

PREFACE

Solid State Ionics is an interdisciplinary branch of science and technology which deals with solid state materials and devices based on the ion motion in the solids with exceptionally high ionic conductivity ($\sim 10^{-4}$ - 10^1 S cm⁻¹ at room temperature) comparable to that of liquid electrolytes. Such materials are known as 'Superionic Solids' or 'Solid Electrolytes' or 'Fast Ion Conductors'. These materials show tremendous promises in the development of solid state electrochemical devices viz. batteries, fuel cells, supercapacitors, sensors, electrochromic displays etc. This discipline started in 1967 with the discovery of two groups of solid systems viz. MAg₄I₃ (M = Rb, K, NH₄) and Na-β-alumina exhibiting exceptionally high Ag⁺/Na⁺-ion conduction at room/moderately high temperatures. Since then, a large number of good ion conducting solid systems, involving variety of ions viz. H⁺, Li⁺, Ag⁺, Cu⁺, Na⁺, F⁻, O²⁻ etc. as the principal charge carriers, have been developed in the form of (i) crystalline/polycrystalline solids, (ii) glasses, (iii) composites, and (v) polymer electrolytes. In the recent years, ion conducting polymer electrolytes has attracted attention as they show excellent technological potentials to develop all-solid-state electrochemical devices. Infact, the batteries based on ion conducting polymer electrolytes could be realized only after Armand et al. [1979] who demonstrated the first practical polymer battery using poly (ethylene oxide) (PEO) complexed with Li-salt as electrolyte. Subsequently, a large number of polymer electrolyte materials have been discovered. The polymer electrolytes, developed so far, can be divided into five classes as: (i) polymer-salt complexes or dry solid polymer electrolytes, which are prepared by complexing/dissolving ionic salts into high molecular weight polymer hosts viz., PEO etc., (ii) plasticized polymer electrolytes, which are prepared by adding small amounts of low-molar-mass polar liquids into dry polymer electrolytes, (iii) rubbery electrolytes or 'polymer-in-salt' systems in which a small amount of high-molecular-weight polymers, e.g. poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), etc. are dissolved in low temperature molten salt mixtures, (iv) gel polymer electrolytes, which are prepared by incorporating large amount of a nonaqueous electrolyte solution within an inert polymer matrices, and (v) composite polymer electrolytes (CPEs), which are prepared by the dispersion of nano-/micro-sized ceramic particles or dual-phase block copolymers into the polymer-salt complexes.

The conventional gel polymer electrolytes, one of the five broad categories mentioned above, although exhibit high ambient conductivities, but suffer from a number of limitations viz. poor mechanical stability, increase in interfacial impedance due to rapid growth of passivation layer at the metal electrode/electrolyte interface, poor thermal stability due to gas evolution etc. Further, due to the use of liquid components viz. organic plasticizers

(ethylene carbonate, propylene carbonate etc.), there always exist significant problems of volatility and flammability with these systems. To overcome these discrepancies two new approaches have been considered. One of them is dispersion of micro/nanosized ceramic filler particles into polymer gel electrolytes, and second one is the use of nonflammable and nonvolatile ionic liquids in place of organic plasticizers, which allow the formation of much safer polymer gel electrolytes with wider electrochemical window, higher ionic conductivity and excellent thermal stability.

Most of the R & D activities in the battery technology are focused on the development of lithium based polymer electrolyte batteries worldwide. Since, Li-metal (used as anode) is very reactive and it is difficult to handle the Li-battery fabrication especially in the ambient humid conditions. The battery applications of the polymer electrolytes also put forward several problems such as formation of an insulating passivating layer at the anode/electrolyte interfaces, dendritic growth within the electrolyte and above all, they are expensive. In recent years, composite polymer electrolyte systems dispersed with micro/nano ceramic filler particles in the polymer matrix and ionic liquid based gel polymer electrolytes are attracting more attention. The dispersion of filler particles not only reduces the Li^+ reactivity, but enhances the ionic conductivity from that of the undispersed polymer electrolytes as well as increases the mechanical strength with enhanced electrode/electrolyte interfacial activity. Moreover, due to problems associated with the lithium based battery systems attempts have been made to look for other alternatives which are safer to handle, more economical and environmental friendly viz. proton battery system, magnesium based battery systems etc.

Recently, some magnesium ion containing polymer electrolytes and gels have been reported which show potential applicability to fabricate solid state rechargeable magnesium batteries with much cheaper Mg as anode and Mg_xMO_y / Mg_xMS_y as cathode. The rechargeable magnesium polymer batteries have some inherent advantages over their lithium counterpart. These include: (i) low cost and natural abundance of magnesium, (ii) non-toxicity, non-hazardous nature of Mg than lithium, (iii) ionic radius of Mg^{2+} ions comparable to Li^+ ions, (iv) its comparable value of redox potential (-2.3 V vs. SHE), and (v) low electrochemical equivalence (12.2 g eq^{-1}) and high theoretical energy density of $\sim 1900 \text{ Wh Kg}^{-1}$. The magnesium based rechargeable batteries are in the early stage of development. However, the practically achievable energy density of batteries with magnesium anode in combination with cathodes like Mg_xMO_y or Mg_xMS_y is $> 100 \text{ Wh Kg}^{-1}$, which is more than Pb-acid or Ni-Cd batteries but less than Li-batteries. Nevertheless, this can be compensated from the fact that magnesium is cost effective and safer than lithium.

The present thesis work is devoted to the synthesis, characterization and device application aspects of some new H^+ - and Mg^{2+} -ion conducting polymer electrolyte systems.

The electrolyte materials have been characterized and optimized their electrical, thermal, mechanical and electrochemical properties using various physical techniques viz. XRD, SEM, FTIR, DTA/DSC/TGA, a.c. impedance spectroscopy, d.c. polarization etc. Using these optimized polymer electrolyte materials, all-solid-state batteries have been fabricated and characterized. The entire thesis is organized in seven chapters as summarized below:

Chapter 1 gives a general introduction of the broad subject area “Solid State Ionics” and briefly reviews various superionic solids, in general, and polymer electrolytes, in particular. Different types of polymer electrolyte materials and their possible ion conduction mechanisms have been described in brief. A brief overview of different battery systems along with other applications of polymer electrolytes are given in this chapter. At the end of the chapter, the scope of the thesis has been presented.

Chapter 2 deals with the detailed description of the experimental techniques used in the present investigations. Various routes adopted for synthesis of H^+ and Mg^{2+} ion conducting polymer electrolytes have been discussed. Various morphological/structural, thermal, electrical and electrochemical techniques have been adopted for the characterization of these newly synthesized polymer/gel electrolytes. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies have been carried out for the study of morphological and structural changes in the polymer electrolytes. Thermal analysis and the phase transition behavior have been studied by DSC/TGA techniques. FTIR spectroscopic studies have been carried out to probe ion-polymer interaction and possible conformational changes in host polymer in the polymer electrolytes at the microscopic level. The polymer electrolytes are electrically characterized by measuring the electrical conductivity evaluated by impedance spectroscopy and ionic transference number by d.c. polarization and combined a.c./d.c. methods. Cyclic voltammetry has been carried out to study the electrochemical stability of the electrode/electrolyte interfaces. Finally, techniques have been discussed to characterize of proton and magnesium batteries.

Chapters 3 describes the comparative studies on proton conducting nanocomposite polymer electrolyte system, PEO: NH_4HSO_4 dispersed with nanosized SiO_2 prepared by a novel hot-press and the solution cast techniques. SEM, XRD, DSC, FTIR spectroscopy, ionic transport number (t_{ion}) and electrical conductivity (σ) measurements have been carried out on hot-press films and the results have been compared with the nanocomposite films prepared by the standard solution cast technique. On the basis of various studies, it has been observed that the hot-press technique, which is a solvent-free/dry and cost effective method, can be adopted as an alternative to the ‘solution-cast’ preparation method of the polymer electrolytes.

Chapters 4 describes the results of morphological/structural, thermal, spectroscopic and electrical/electrochemical studies on the following Mg^{2+} ion conducting composite gel polymer electrolyte systems:

PVdF-HFP + EC:PC (1:1 v/v) + $Mg(ClO_4)_2$ dispersed with nanosized SiO_2

PVdF-HFP + EC:PC (1:1 v/v) + $Mg(ClO_4)_2$ dispersed with micro- & nano-sized MgO

The composite gel polymer electrolyte have been optimized using different physical techniques such as impedance spectroscopy/electrical conductivity as a function of composition and temperature, d. c. polarization technique for total ionic transport number measurement, combined a. c. and d.c. technique for Mg^{2+} ion transport number measurement, cyclic voltammetry for the measurement of the electrochemical stability of the gel composite systems.

Chapter 5 deals with the studies on ionic liquid based Mg^{2+} ion conducting gel polymer electrolyte system EMI-triflate (EMITf) - $Mg(CF_3SO_3)_2$ + PVdF-HFP. The results of various experimental investigations based on SEM, XRD, TGA/DSC, FTIR spectroscopy, impedance spectroscopy/electrical conductivity as a function of composition and temperature, ionic transport number (t_{ion}), cyclic voltammetry have been discussed.

Chapter 6 describes the fabrication and characterization of proton and magnesium batteries based on optimised proton and Mg^{2+} ion conducting polymer/gel electrolytes. The cell performance studies on the proton batteries fabricated using optimized proton conducting nanocomposite polymer electrolyte, sandwiched between Zn-composite anode and $MnO_2 + C$ or $PbO_2/V_2O_5 + C$ as cathode, have been carried out under different load conditions. Some important cell parameters, calculated from the plateau region of different cell potential discharge profile, have been presented.

Further, the fabrication of rechargeable magnesium batteries using Mg-metal as anode and MnO_2 , MoO_3 , polyaniline (bulk and nanofibres) as cathodes with optimized gel polymer electrolytes have been described. The performance characteristics of these batteries in term of the open circuit voltage (OCV) and charge-discharge characteristics have been given. Various parameters of the typical batteries such as discharge capacity, specific energy, specific power have been evaluated and presented.

Chapter 7 finally, summarises the studies reported in this thesis.