PREFACE

The field of Solid State Ionics, in the recent times, has emerged as an area of interdisciplinary activity. It is a branch of materials science encompassing the study of physical, chemical and technological aspects of the solids exhibiting rapid/fast ion movements within the bulk. Solid state ionic materials, commonly referred to as 'Superionic Solids' or 'Fast Ion Conductors' or 'Solid Electrolytes', exhibit exceptionally high ionic conductivity at room temperature close to in the range of that exhibited by liquid/aqueous electrolytes. Hence, these materials show tremendous technological potentials to develop variety of solid state electrochemical devices viz. mini/micro batteries, fuel cell, sensors, supercapacitors, memory/electrochromic display devices etc. Being all solid-state components, the miniaturization of these devices can also be practically realizable. More ever, all the major limitations of the liquid/aqueous electrolyte based electrochemical devices viz. limited temperature range of operation, electrode corrosion, bulky in size, less ruggedness etc. can be tackled with most conveniently using these materials as solid electrolytes. The field of solid state ionics came into existence around the last quarter of 20th century. To be more specific, the year 1967 has been marked as the birth of this exciting area of research after the discovery of two groups of solid electrolyte systems viz. MAg_s_i3 (where $M = Rb, K, NH_4$) and Na - $\beta$ - alumina, which exhibited exceptionally high Ag$^+$ - and Na$^+$ - ion conduction ($\sim 10^1$ Scm$^{-1}$) at room/ moderatley-high temperatures. Afterwards, the activity in this area took a rapid pace, consequently, a large number of superionic solids involving different kinds of cations and anions as mobile species such as H$^+$, Li$^+$, Na$^+$, K$^+$, Ag$^+$, Cu$^+$, F$^-$, O$^2$ etc. has been discovered in the last $\sim 4$ decades. On the basis of microstructure and physical properties, these materials have been broadly classified having different phases such as: crystalline/polycrystalline, polymeric, 2-phase composite, glass/amorphous electrolytes etc. The present investigation has been mainly focused on the synthesis of a few new Ag$^+$ ion conducting solids in glassy/amorphous phase including polymeric electrolytes. The glass electrolyte materials are prepared, in general, by melt-quenching the homogeneous molten mixture of following three basic constituent chemicals in appropriate molar wt (%) expressed by the following compositional formula:

$$MX: M_2O: A_3O_y$$
where MX : Host Salt viz. AgI, LiI, CuI etc; M₂O : Glass Modifier (GM) viz. Ag₂O, Cu₂O, Li₂O, Na₂O, K₂O etc. and AₙOₙ : Glass Modifier (GM) viz. B₂O₃, MoO₃, WO₃, V₂O₅, P₂O₅, As₂O₃ etc.

For the preparation of fast Ag⁺ ion conducting glasses, AgI has been used traditionally as host salt with a common glass modifier Ag₂O and any one of the glass formers. Attempts have also been made to mix two or more glass formers in order to achieve higher conductivity enhancements due to ‘Mixed Former Effect (MAE)’. However, at the present laboratory, a new host compound: ‘a quenched [0.75 AgI: 0.25 AgCl] mixed system/ solid solution’ was discovered in 1994 as an ‘alternative host’ in place of traditional host AgI. This newly investigated host exhibited transport characteristics identical to those of AgI viz. β → α like phase transition at a substantially lower temperature (~135°C) as compared to β → α transition of AgI at ~147°C, relatively higher ionic conductivity at room temperature etc. Moreover, the new host yielded superionic systems in glassy/composite/polycrystalline phases having superior electrolytic characteristics as compared to those prepared in the identical manner using the conventional host AgI. The present work reports the synthesis of the following two new Ag⁺ ion conducting glass electrolyte systems using the alternate host salt mixed with GM: Ag₂O and GFs : V₂O₅ and P₂O₅ in different mol wt. (%) compositions:

[A] Silver-vanadate glass electrolyte systems: x [0.75 AgI: 0.25 AgCl]: (1-x) [Ag₂O:V₂O₅]
[B] Silver-phosphate glass electrolyte systems: x [0.75 AgI: 0.25 AgCl] (1-x) [Ag₂O:P₂O₅]

For the sake of direct comparison of room temperature conductivity values of the above newly synthesized glass electrolytes, following two glass electrolyte systems have been synthesized in the identical manner using the traditional host salt AgI:

- x AgI : (1-x) [Ag₂O:V₂O₅]
- x AgI : (1-x) [Ag₂O:P₂O₅]

A twin-roller quencher with cooling rate ~ 10² K/s was employed for the formation of the glassy phase. The Optimum Conducting Composition (OCC) of the above glass electrolyte systems have been identified from the compositional dependent conductivity studies.
In addition to above Ag⁺ ion conducting solid electrolyte systems in glassy/amorphous phase, the present thesis also includes a preliminary investigation on two new Ag⁺ ion conducting PEO (polyethyleneoxide) based polymer electrolyte materials. Please note, these studies on Ag⁺ in conducting polymer electrolyte systems are the supplementary addendum to the present work besides what has been mentioned in the original synopsis. Following two polymer electrolyte films have been casted using a novel hot-press method instead of the usual solution-cast method:

[C] Solid Polymer Electrolyte (SPE): PEO: AgI
[D] Nano-Composite Polymer Electrolyte (NCPE): (PEO: AgI): SiO₂

Firstly, SPE films of different salt concentration (in wt %) were hot-press casted. The highest conducting composition at room temperature was identified from salt-concentration dependent conductivity studies. Afterwards, using this SPE composition as 1st-phase polymer host, NCPE films were hot-press casted by dispersing nano dimension (~8 nm) particles of SiO₂ into it as 2nd-phase dispersoid. Further, the Optimum Conducting Composition (OCC) of NCPE was identified from the SiO₂-concentration dependent conductivity study.

The material characterization and the identification of the glassy phase on the above newly synthesized OCC glass electrolytes were done with the help of XRD and DTA studies. The ionic mobility (μ) measurements were carried out by d.c. polarization Transient Ionic Current (TIC) technique. Subsequently, the mobile ion concentration (n) values have been determined from the σ and μ data. The ionic transference number (tᵢ₀ᵣ₉) values have also been determined from the TIC ‘current vs. time’ plots and subsequently, ionic drift velocity (v_d) values have been evaluated for different OCC samples. The temperature dependent studies on these basic ionic parameters viz. σ, μ, n, tᵢ₀ᵣ₉, v_d have been done to evaluate the respective energies involved in the different thermally activated processes. On the basis of these experimental findings, the ion transport behaviour in all the above newly investigated solid electrolyte systems have been discussed in the light of existing theoretical models. Finally, using OCC glasses as electrolytes, solid state batteries have been fabricated and cell-potential discharge performances have been tested under varying load conditions. The total work done in the present Ph.D. programme has been presented in seven chapters of this thesis and summarized below in brief.
Chapter 1 has been exclusively devoted for reviewing the field of solid state ionics extensively including the historical background and recent progress made during the development of this new area of multidisciplinary research activity. Variety of solid state ionic materials, discovered so far since the inception of this new area of materials science, and their broad classifications into various phases have been presented. Fast ion conduction in these solids is an exotic phenomenon, hence, various theoretical concepts, suggested to explain the ion transport mechanism in different superionic solid systems, have been briefly reviewed. Since the work in the present thesis mainly related to investigations on a few new Ag\(^+\) ion conducting glasses, thus this phase has been reviewed relatively in a greater detail separately also incorporating an elaborate discussion on the theoretical aspects for ion conduction. At the end of this chapter, a brief description on application aspects of these materials has been presented along with the relevance/ scope of the present work.

Chapter 2 reports the materials designing aspects for obtaining Ag\(^+\) ion conducting glasses as well as PEO - based polymer electrolyte films, as mentioned above. It also reports various techniques employed for material characterization/ phase - identification and characterization of the ion transport behaviour in the newly synthesized solid electrolyte systems including the fabrication of solid state batteries as well as study of the cell - potential discharge performances. It also describes an alternative electrochemical cell potential method employed for evaluating the ionic transference number.

Chapters 3 and 4 report the results of various experimental studies done to characterize the materials and ion transport properties in the newly synthesized glass electrolyte systems [A] and [B]. Compositional dependent conductivity studies reveled the following compositions as Optimum Conducting Compositions (OCCs) at room temperature:

- Silver - vanadate glass electrolyte: 0.8 [0.75 AgI: 0.25 AgCl]: 0.2 [Ag\(_2\)O:V\(_2\)O\(_3\)] (Chapter 3)
- Silver - phosphate glass electrolyte: 0.75 [0.75 AgI: 0.25 AgCl]:0.25[Ag\(_2\)O:P\(_2\)O\(_5\)] (Chapter4)

Materials characterization/ phase identification has been done on the above OCCs using XRD and DTA studies, as mentioned. Ion transport characterization has been done by measuring \(\sigma, \mu\).
employing different experimental techniques and plausible explanations have been given for the mechanism of ion transport in these newly synthesized glass electrolyte systems in the light of proposed theoretical models for glass electrolytes.

Chapter 5 reports the device application aspect of the above newly synthesized fast Ag\(^+\) ion conducting glasses. Using the above OCC glasses as electrolytes, solid state batteries have been fabricated in the following cell configuration:

**Cell I** : Ag - metal / 0.8 [0.75 AgI: 0.25 AgCl]: 0.2 [Ag\(_2\)O:V\(_2\)O\(_5\)] / (C+I\(_2\))

**Cell II** : Ag - metal / 0.75 [0.75 AgI: 0.25 AgCl]: 0.25[Ag\(_2\)O: P\(_2\)O\(_5\)] / (C+I\(_2\))

where Ag - metal and (C+I\(_2\)) in 1:1 wt (%) have been used as anode and cathode respectively. The cells have been discharged under varying load conditions to study the performances of the device and some important cell parameters were calculated in the plateau region of the cell potential profiles. \(t_{\text{ion}}\) has also been determined, as mentioned and compared with the value obtained earlier using dc polarization method.

Chapter 6 briefly highlighted the merits of the novel hot-press/ solvent free/ dry technique over the usual solution - cast method traditionally used for the formation of polymer electrolyte membranes. Using hot-press technique, developed at the present laboratory for the first time, Ag\(^+\) ion conducting polymer electrolyte films has been casted, as mentioned. On the basis of compositional dependent conductivity studies at room temperature, following highest conducting polymer electrolytes films have been identified as highest conducting composition:

- Highest Conducting SPE film: 20 PEO: 80 AgI
- Optimum Conducting Composition (OCC) NCPE film: (20 PEO: 80 AgI): 10 SiO\(_2\)

As consequences of dispersal of SiO\(_2\) nano particles as II\(^{nd}\) - phase dispersoid in to I\(^{th}\) - phase polymer electrolyte host: (20 PEO: 80 AgI), a two fold conductivity enhancement has been achieved further along with a substantial improvement in the mechanical strength of the film. The mechanism of ion transport in these polymer electrolyte membranes has been explained on the basis of experimental measurements on various ionic parameters \(\sigma, \mu, n, t_{\text{ion}}\) etc. employing
similar techniques, as mentioned. Polymer electrolyte films can be potentially employed to fabricate thin film micro batteries. This study is currently undergoing in the present laboratory. Hot-press is an emerging new method which can be potentially employed for casting of polymer electrolyte membranes complexed with different kinds of ionic salts in variety of polymeric hosts, for which the usual solution-cast-method has its own limitations, as discussed in this chapter.

Chapter 7 finally summarizes the entire work of the present thesis once again.