ELECTROCHEMICAL STUDIES OF SPINEL CATHODE MATERIAL AND NANOCOMPOSITE POLYMER ELECTROLYTE

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Introduction:

Since several years, “Electrolytes” have been playing a key role in various fields of industrial as well as household applications owing to which the study of preparation and applications of these electrolytes in appropriate devices and appliances have become a keen interest nowadays.

These electrolytes are basically of two major types, i.e. solid and liquid electrolytes and their selection in various applications is based on their conductivity yielding capacity. Hence, the conductivity provided by an electrolyte plays a major role in deciding the performance of an appliance or a device. The major importance is being given to the electrolytes possessing higher conductivity values. Many efforts are being made since long in order to improve the conductivity of both i.e. liquid and solid electrolytes.

The liquid electrolytes are capable of yielding very high value of conductivity and hence, are being used in various applications. However, these electrolytes at times show leakage problems after a long time span which deteriorates the appliances’ performance. Hence, it became essential to prepare such electrolytes which not only provide the considerable conductivity as that of liquid electrolytes but also minimizes the limitation of leakage. These conditions can be fulfilled by an alternative class of electrolytes called Solid Electrolytes.

The solid electrolytes are basically divided into mainly four types, viz., gel electrolytes, glassy solid electrolytes, solid ceramic electrolytes and solid/dry polymer electrolytes. Out of these, solid polymer electrolytes have become highly attractive since last two decades [1]. Basically when polymers are used in the preparation of electrolytes, such prepared electrolytes are termed as *“Polymer Electrolytes”*. Wright and co-workers [2] were the first to study *“Polymer Electrolytes”*. The interesting and essential properties such as good mechanical strength, easy processability, dimensional nature, electrochemical and mechanical stability, design flexibility, light weight, low cost, etc., make these polymer electrolytes highly applicable in various applications such as electrochromic displays, sensors, fuel cells, high energetic batteries etc. [1, 3-6].

Certain natural occurring biodegradable polymers such as chitosan, protein molecules, natural fibres such as Kevlar fibres, etc., are commonly used in the preparation of electrolytes. However, few such biodegradable polymer electrolytes show certain limiting properties which make them unsuitable for various applications. Hence, instead of biodegradable polymers, a substitute in the form of non-biodegradable polymers is used in preparation of most of the polymer electrolytes. The basic and common non-biodegradable host polymers which are used in the preparation of electrolytes are majorly polyethylene oxide (PEO), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), polyvinyledene fluoride (PVdF), polyvinyl chloride (PVC), polyacrylamide (PAM), etc. Hence, the problems occurring in case of certain biodegradable polymer electrolytes can be now minimized by using the non-biodegradable polymer electrolytes which can in turn improve the appliances' performance.

Although, the non-biodegradable polymer electrolytes show certain properties better than the biodegradable polymer electrolytes, the fact i.e. these non-biodegradable polymer electrolytes at times possess several unwanted factors, which can in turn deteriorate the conductivity and other electrolytic properties, cannot be neglected. Some of these factors include the semicrystalline/crystalline nature of polymers, rigid polymeric chain matrix, high viscosity of polymers, high melting temperatures of polymers, etc., owing to which these electrolytes at times show low conductivity values [7, 8]. Hence, many efforts such as blending of two or more host polymers, incorporation of certain additives such as plasticizers and nano-fillers and irradiation techniques are being carried out in order to improve the electrolytic properties and conductivities of these polymer electrolytes [9-11]. In addition to the selection of these techniques, the choice of the constituents such as host polymers, plasticizers, salts used as a dopant and nano-fillers should be done carefully in the electrolyte preparation as these constituents as well as their amount decide the conductivity and other properties of the electrolyte. Moreover, there also exists a possibility in few polymer electrolytes wherein plasticization may lead to deterioration of electrolytic properties. Hence, in order to minimize such a limitation of the polymer electrolytes, nano-fillers are dispersed in the electrolytes during their preparation. The addition of nano-fillers enhances conductivity and mechanical properties of the electrolytes. Such polymer electrolytes wherein nano-fillers are incorporated are known as *"Polymer Nanocomposites"* wherein, there exists an interaction between the dispersed nano particles and polymer matrices. Usually, these nano sized filler particles lead to a considerable improvement in the polymer composite's properties than that observed for the micro sized filler particle based polymer composite. However, at times, the high amount of filler addition also leads to the deterioration of the properties of these electrolytes [12-14]. Hence, in the preparation of the polymer nano-composite the amount of this nano-filler should be decided gently in order to obtain the best properties of these electrolytes. Apart from the above, another technique called *"Irradiation"* is also adapted to improve the electrolytic properties. In this method, the electrolytes are exposed to certain suitable radiations such as electron beam, heavy ions, gamma rays, etc., which in turn affect and improve the conductivity as well as other properties of the electrolytes.

Considering all these factors and conditions, the selection and preparation of the present polymeric systems, has been done carefully in order to obtain the best considerable conductivity and other electrolytic properties for application purpose [15].

The application of solid polymer electrolytes to solid state batteries has become one of the favourite areas of research nowadays [16]. These batteries are thus, the energy sources for such devices [17]. Solid state battery is basically an assembly which includes anode, electrolyte and cathode, all in solid form and can be used in certain biomedical and electronic devices wherein enough memory backup is required. The selection of anode, cathode and the electrolyte in the battery fabrication should be done gently as the assembly of these components ultimately decides electrochemical performance and on the basis of this performance, the suitability of the thus, prepared battery for the application purpose can be determined. The anodes of these batteries are usually chosen as the pure metals whereas; the cathodes are formed using suitable techniques such as co-precipitation method, solid state combustion method and sol gel method etc. Out of all these techniques, the solid state reaction is quite preferable for the cathode preparation. In solid state reaction technique, the solid reactants are used as the starting materials. When these materials are mixed together, the mixture of the reactants (solids) yields the polycrystalline solid compound. However, these solid crystalline compounds are unable to get formed at room or low temperatures over normal time scales. The reaction amongst the solids occurs when the reactants are heated at very high temperatures of nearly 1000 °C to 1500 °C [18-22].

Objectives of the present work:

The major objectives of the present work include:

- *Preparation of PVA-PEO blend polymer electrolytes with nano-filler having different plasticizers and salts.*
- *Investigation of the electrochemical properties of the prepared nano-composite polymer electrolytes and study of different parameters of an electrochemical battery using the suitable cathode.*

Brief discussion about the present research work:

In the present work, polyvinyl alcohol is selected as a host polymer. This is a semicrystalline and one of the most commonly used polymers in the polymer electrolyte preparation. Moreover, its advantageous properties such as excellent film forming, adhesive and emulsifying properties [23], interesting physical properties arising due to presence of -OH groups and hydrogen bond formation [24], non-toxic nature, good water solubility, good film forming capacity, possible coupling of charge transport with the motion of its hydroxyl group, thermal stability over large temperature range of 173-473 K [6, 25], excellent chemical resistance, thermal and mechanical properties, ease of preparation of electrolytes using it, high hydrophilic properties, relatively low cost [26], good film forming ability, nontoxic nature [27], high dielectric strength, dopant-dependent electrical properties, good charge storage capacity [28], etc., led to the curiosity and interest in selecting PVA as the host polymer in the preparation of present electrolyte systems. However, in addition to the advantageous properties, PVA also possesses certain unfavourable properties which may degrade the overall electrolytic properties. Usually, host polymers used in the preparation of polymer electrolytes should possess certain advantageous properties such as flexible polymer chains, low melting points, low glass transition temperatures, etc., which can enhance the electrolytic properties. However, it is totally reverse in the present case wherein, the host polymer PVA is a highly crystalline and rigid polymer with high melting point (219 °C) [23, 27, 29, 30] which makes the PVA matrix highly viscous which is not a viable condition for the electrolytic properties. Hence, PVA may be blended with another polymer like PEO to obtain better and beneficial properties. Hence, in the present polymer blend system, polyethylene oxide (PEO) is chosen for blending with PVA for preparation of electrolytes. PEO is basically a semicrystalline polymer having linear chained molecular structure [31, 32] and possesses flexible chained single helical structure which allows high and fast mobility of ions through the polymer electrolytes [33-35]. Salvation of inorganic salts is high resulting in higher ionic conductivities. Electrochemical stability and its structure supporting easy ion migration make PEO attractive as a host polymer [3, 36]. Owing to all such properties, PEO deserves a good polymer pair for blending with PVA.

PVA-PEO blends plasticised with PEG and/or EC and dispersed with nano-particles are prepared by solvent cast technique and their electrical, dielectric, relaxation and various other characterisation properties are analysed in the present research work. Two salts i.e. silver nitrate ($AgNO_3$) and lithium trifluoromethanesulfonate ($LiCF_3SO_3$) are selected for dissolving in these blends. The plasticizers polyethylene glycol (PEG) and ethylene carbonate (EC) and the nano filler aluminium oxide (Al_2O_3), are incorporated.

Finally, the solid state battery has been fabricated using the structure *Anode/Polymer Electrolyte/Cathode* to measure the charge, discharge and other electrolytic parameters. Suitable cathodes for the present electrochemical studies are prepared using the solid state reaction technique. Majorly silver and lithium salt batteries are prepared and tested in the present study.

For the fabrication of silver battery, silver oxide (Ag_2O) has been selected as cathode and pure silver metal is taken as anode. Ag_2O with decomposition temperature of 420 °C (700 K) is thermally quite stable [37-39]. These silver oxide electrodes are highly active [40].

The lithium battery is designed using the spinel lithium manganese oxide, also known as lithium manganate or lithium-ion-manganese ($LiMn_2O_4$) as cathode and pure lithium metal as anode. Spinel $LiMn_2O_4$ is preferred over other cathodes as it is abundant resource, non-toxin, non-polluting, safe, cheap, easy to prepare, possesses high energy density and 3-D framework which improve battery performance. $LiMn_2O_4$ is having cubic spinel type structure Fd3m space group at room temperature and whose formula resembles the standard formula of spinel i.e. AB_2O_4 where, 'A' is monovalent Li metal and 'B' is 'Mn'. The oxidation states of 'Mn' usually range from +2 to +7; however, +2 is its most stable oxidation state. In the crystal structure of spinel $LiMn_2O_4$, the oxygen ions are arranged in 32e sites, lithium ion occupies tetrahedral 8a sites and the octahedral sites are occupied by Mn^{+3} and Mn^{+4} ions. In such a cubic phase, usually at 4 V, the lithium gets extracted from and inserted into the tetrahedral 8a sites and this process is associated with the $Mn^{3+} \leftrightarrow Mn^{+4}$ oxidation-reduction process [41-47].

The present research work done is described in the 7 major chapters of the thesis. The basic contents covered by each of these chapters are discussed chapter-wise as follows:

Chapter-1 of the thesis is *"Introduction"*. The chapter begins with a brief discussion on electrolytes and their types.

Two major types of electrolytes which include solid and liquid electrolytes are introduced here. Out of these two types of electrolytes, the solid electrolytes are mainly focussed. These solid electrolytes are subdivided into glass electrolytes, ceramic electrolytes, polymer electrolytes, etc.

In the later part of this chapter different types of polymer electrolytes such as polyelectrolyte, gel polymer electrolyte, solid polymer electrolytes, etc., are discussed.

After an insightful classification of electrolytes and their types, the general characteristics of the constituents such as host polymers, salt for complexation, plasticizer and nano-fillers that are used in the preparation of the solid polymer electrolytes are briefly introduced.

The concluding part of this chapter describes a few devices such as electrochemical sensors, electrochromic display devices, conventional cells, fuel cells, memory devices, super capacitors and solid state batteries, etc., wherein these polymer electrolytes, especially solid polymer electrolytes are applied.

Chapter-2 is *"Theoretical details"*, mainly describes general theories, theoretical models and formalisms.

These theories and models throw light on the ion conduction mechanism in the polymer electrolytes.

The Complex Impedance Data Analysis, Modulus Formalism and Dielectric formalism which provide an insight on conductivity and ion transport mechanism, are discussed.

These formalisms also explain the dielectric relaxation phenomena that usually occur in the polymeric electrolytes.

Chapter-3 is *"Experimental"*, discusses about the materials and techniques used in the present polymeric electrolyte sample preparation and the characterization of these prepared specimens.

This chapter also describes the preparation of the silver and lithium cathodes which are employed in the fabrication of the battery.

Here, Ag_2O and spinel $LiMn_2O_4$ cathodes are prepared by *"Solid State Reaction Method"*.

Different experimental techniques used in the present thesis are described which include Complex Impedance Spectroscopy (CIS), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FT-IR), Transport Number Measurement and Battery Parameters.

Chapter-4 is *"Characterization Studies"*. In this chapter, the results of characterization studies viz., SEM, XRD, FT-IR, DSC and Transport number measurements of all the prepared solid polymer electrolytes have been discussed.

Chapter-5 is *"Conductivity, Modulus & Dielectric Analysis"* which mainly discusses conductivity, electric modulus and dielectric properties of the solid polymer electrolytes.

The dependency of conductivity on temperature, frequency and composition along with the ion-conduction mechanism are explained in detail. This study is carried out by investigating the Complex Impedance plots and dc/ac Conductivity Analysis using complex impedance analysis.

The later part of this chapter includes the analysis of frequency dependent electric modulus, relaxation time and scaling of modulus which throws light on the relaxation dynamics of the present solid polymer electrolytes.

The discussion is finally followed by the description of the behaviour of dielectric constant and dielectric loss factors with frequency.

Chapter-6 is *"Electrochemical Studies"*. This chapter deals with the electrochemical testing of the silver and lithium batteries prepared for the present work by carrying out charging-discharging studies, etc.

Chapter-7 is *"Conclusion/Summary"* The final chapter of the present thesis provides a summary of the entire work and the conclusion of the thesis. The list of publications is followed by Chapter-7.

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