ELECTROCHEMICAL STUDIES OF SPINEL CATHODE MATERIAL AND NANOCOMPOSITE POLYMER ELECTROLYTE

SUMMARY OF THESIS

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SUMMARY

'Solid State Ionics' is a field of Science and Technology which mainly deals with ionically conducting liquid and solid electrolytes. Inspite of showing appreciably high ionic conductivity, liquid electrolytes depict leakage problems after a certain time span which in turn hampers performance of electrochemical devices in which they are employed. This limitation has provoked a need of choosing an alternative such as *'Solid Electrolyte'* towards liquid electrolytes which not only solves leakage problems but also shows ionic conductivity comparable to these liquid electrolytes. All this discussion is briefly carried out in ***Chapter 1*** which is ***'Introduction'.*** The chapter further discusses types of solid electrolytes viz. glass, ceramic and polymer electrolytes. Amongst these solid electrolytes, the present research work mainly focuses on polymer electrolytes which can be further classified into polyelectrolytes, rubbery polymer electrolytes, gel polymer electrolytes, solid polymer electrolytes, plasticized polymer electrolytes, composite/nano-composite polymer electrolytes, plasticized composite/nano-composite polymer electrolytes and blend polymer electrolytes. These polymer electrolytes can be successfully applied in non-battery applications such as sensors and electrochromic display devices as well as in battery applications viz. fuel cells, solar cells, electrochemical capacitors and supercapacitors and especially in solid state batteries.

Considering this discussion, five different blend series are prepared in the present research work using commercially available polyvinyl alcohol (PVA) and polyethylene oxide (PEO) as host polymers, silver nitrate ($AgNO_3$) and lithium trifluoromethansulfonate (lithium triflate) ($LiCF_3SO_3$) as dopant salts, polyethylene glycol (PEG) and ethylene carbonate (EC) as plasticizers and aluminium oxide (alumina) (Al_2O_3) as nano-filler respectively, and investigated in detail. Composition for each PVA-PEO blend polymer series is as follows.

1) ***PPAP Series:*** $[PVA_{(100-x)} : PEO_{(x)}]$ – 5 wt% $AgNO_3$ – 10 wt% PEG
where, x = 10 % to 50 % in the steps of 10

2) ***PPAPA Series:*** $[PVA_{(50)} : PEO_{(50)}] - 5$ wt% $AgNO_3 - 10$ wt% PEG – x wt% Al_2O_3
where, x = 2 wt% to 10 wt% in the steps of 2

3) ***PPLE Series:*** $[PVA_{(50)} : PEO_{(50)}] - 5$ wt% $LiCF_3SO_3$ – x wt% EC
where, x = 2 wt% to 10 wt% in the steps of 2

4) ***PPEL Series:*** $[PVA_{(50)} : PEO_{(50)}] - 6$ wt% EC – x wt% $LiCF_3SO_3$
where, x = 3 wt% to 11 wt% in the steps of 2

5) ***PPELA Series:*** $[PVA_{(50)} : PEO_{(50)}] - 6$ wt% EC – 9 wt% $LiCF_3SO_3$ – x wt% Al_2O_3
where, x = 2 wt% to 10 wt% in the steps of 2

The chapter further throws light on the objectives of the thesis which cover the studies and investigations on:

(i) physical, thermal, structural, microstructural and morphological properties of the as prepared silver ion (Ag^+) and lithium ion (Li^+) conducting blend polymer electrolytes and lab-made cathode materials.

(ii) experimental studies on transport and electrical properties viz. impedance, ac/dc conductivity, dielectric and relaxation properties of these PVA-PEO blends.

(iii) electrochemical properties of the as prepared cathode materials and optimized blend polymer electrolytes.

(iv) suitability of the optimized Ag^+ and Li^+ conducting blend polymer electrolytes as well as Ag_2O and $LiMn_2O_4$ cathode materials in the respective Ag^+ and Li^+ solid state primary polymer batteries.

Chapter 2 is ***'Theoretical Details'*** which provides an insight regarding the ionic conductivity and ion conduction mechanism taking place in solid electrolytes especially, in polymer electrolytes, by using various theories and theoretical models viz. temperature dependent Arrhenius, Vogel-Tamman-Fulcher (VTF) and William-Landel-Ferry (WLF) theories of conductivity, Rouse Model, Amorphous Phase Model, Effective Medium Theory, Free Volume Theory, Configurational Entropy Model, Jump Relaxation Model and Percolation Model. Further part of the chapter throws light on (a) non-destructive technique

called *'Complex Impedance Spectroscopy (CIS)'* which measures *'Impedance'* of a cell considered over wide range of frequencies and temperatures in a single experiment, (b) Dielectric Spectroscopy which informs about relaxation phenomenon and dielectric response of ion-conducting polymer electrolytes and (c) *'Electric Modulus (M^*)'*, an electric analog of dynamic mechanical modulus or mechanical shear modulus that is mainly put forward to analyse relaxation processes taking place in solids.

Chapter 3 is ***'Experimental'*** which discusses about the preparation of blend specimens of the previously mentioned PVA-PEO series and silver oxide (Ag_2O) and lithium manganese oxide ($LiMn_2O_4$) cathode materials. The later part of the chapter includes a general discussion on various experimental techniques viz. X-ray diffraction (XRD), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). These techniques respectively, throw light on various physical, thermal, structural, microstructural and morphological properties of the as prepared blend polymer electrolyte specimens and cathode materials (as discussed in later chapters). dc polarization technique, which measures the ionic transport number of the blend specimens to obtain an information as to which of the mobile species (ions or electrons) provide what fraction of conductivity and current individually, is discussed. Various electrical properties such as impedance spectroscopy and its principles, complex impedance, complex conductivity, complex dielectric permittivity and complex modulus function, along with their respective real and imaginary parts are also mentioned in short. Final part of the chapter includes battery essentials of the as assembled Ag^+ and Li^+ primary polymer batteries and gives an idea about the related battery parameters and battery components.

Chapter 4 is ***'Characterization Studies'*** which explains the results of characterization studies of all the as prepared polymer electrolyte specimens of PVA-PEO blend series, that are carried out by using X-ray diffraction (XRD), differential scanning calorimetry (DSC),

Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). All these characterization studies (i) confirm the formation of PVA-PEO blends, (ii) inform about interaction, complexation, miscibility and compatibility amongst host polymers and other constituents in blends and (iii) investigate the variations taking place in degree of crystallinity/amorphicity of the blend matrices with respect to various concentrations of respective polymers, salt, plasticizer and nano-filler incorporated therein. Ionic transport numbers of these blend specimens measured using dc polarization technique, are thoroughly investigated. Further, XRD and FT-IR studies of the as prepared $LiMn_2O_4$ powder are carried out which infer the formation of spinel phase of $LiMn_2O_4$ cathode material.

Chapter 5 which is ***'Conductivity, Modulus & Dielectric Analysis'*** discusses about the influence of concentrations of various constituents viz. polymers, salt, plasticizer and nano-filler and temperature on impedance, ac/dc conductivity, relaxation and dielectric properties of the as prepared specimens of each PVA-PEO blend series. Additionally, temperature-wise and concentration-wise scaling of ac conductivity and modulus as well as calculations of other electrical parameters such as conduction hopping frequency and relaxation time are done and investigated in detail.

Further, as discussed in ***Chapter 6*** i.e. ***'Electrochemical Studies',*** the optimized Ag^+ and Li^+ conducting blends are considered as electrolytes in the fabrication of respective Ag^+ and Li^+ primary polymer batteries in which Ag_2O and $LiMn_2O_4$ are respectively, employed as cathodes and pure silver (Ag) metal and graphite electrode are used as respective anodes. Ag^+ and Li^+ primary polymer battery assemblies are respectively, written as:

Ag // $PVA_{(50)}$: $PEO_{(50)}$] – 5 wt% $AgNO_3$ – 10 wt% PEG – 6 wt% Al_2O_3 //Ag_2O

Graphite // [$PVA_{(50)}$: $PEO_{(50)}$] – 6 wt% EC– 9 wt% $LiCF_3SO_3$ – 10 wt% Al_2O_3 // $LiMn_2O_4$

The chapter thoroughly focuses on the investigations of discharge characteristics of both these batteries at different loads of 330 Ω, 1 kΩ, 2.2 kΩ, 3.3 kΩ and 4.7 kΩ that are applied in

batterys' external circuits. This study provides an insight regarding the performances of both these batteries at every load condition. Battery parameters including 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 and all these parameters are found to improve substantially with increasing loads. This indicates that performance of both these Ag^+ and Li^+ primary polymer batteries continuously enhances as the loads are added. At each particular load, all the battery parameters of Li^+ battery are found to be significantly higher than those of Ag^+ battery. Still, none of these primary polymer batteries meet the requirements of the respective commercial Ag^+ and Li^+ primary polymer batteries, which indicate that the works based on the present batteries, may be considered as preliminary results only. Extensive efforts are required for improving the performance characteristics of the present Ag^+ and Li^+ primary polymer batteries for their successful applications in future.

Final chapter, ***Chapter 7*** of present thesis is ***'Conclusion'*** which provides summary and conclusion of the present research work. This chapter highlights the (i) experimental investigations and related inferences of the as prepared PVA-PEO blends and Ag_2O and $LiMn_2O_4$ cathode materials and (ii) applicability of the optimized Ag^+ and Li^+ conducting blends and cathode materials in the respective lab-fabricated Ag^+ and Li^+ primary polymer batteries. This chapter also mentions the scope of future research works.

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