Chapter – 7

Summary and Conclusions

Summary and Conclusions

Present thesis covers the work done on the synthesis and characterization of proton conducting polymer electrolytes and Mg^{2+} ion conducting gel polymer electrolytes (composite and ionic liquid based) for their applications in solid state batteries. The nanocomposites of proton conducting polymer electrolyte system have been prepared by a novel hot-press (extrusion) technique, which is the least expensive/solvent-free/dry process of polymer electrolyte preparation. The nanocomposite films have also been prepared using standard 'solution-cast' method for comparison. The Mg^{2+} ion conducting composite gel polymer electrolytes have been prepared and characterized in view of their improvement in thermal, electrical and electrochemical properties. In addition, the ionic liquid based magnesium ion conducting gel polymer electrolytes have also been prepared and optimized their characteristics. The proton and magnesium ion conducting polymers have been used as electrolytes in solid state proton and magnesium batteries, respectively.

7.1 Experimental Techniques used in the Present Studies

7.1.1 Materials preparation

The materials prepared in the present investigation are summarized as below:

(i) The proton conducting nanocomposite polymer electrolytes have been prepared by a novel hot-press (extrusion) technique as well as standard solution cast method.

(ii) The Mg^{2+}-ion conducting composite gel polymer electrolytes and ionic liquid based gel polymer electrolytes have been prepared in the form of free-standing films by solution cast method.

(iii) Electronically conducting polymer, polyaniline, for their application as cathode material in battery, has been synthesized by chemical oxidation of aniline monomer whereas polyaniline nanofibres of diameters of ~100 nm and lengths of ~ 450 nm has been synthesized by chemical polymerization method.

7.1.2 Physical characterization

Various experimental techniques were used in the present investigation to study the morphological/structural, thermal, electrical and electrochemical properties of these newly synthesized polymer electrolyte materials. The proton and magnesium batteries based on the optimized electrolyte materials were characterized using galvanostatic charge-discharge methods. These are summarized as below:

(i) Scanning Electron Microscopy (SEM)/Atomic Force Microscopy (AFM) and X-ray diffraction (XRD) studies have been carried out for the morphological and structural changes in the polymer electrolytes.

(ii) Thermal analysis of these polymer electrolytes has been carried out by Differential Scanning Calorimetry (DSC)/Thermo-Gravimetric Analysis (TGA) techniques to check their thermal stability.

(iii) FTIR spectroscopy has been carried out to probe ion-polymer and filler-polymer interactions in the polymer electrolytes at the microscopic level.

(iv) The electrical conductivity measurements have been carried out by impedance spectroscopy (IS) using irreversible/blocking (stainless steel, SS) electrodes and reversible (Mg-foil) electrodes in the case of Mg^{2+} ion conducting electrolytes. Bulk electrical conductivity was evaluated from the complex impedance plots as a function of composition and temperature.

(v) The electrochemical window of gel polymer electrolytes has been evaluated by linear sweep voltammetry (LSV), whereas electrochemical stability at the electrode/electrolyte interfaces has been tested by cyclic voltammetric studies.

(vi) The ionic transference number (t_{ion}) has been determined by d.c. polarization method using SS blocking electrodes. The cationic transport number (t_+) in Mg^{2+} ion conducting gel polymer electrolytes has been evaluated by the combination of ac/dc method.

(vii) The proton batteries have been studied by discharging them through different load resistances, whereas, the performance of Mg-cells have been studied by a charge-discharge cyclic tests under constant current conditions.

7.2 Studies on Proton Conducting Nanocomposite Polymer Electrolytes

The proton conducting nanocomposite polymer electrolyte films of the following composition have been prepared by hot-press (extrusion) technique:

$$PEO:NH_4HSO_4\ (80{:}20\ w/w) + x\ wt\%\ SiO_2$$

The nanocomposite films have also been prepared by solution cast method for the comparison of their various properties. In addition, another composition has been prepared by solution cast method:

$$PEO:NH_4HSO_4\ (92{:}8\ w/w) + x\ wt\%\ SiO_2$$

A wide variety of techniques have been used to characterize the nanocomposite polymer electrolyte materials and a comparative studies have been carried out on the materials

prepared by two different method. On the basis of various electrical, thermal and structural studies, following conclusions have been drawn:

(i) The complexation of the salt NH_4HSO_4 in the polymer PEO and formation of nanocomposite polymer electrolyte phase have been confirmed by SEM, XRD, FTIR and DSC studies.

(ii) The dispersion of nanosized filler particles SiO_2 in the polymer electrolyte hosts PEO: NH_4HSO_4 (80:20 w/w) and PEO: NH_4HSO_4 (92:8 w/w) resulted into conductivity enhancement at room temperature. The conductivity value of hot-press nanocomposite film is very close to that of solution cast film.

(iii) The hot-press technique which is a least expensive/solvent-free/dry procedure can be preferred over the solution cast method.

(iv) The total ionic transference number has been found to be ~0.97-0.98 which indicates that the charge carriers are predominantly ions (protons) in the polymer electrolyte nanocomposite materials under study.

7.3 Studies on Mg^{2+} Ion Conducting Composite Gel Polymer Electrolytes

The effect of addition of a micro and nano-sized MgO as active fillers and nanosized passive filler SiO_2 in the PVdF-HFP based Mg^{2+} ion conducting gel polymer electrolyte has been investigated using various experimental techniques namely XRD, SEM/AFM, FTIR, thermal analysis by DSC/TGA, impedance spectroscopic analysis, cyclic voltammetry and transport number measurements. The Mg^{2+} ion conducting composite gel polymer electrolyte systems have been prepared with the following compositions:

[PVdF-HFP + EC:PC (1:1 v/v) + 1.0 M $Mg(ClO_4)_2$] + x wt.% nanosized SiO_2

[PVdF-HFP + EC:PC (1:1 v/v) + 1.0 M $Mg(ClO_4)_2$] + x wt.% micro- & nano-sized MgO

Various experimental studies like electrical conductivity, transport number measurements, cyclic voltammetry supports that MgO act as active filler whereas SiO_2 plays a role of passive filler in the present composite gel polymer electrolyte systems.

On the basis of various structural, thermal, electrical and electrochemical studies, following conclusions have been drawn:

(i) The addition of nanosized MgO is beneficial in inducing consistent improvements in liquid electrolyte retention as well as in the overall chemical, physical and electrochemical properties as compared to the addition of micro-sized MgO.

(i) The composite nature of the gel electrolyte films due to the dispersion of various filler particles has been confirmed from XRD and SEM results.

(ii) Substantial conformational changes in the crystalline texture of the host polymer PVdF-HFP have been observed due to the immobilization of liquid electrolyte in the gel polymer electrolyte. The existence of free anion and filler-polymer interaction has also evidenced from the FTIR studies.

(iii) The composite gel electrolytes offers high ionic conductivity ($\sigma \sim 10^{-3}$ S cm^{-1} at room temperature) with wider electrochemical potential window (~ 3.5 V) and good thermal stability having single phase behaviour for the temperature range from -70^0 to 80 ^{0}C.

(iv) The studies based on the ac impedance spectroscopy and cyclic voltammetry indicate the existence of electrochemical equilibrium between Mg metal and Mg^{2+} ions and hence, confirm Mg^{2+} ion conduction in the composite gel polymer electrolytes.

(v) The Mg^{2+} ion transport number has become almost doubled due to the addition of 10 wt.% MgO nanoparticles. The enhancement has been explained on the basis of the formation of space charge (double layer) regions due to the presence MgO:Mg^{2+} like species, which supports the Mg^{2+} ion motion.

7.4 Studies on Ionic Liquid based Mg^{2+} Ion Conducting Gel Polymer Electrolytes

Experimental investigations on a novel Mg^{2+} ion conducting gel polymer electrolyte system based on room temperature ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) have been carried out. The solution of magnesium trifluoromethanesulfonate, $Mg(CF_3SO_3)_2$ in ionic liquid has been immobilized in the polymer matrix, PVdF-HFP to form gel polymer electrolyte films. A variety of experiments, namely XRD, thermal analysis, FTIR, SEM, complex impedance analysis, conductivity versus temperature and composition, transference number and cyclic voltammetry have been carried out to characterize the gel polymer electrolyte and to establish ion transport behavior in the material. On the basis of these studies, following conclusions have been drawn:

(i) The polymer gel electrolyte film is flexible and free standing with good mechanical strength. The films offer high ionic conductivity ($\sigma \sim 10^{-3}$ S cm^{-1} at room temperature) with a wider electrochemical potential window (~ 3.5 V) and excellent thermal stability having single phase behaviour for the temperature range from -30^0 to 110 ^{0}C.

(ii) There are substantial conformational changes in the crystalline texture of the host polymer PVdF-HFP, observed due to the immobilization of ionic liquid/Mg-salt in the gel polymer electrolyte. The existence of free anions and ion (particularly triflate anion)-polymer interaction has also evidenced from the FTIR studies.

(iii) The studies based on the a.c. impedance spectroscopy and cyclic voltammetry indicate the existence of electrochemical equilibrium between Mg metal and Mg^{2+} ions and hence, confirm Mg^{2+} ion conduction in the polymer gel electrolyte.

(iv) The Mg^{2+} ion transport number has been observed to be ~ 0.26, which indicates a lower contribution to the overall ionic conductivity. The other possible mobile ions are ionic liquid components and triflate anions, which are common to both the ionic liquid and magnesium salt, in the present studies.

(v) The present ionic-liquid-based polymer gel electrolyte appears to be an excellent substitute to the liquid electrolyte in electrochemical devices, particularly in rechargeable magnesium batteries.

7.5 Proton and Mg^{2+} Ion Conducting Polymer Electrolytes based Solid-State Batteries

The proton batteries have been fabricated using optimised nanocomposite polymer electrolytes with ($Zn+ZnSO_4.7H_2O$) composite anode and MnO_2+C, $PbO_2+V_2O_5$+C cathodes. Proton batteries have been studied by discharging them through different load resistances and various parameters such as discharge capacity, specific power and specific energy have been evaluated. The cell potentials remained stable, after the usual initial potential drop due to polarization effect, for long time with low current drain (~ 1μA). However, it gets discharged more quickly during higher current drain or with low load resistance and thus, the cells are found suitable for low current density applications.

The magnesium batteries using the optimised composite gels and ionic liquid based gel polymer electrolytes have been fabricated with different configurations of the anode (Mg and C+Mg) and cathode (MnO_2, MoO_3, bulk and nanofibres of polyaniline) materials. The magnesium batteries have been characterized by charge-discharge studies at room temperature (~ 20 °C) under different constant current conditions. The electrochemical impedance of the Mg-cells has also been measured by a.c. impedance spectroscopy technique. On the basis of these studies following conclusions have been highlighted:

(i) The studies suggest the usefulness of composite gel polymer electrolytes and ionic liquid based gel polymer electrolyte in the development of magnesium batteries.

(ii) The poor rechargeability of Mg cells has been observed, probably due to the passivation film formation of Mg/gel electrolyte interface.

(iii) Electronically conducting polymer, polyaniline, has been found to be a good cathode material for magnesium batteries, particularly, in its nano-fibrous form.

(iv) Carbon anode material (mixed with Mg powder) can be used to develop Mg-ion rechargeable batteries analogous to Li-ion battery systems.

(vi) These studies show the prospects of rechargeable magnesium batteries with solid-like gel polymer electrolytes.

7.6 Scope of Future Work

In addition to the studies carried out in the present thesis, there is a lot of scope for future work in the area of gel polymer electrolyte based electrochemical devices, particularly on development of rechargeable magnesium or magnesium-ion batteries. These are summarised as follows:

(i) There is a need to explore more Mg^{2+} ion conducting polymer/gel polymer electrolytes with other polymer hosts and salts.

(ii) Some other ionic liquids can be used as a solvent to form Mg^{2+} ion conducting gel polymer electrolytes to obtain their better thermal and electrochemical stability.

(iii) Efforts are needed to enhance the target ion (Li^+, Na^+, Mg^{2+} etc.) transference number in ionic liquid based gel polymer electrolytes for battery applications. Zwitterionic liquid may be a non-volatile polar solvent to form high target ion conducting gel polymer electrolyte, since the zwitterionic salt dissociates into ions but did not migrate along with the potential gradient.

(iv) The reversible negative magnesium-metal electrode was scarcely investigated and is still poorly understood so more studies are required.

(v) Various insertion and spinel materials can be used a cathode material in rechargeable magnesium batteries, in order to improve the cyclic performance.

(vi) Studies are required in detail regarding the use of conducting polymers as cathode materials in the rechargeable magnesium batteries. Other conducting polymer viz. polypyrrole, Poly(ethylenedioxythiophene) (PEDOT) may also be examined as a cathode materials in Mg-battery systems.