PREFACE

It is well known that most of the scientific and technological advancements are always associated with an effective use of materials in devices. Semiconductor based technology has brought dramatic changes in the life-style of the mankind in the last few decades. While, Solid State Ionics, which deals mainly with the physics, chemistry and technological aspects of the fast ion conducting solids, is in the process of refinements. These solids show tremendous promises for use in several solid state electrochemical devices such as solid state batteries, fuel cells, sensors, electrolyzers, electrochromic display devices, memory devices etc. The fast ion conducting solids, also termed as Superionic Solids or Solid Electrolytes are new class of materials which exhibit exceptionally high ionic conduction at room/moderately-high temperatures. The ionic conductivity is comparable to that of liquid electrolytes, hence, many of the major limitations of liquid electrolyte based devices can be easily overcome by the use of solid electrolytes.

The field of solid state ionics experienced rapid growth in the last few decades, both in terms of industrial applications and academic interests. A large number of fast ion conducting solids with various ion species viz. H\(^+\), Li\(^+\), Na\(^+\), K\(^+\), Ag\(^+\), Cu\(^+\), F\(^-\), O\(^2-\) etc. have been investigated and tested for different device applications. On the basis of microstructure and physical properties, these solids are now broadly classified into different phases such as crystalline/polycrystalline, glassy/amorphous, polymeric, composite. Amongst the various fast ion conductors, AgI-based solids exhibit very high Ag\(^+\) ion conduction at room temperature. AgI was used as host-salt, in general, in the preparation of the majority of fast Ag\(^+\) ion conducting glass and composite electrolyte systems. As a part of the present work, we investigated a new salt: a quenched/annealed \(0.75\text{AgI}:0.25\text{AgCl}\) mixed-system/solid solution as an alternate host which can replace the conventional salt AgI. The new host compound not only exhibits transport characteristics similar to AgI but it has several transport parameters...
superior to conventional salt AgI. Using this alternate compound as host- matrix, this thesis reports the synthesis and characterization of two new 2-phase composite electrolyte systems: \( (1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{Al}_2\text{O}_3 \) & \( (1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{SnO}_2 \). Much better enhancements in the room temperature conductivity were obtained in these systems than with those prepared identically using the conventional host-salt AgI. Characterization of transport properties viz. the electrical conductivity \( (\sigma) \), ionic mobility \( (\mu) \), mobile ion concentration \( (n) \), ionic transference number \( (t_{\text{ion}}) \), ionic drift velocity \( (v_d) \) and thermoelectric power \( (\theta) \) etc. were carried out by different techniques. Phase identification/material characterization was done by XRD, IR, DTA studies which confirm the coexistence of two separate phases in the optimum conducting compositions. The optimum conducting composites are, then, used as solid electrolytes for the fabrication of solid state batteries and to study the discharge characteristics under varying load conditions and cathode preparations. The entire thesis has been divided into seven chapters.

In Chapter 1, an introduction to the field of Solid State Ionics is presented along with a general review of superionic solids reported in the literature. This chapter also discusses the classification, basic notions of transport mechanism, theoretical aspects, electrochemical device applications etc. As composite electrolyte systems concerned the investigation of the present work, this phase has been dealt with very extensively. At the end of the chapter, the scope of the present thesis is outlined.

Chapter 2 gives detail descriptions of various experimental procedures actually used in the present work. These include: preparation of the new/alternate host \([x\text{AgI}:(1-x)\text{AgCl}]\) and composite electrolyte systems: \((1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{Al}_2\text{O}_3 \) & \((1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{SnO}_2 \); material characterization/identification of the phases by X-ray diffraction (XRD), infrared (IR), differential thermal analysis (DTA); transport property characterization such as electrical conductivity \( (\sigma) \) by impedance spectroscopy (IS), ionic mobility \( (\mu) \) by transient ionic current (TIC) technique, mobile ion concentration \( (n) \), ionic transference number \( (t_{\text{ion}}) \) & ionic drift velocity \( (v_d) \) by Wagner's depolarization method and thermoelectric power \( (\theta) \) studies. At the end of the chapter, fabrication of solid state batteries and procedures adopted for discharge characteristic studies including the determination of ionic transference number by electrochemical cell potential method, are given.

The experimental results of various transport property studies performed on the new and alternate host compound: a quenched/annealed \([0.75\text{AgI}:0.25\text{AgCl}]\) mixed-system/solid solution are discussed in the Chapter 3. The quenched composition
[0.75AgI:0.25AgCl] exhibited relatively higher room temperature conductivity than the annealed one as well as conventional host AgI. The results of various structural, thermal, transport property characterizations are explained on the basis of existing theories.

Chapters 4 & 5 report our results of transport property studies on Ag\(^+\) ion conducting composite electrolyte systems: \((1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{Al}_2\text{O}_3\) & \((1-x)[0.75\text{AgI}:0.25\text{AgCl}]:x\text{SnO}_2\) respectively. For direct comparison of extent of conductivity enhancements at room temperature in these systems, composite electrolytes: \((1-x)\text{AgI}:x\text{Al}_2\text{O}_3\) & \((1-x)\text{AgI}:x\text{SnO}_2\) were also prepared in the identical manner. The compositional variation of room temperature conductivity revealed that the highest conductivity enhancements at room temperature were obtained for the compositions: 0.7[0.75AgI:0.25AgCl]:0.3Al\(_2\)O\(_3\) & 0.8[0.75AgI:0.25AgCl]:0.2SnO\(_2\) prepared by melt-quench technique with soaking time \(\sim 15\) min. The conductivity enhancements in these composite systems are strong-preparation-route dependent, \(\sigma\) vs \(x\) studies also revealed that the new host compound is a better choice in place of conventional salt AgI. The material characterization/phase identification studies confirmed the coexistence of two separate phases in both the composite systems. Results of various transport characterization studies performed on the optimum conducting compositions are explained on the basis of existing theories/models proposed for 2-phase composite electrolyte systems.

Chapter 6 discusses our results on discharge characteristic studies performed on the batteries fabricated using the optimum conducting compositions: 0.7[0.75AgI:0.25AgCl]:0.3Al\(_2\)O\(_3\) & 0.8[0.75AgI:0.25AgCl]:0.2SnO\(_2\) as electrolytes. Ag-metal was used as anode, while several cathode compositions such as \([\text{C}+\text{l}_2]\); \([\text{C}+\text{Kl}_2]\); \([\text{C}+(\text{CH}_3)_4\text{N}]\); \([\text{C}+(\text{C}_2\text{H}_5)_4\text{N}]\) were employed as cathodes. The batteries were discharged under various load conditions. It was observed that the batteries using \([\text{C}+\text{l}_2]\) cathode exhibited stable potentials for over 50-85 h at low current drain state i.e. at high loads \((\sim 1\ \text{M}\Omega)\). Further, measurements of ionic transference number by electrochemical cell potential method indicated that \(t_{\text{ion}}\sim 1\) as observed earlier by Wagner's dc polarization method.

Finally, Chapter 7 summarizes once again the important results of various measurements carried out in the present thesis.