CHAPTER VIII
BRIEF SUMMARY AND CONCLUSION

The investigations discussed in the present work, relate to the analysis of PVdC-AN/PMMA polymer electrolyte membranes for lithium battery applications. All polymer electrolyte films were prepared by solution casting technique. Having discussed the results obtained from various characterization studies, a brief summary of the work is being presented.

The initial investigation commenced with optimisation of the blend ratio. Conductivity has been further improved by the addition of plasticizer and imparting different plasticizers. The effect of different lithium salts with various anion sizes on the gel membranes is also explained.

The comparison between X-ray diffraction patterns of pure samples and the prepared electrolyte membranes proves the change in phase of the materials while blending i.e. crystalline to amorphous. The absence of crystalline peaks of salts in the X-ray diffraction pattern indicates the complete dissolution of lithium salt, and the dispersion of polymer occurred at the molecular level.

The FT-IR studies suggest that the cations are coordinated to the ether oxygens (C=O, C–O–C) and nitrile groups (C≡N) in the polymer chains. A positional change in the vibrational frequency of functional groups in polymers ascertains the complex formation. Thus, the shift in the existing peaks of vibration and appearance/disappearance of peaks in the FT-IR spectra confirm the complex formation.

The electrochemical analysis on the electrolyte membranes is considered as the basic parameter which helps to find out the change in impedance and hence the
ionic conductivity. The mobility of ions, segmental mobility and flexibility of polymers, anion size, etc. have a major role on conduction. Among the various compositions of blend, 50:50 wt.% of PVdC-AN/PMMA with fixed ratio of LiClO$_4$ has the ability to fulfil the expected properties such as conductivity and thermal stability. The optimum ionic conductivity value obtained was $0.256 \times 10^{-7}$ S cm$^{-1}$. This optimized composition of PVdC-AN/PMMA blend has been chosen for the entire investigation. Since the incorporation of plasticizer significantly alters the behaviour of the polymers, the effect of plasticizer (EC) concentration has been analysed. A conductivity of $0.398 \times 10^{-6}$ S cm$^{-1}$ at 303 K has been achieved for high plasticizer content electrolyte membrane PVdC-AN (46)- PMMA (46)- EC (60)- LiBF$_4$ (8) wt.%.

The effect of anion towards the electrochemical behaviour indicates that LiAsF$_6$ doped complex gives high conductivity value. However, due to the high toxicity of LiAsF$_6$, the remaining works have been carried out with LiClO$_4$ salt. Further investigation on the addition of different plasticizers (EC, PC, gBL, DMSO) into PVdC-AN/PMMA/LiClO$_4$ complex show an enhanced conductivity for all the membranes and comparatively high conductivity has been obtained ($0.176 \times 10^{-5}$ S cm$^{-1}$) for EC+gBL combination.

The ionic conductivity ($\sigma$) vs composition, temperature, and frequency were also investigated. The non-linear behaviour of the temperature dependence plot is attributed to the amorphous phase which could be described by the VTF relation for almost all the samples investigated.

The dielectric loss ($\varepsilon'$), electric modulus ($M''$), and conductance studies as the function of frequency evidence the mechanism of ion transport. The plotting of AC data in terms of impedance ($Z^* = Z' - iZ''$), dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) and electric modulus ($M^* = M' + iM''$) helps to distinguish the different relaxation processes.
occurred in the materials on the application of electric field. The comparison of the experimental data in the $\varepsilon^*$ and $M^*$ is thus useful to differentiate long-range conduction processes from the localized dielectric relaxation. The analysis of the effect of different lithium salts on the electrolyte complexes indicates that larger and more polarized anions generally lead to a higher conductivity. The AC impedance and conductance spectra were found to correlate well with each other for all the samples studied.

The thermal analysis of the samples was carried out by thermogravimetry, differential thermal analysis, and differential scanning calorimetry for finding the thermal stability and decomposition temperature. Thermal analysis of all the samples reveals appreciable thermal stability and also found that there is a problem of the reduction in decomposition temperature while the plasticizers were added to the polymer blend. Even though vinylidene chloride polymers are highly resistant to oxidation, they have undergone degradative dehydrochlorination on the application of heat. DSC analysis of the samples explains the phase transition of the membranes and chemical reactions involved while heating.

Further, there is a scope to synthesize a new high conducting composite polymer electrolyte by the addition of appropriate new plasticizers and/or fillers. The incorporation of ionic liquids into the polymer matrix could also lead to higher conductivity. The practical application is possible only after a detailed study regarding the compatibility with Li metal, charge-discharge behaviour, cyclic performance, etc. of the polymer membranes. Improvement of mechanical properties of electrolytes in terms of flexibility to achieve good contact at the interface can also be attempted in future.
To wrap up, electrolyte membrane with desired properties has been identified for possible applications in batteries, electrochromic windows, sensors, etc. on the basis of parameters such as impedance response, dielectric response, thermal stability, and spectral analysis.