Ch. 7: Conclusion

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Conclusions emerging from the experimental results of the as prepared PVA-PEO blend polymer electrolytes and Ag^+ and Li^+ primary polymer batteries are presented in this chapter.

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In the present thesis work, silver ion (Ag^+) and lithium ion (Li^+) conducting PVA-PEO blend polymer electrolytes prepared using solution cast technique and lab-made Ag_2O and $LiMn_2O_4$ cathode materials are characterized using various physical techniques viz. X-ray diffraction, differential scanning calorimetry, Fourier transform infrared spectroscopy and scanning electron microscopy. Experimental results of transport and electrical properties viz. impedance, ac/dc conductivity, dielectric and relaxation properties of these blend specimens are investigated. Suitability of the optimized Ag^+ and Li^+ conducting PVA-PEO blend electrolytes in the respective Ag^+ and Li^+ solid state primary polymer battery applications is studied and presented. Conclusions emerging from the experimental results of these PVA-PEO blend polymer electrolytes and Ag^+ and Li^+ primary polymer batteries are as discussed.

In the firstmost '[$PVA_{(100-x)}$: $PEO_{(x)}$] – 5 wt% $AgNO_3$ – 10 wt% PEG' (PPAP) series, the ratio of PVA and PEO host polymers is optimized to find the effect of blending. XRD and FT-IR results confirm the formation of PVA-PEO blend phase at all PVA-PEO ratios in the blends. Addition of PEO in blends gradually makes the blend phase homogeneous, reduces crystallinity of blend matrices and increases amorphous phases therein. Ether linkages with oxygen atoms in PEO structure improve flexibility of blend matrix and promote $AgNO_3$ salt dissociation to enhance number of free Ag^+ and NO_3^-. The increase in number of free charge carriers as well as dipolar orientations of polymeric macromolecules activates the conduction and localization processes and substantially improves ionic transport number, dc conductivity and dielectric parameters (dielectric constant and dielectric loss) with respect to PEO's addition in blends. For all blends of PPAP series, dc conductivity shows Arrhenius behaviour with rising temperature. Ion dynamics gradually starts following the same mechanism at all temperatures as PEO is added in blends but depend upon PEO concentration. Relaxation dynamics depend upon temperature and PEO concentration. Optimized Ag^+ conducting blend specimen of PPAP series with 50 % of PEO is then incorporated with Al_2O_3 nano-filler to prepare PPAPA series given as '[$PVA_{(50)}$: $PEO_{(50)}$] – 5 wt% $AgNO_3$ – 10 % PEG – x wt% Al_2O_3'.

Incorporation of Al_2O_3 nano-filler in blends of PPAPA series results in uniform miscibility and compatibility amongst host polymers at temperatures nearby or beyond PEO's melting temperature. Uneven dispersion of Al_2O_3 nano-filler upto 6 wt% in blends of PPAPA series leads to some structural reorganization such that it improves free volume of blend matrices which promotes mobility of free Ag^+ and NO_3^- and alignment of dipoles of macromolecular chains that participate in conduction and polarization processes and finally results in significant enhancement of blends' dc conductivity, transport and dielectric properties. At Al_2O_3 > 6 wt%, formation of neutral aggregates of filler particles restricts the mobility of free Ag^+ and NO_3^- and polymeric chain segments through blend matrices by blocking the conducting pathways and slows down the conduction and dielectric processes which deteriorate the transport and electrical properties of these blends. Vogel-Tamman-Fulcher (VTF) behaviour of dc conductivity with rising temperature depicted by the nano-filler 'based' blends is completely different from the Arrhenius behaviour shown by the nano-filler 'free' blends of PPAP series. Both ion dynamics and relaxation dynamics of these blends depend upon temperature. Relaxation dynamics depend upon Al_2O_3 concentration but ion dynamics remain independent of the same. Optimized nano-composite blend of PPAPA series with 6 wt% of Al_2O_3 is further chosen as electrolyte in fabricating 'Ag // [$PVA_{(50)}$: $PEO_{(50)}$] – 5 wt% $AgNO_3$ – 10 wt% PEG – 6 wt% Al_2O_3 //Ag_2O' primary polymer battery.

Ag^+ conducting blend specimens get oxidized owing to the 'silver' component present therein, which may deteriorate their mechanical, electrolytic and electrochemical properties in long term usage. This limitation is overcome by replacing $AgNO_3$ salt with a suitable $LiCF_3SO_3$ salt to form a new Li^+ conducting PPLE series, given as '[$PVA_{(50)}$: $PEO_{(50)}$] – 5 wt% $LiCF_3SO_3$ – x wt% EC' at the optimized PVA-PEO ratio. Likewise Ag^+ conducting specimens, the XRD studies of Li^+ conducting blends confirm the formation of PVA-PEO blend phase therein. Homogeneity in this blend phase continuously enhances with increasing temperature due to gradual melting of PEO. EC's high dielectric constant aids in activating the process of $LiCF_3SO_3$ salt dissociation to the increase number of free Li^+ and $CF_3SO_3^-$ and making the blend phase substantially amorphous and flexible, with its addition in the blends upto 6 wt%. This consistently favours effortless migration of cations and easy orientation of dipoles of polymeric macromolecules through blend matrix and improves blends' transport and electrical properties. At EC > 6wt%, the neutral aggregates of Li^+ and $CF_3SO_3^-$ block the conducting pathways, hamper the mobility of free charge carriers and dipolar orientations governing the conduction and dielectric processes and in turn degrade their transport and electrical properties. Likewise blends of PPAPA series variation in dc conductivity of blends of PPLE series, follows VTF behaviour with rising temperature. Both ion dynamics and relaxation dynamics follow different mechanisms throughout the temperature range and EC contents. Optimized blend with 6 wt% of EC is further selected as the base electrolyte for preparing next PPEL series given as '$[PVA_{(50)} : PEO_{(50)}]$ – 6 wt% EC – x wt% $LiCF_3SO_3$'.

Initial addition of $LiCF_3SO_3$ salt in blends of PPEL series upto 9 wt% substantially leads to betterment in complexation amongst salt and polymeric group and compatibility and miscibility amongst PVA and PEO host polymers. This also enhances amorphicity of blend matrices and leads to significant dissolution $LiCF_3SO_3$ salt to increase the number of free Li^+ and $CF_3SO_3^-$ conducting through these matrices. In addition to systematic increase in the number of free charge carriers, these factors facilitate easy alignment of dipoles of polymeric macromolecules participating in conduction and localization processes which further enhance transport and electrical properties of blends. At $LiCF_3SO_3$ > 9 wt% neutral aggregates of Li^+ and $CF_3SO_3^-$ are formed which lower the number of free Li^+ and $CF_3SO_3^-$ and obstruct the mobility of remaining free charge carriers and polymeric chain segments from participating in conduction and localization processes by blocking the conducting pathways. These phenomena in turn deteriorate the dc conductivity, ionic transport number and dielectric parameters at $LiCF_3SO_3$ = 11 wt% in blends. Likewise PPLE series, dc conductivity of blends of this PPEL series also shows VTF-like variation with rising temperature. Both ion dynamics and relaxation dynamics depend upon temperature and $LiCF_3SO_3$ salt content. Blend with 9 wt% of $LiCF_3SO_3$ salt depicting optimum transport and electrical properties is chosen as base electrolyte for the preparation of latest nano-composite PPELA series given as '[$PVA_{(50)}$: $PEO_{(50)}$] – 6 wt% EC – 9 wt% $LiCF_3SO_3$ – x wt% Al_2O_3'.

Incorporation of Al_2O_3 nano-filler upto 6 wt% in the blends of PPELA series initially makes the PVA-PEO blend matrix significantly inhomogeneous and forms neutral aggregates of filler particles which in turn block the conducting pathways and hinder mobility of free Li^+ and $CF_3SO_3^-$ and segments of polymeric chain via these conducting pathways. This slows down the conduction and localization processes and degrades blends' dc conductivity, transport and dielectric properties. At Al_2O_3 > 6 wt%, random distribution of nano-filler particles systematically increases compatibility and miscibility amongst host polymers, makes PVA-PEO blend phase gradually homogenous and creates free volume in blend matrix. This avails conducting pathways for transport of free Li^+ and $CF_3SO_3^-$ and polymeric chain segments, leads to effortless localization of free charge carriers and dipolar alignment and enhances transport and electrical properties of blends. dc conductivity of blends of this series shows VTF behaviour with rising temperature except for the optimum conducting specimen with 10 wt% of Al_2O_3, wherein it obeys Arrhenius rule. Ion dynamics and relaxation dynamics depend upon temperature and Al_2O_3 content and follow different mechanisms for the same. The blend with 10 wt% of Al_2O_3 of this series depicting optimum ionic transport number, dc conductivity and dielectric parameters is further chosen as electrolyte in fabricating ‘Graphite // [$PVA_{(50)}$: $PEO_{(50)}$] – 6 wt% EC – 9 wt% $LiCF_3SO_3$ – 10 wt% Al_2O_3 // $LiMn_2O_4$’ primary polymer battery.

Linear increment in conduction hopping frequency and linear decrement in relaxation time with rising temperature for all Ag^+ and Li^+ conducting blend specimens infer that both, ionic conduction and ionic relaxation are thermally activated processes.

Testing of respective prototype Ag^+ and Li^+ primary polymer batteries is successfully carried out in open atmosphere at room temperature. Various electrochemical battery parameters (plateau voltage, discharge capacity, specific capacity, electrical energy, specific power and specific energy) are calculated at the working region (plateau region) for each applied load in the external circuit of these batteries. Battery parameters of both these batteries significantly improve with addition of loads. At each particular load, the battery parameters of Li^+ battery are significantly higher than those of Ag^+ battery. As the presented works on batteries do not fulfil the requirements of the respective commercially available batteries, they may be considered as preliminary results only. Extensive efforts are needed to be done in order to enhance the performance characteristics of the present Ag^+ and Li^+ primary polymer batteries for their successful applications in future.

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