PC:DEC plasticizers, and Al_2O_3 nanoparticles have been prepared using the solvent casting technique.

The prepared series in the present work are:

Series (a): PVDF-HFP: PMMA -PC: DEC (1:1)-x wt.% $LiClO_4$,
where x = 2, 4, 5, 7.5, 10

Series (b): PVDF-HFP: PMMA - 10 wt.% $LiClO_4$- x wt.% PC: DEC (1:1),
where x= 20, 30, 40, 50, 60

Series (c): PVDF-HFP: PMMA – 10 wt.% $LiClO_4$- 60 wt.% PC: DEC (1:1)- x wt.%
Al_2O_3, where x = 0.5, 1, 2, 3, 4

The prepared films of the electrolutes are characterized using various techniques i.e. X-ray diffraction (XRD) to observe extent of crustallinity in films, scanning electron microscope (SEM) for surface morphology, differential scanning calorimetry (DSC) for melting, crystallinity and / or glass transition temperature, Fourier transforms infrared spectroscopy (FTIR), Atomic force microscopy (AFM) for surface roughness measurements, Transport number measurement, Cyclic voltammetry (CV), and tensile strength. The effect of $LiClO_4$ salt, plasticizers PC:DEC and dispersed nanoparticles Al_2O_3 on conduction and relaxation mechanism has been studied using the electrochemical impedance spectroscopy technique. The performance of the fabricated Li^+ primary battery is discussed.

It can be concluded from the results and discussions about the present gel polymer electrolyte systems as following;

1. The XRD results show no x-ray peaks of salt when $LiClO_4$ added, indicating the complete dissolution of the salts in the polymer matrix. X-ray also confirms the amorphicity of the electrolyte films containing 7.5 wt.% $LiClO_4$ salt. Beyond 7.5 wt.% of salt, the film shows the increase in crystalline nature. Amorphicity continues to increase as the PC:DEC plasticizers are incorporated from 20 wt.% to 60 wt.% which is due to the trapping of low molecular weight plasticizers resulting in the separation of inter and intra chains of polymers. Further enhancement in the amorphicity has been observed on the incorporation of Al_2O_3 nanofiller up to 2 wt.%.
2. SEM results show the enhancement in the pore size and swelled nature of the GPE up to 7.5 wt.% $LiClO_4$. More embedded small pores filled with liquid electrolytes and enhanced swelled nature of GPE is observed when the amount of PC: DEC plasticizers is added from 20 wt.% to 60 wt.% in the electrolyte films. SEM pictures showed the reduction in the pore size but the number of pores uniformly increased after incorporation of Al_2O_3 nanofiller up to 2 wt.% which has better ability of retention of liquid electrolyte. The disappearance of uniformly distributed pores is observed for GPE with 3 wt.% Al_2O_3 may be due to aggregation of nano-particles or aggregation of dissociated ions.
3. DSC result of all series shows endothermic peaks corresponds to melting temperature. The lowest melting temperature values are recorded for the sample having high amorphicity in all series.
4. FTIR results of all series show the broadening of the spectra and shifting in the band which reveals the change in molecular band structure due change in bond length and vibrations due to incorporation of $LiClO_4$, PC-DEC plasticizers and Al_2O_3 nanofillers in blended polymers PVDF-HFP and PMMA.

5. From the AFM analysis, the minimum roughness height and smooth surface are seen for the optimum GPE sample from each series.
6. The total ionic transport number is found to be ~ 0.96-0.99 which indicates the present gel polymer electrolyte is the ionic conductor. This means, the charge transport in the present GPE is mainly due to ions and a negligible contribution comes from electrons.
7. The electrochemical stability window measures the working voltage range of the substance necessary to measure for the electrochemical application. The samples in series (a), the optimum salt sample i.e GPE with 7.5 wt.% $LiClO_4$ shows the stability window of 4.40 V. In series(b), the highest stability window is observed of 4.89 V for the GPE system containing the maximum amount i.e. 60 wt.% of PC:DEC plasticizers while a maximum electrochemical stability window of 6.00 V is recorded for the nanocomposite gel polymer electrolyte sample having 2 wt.% Al_2O_3.
8. The mechanical strength also improves upon the addition of PC:DEC plasticizers and Al_2O_3 nanoparticles in the gel polymer electrolytes as compared to salt electrolyte films.
9. In series (a), the ionic conductivity of the GPE system is dependent on the salt concentration, which increases with the salt concentration up to 7.5 wt.% $LiClO_4$ and thereafter decreases. The maximum ionic conductivity of 2.83×10^{-4} S cm^{-1} is recorded. The ionic conductivity continues to increase with increasing the PC:DEC plasticizer concentration, and maximum ionic conductivity is of the order of 3.97×10^{-4} S cm^{-1} for 60 wt.% PC:DEC GPE. The highest ionic conductivity of the order of 1.62×10^{-4} S cm^{-1} is obtained when nano particles are dispersed in the nanocomposite gel polymer electrolyte sample having 2 wt.% Al_2O_3.
10. The temperature-dependent ionic conductivity follows Arrhenius behavior. It suggests that it is a thermally activated process and lower activation energy is coupled with a high ionic conducting sample of all series.
11. The AC conductivity spectra have been found to follow Jonscher's universal power law in all the three systems. The scaling of AC conductivity for all the samples at different temperatures follows the time-temperature superposition principle. This suggests that the ion dynamics in the present polymer gel electrolytes are temperature independent. The deviation at the lower frequency side may be due to the electrode-polarization effect. The hopping frequency (ω_p) and mobile ion

concentration (*K*) both are found to be thermally activated like that of dc conductivity.

12. The dominance of space charge polarization (electrode polarization) at lower frequency, the dielectric constant attains higher values while it gradually decreases with frequency and attains lowest value due to the inability of alignment of dipoles in the direction of the applied field at high frequency. The dielectric constant is also composition dependent and maximum values of ε' is obtained for the optimum concentration sample of each series which in good agreement and in consonance with the XRD, SEM, DSC and tensile strength results of the the films.
13. In modulus analysis, the asymmetric and broad nature of the modulus plot indicates the non-Debye nature of ion relaxation and distribution of relaxation time. The shifting of the peak with composition variation is an indication of the change of conductivity relaxation. The conductivity relaxation time (τ) is calculated from the values of f_{max} corresponds to the peak M''_{max} using relation $\omega\tau=1$. A shorter relaxation time is observed for the high conducting gel polymer electrolyte systems. The scaling behavior of the modulus spectra results in a master curve which indicates the conductivity relaxation process is temperature independent.
14. The optimized gel polymer electrolyte systems from each series have been applied for the battery fabrication. The battery performance in terms of current density, discharge capacity, specific power, and specific energy is significantly improved with the load resistance. However, extensive efforts are needed to improve the performance of the present system for its successful battery application as well as commercialization.