EXPERIMENTAL STUDIES ON ION CONDUCTING POLYMER ELECTROLYTES

Synopsis

of

Ph.D. Thesis

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PREFACE

In the recent few years, a special attention has been provided to develop a large number of fast ion conducting materials, whose conductivity is of the order of $10^5-10^1$ S cm$^{-1}$ at ambient temperature, almost comparable to that of liquid electrolytes. These materials are called as Superionic Solids or Solid Electrolytes or Fast Ion Conductors. Depending on the microstructure, composition, phase and its physical properties, the superionic solids are broadly classified into different classes such as crystalline/polycrystalline, amorphous/glassy electrolytes, composite electrolytes and polymer electrolytes.

Recently, the polymer electrolytes have attracted the great attention for the fabrication of various electrochemical devices, because of their unique properties like high ionic conductivity, flexibility, good mechanical stability, thin film casting etc. Since, solid polymer electrolytes suffer from lower conductivity due to more restricted motion of the polymer molecules, it effects the efficiency of the device performance. Due to this reason, much attention has been turned to gel or plasticized polymer electrolytes whose conductivity is approachable to that of the liquid electrolytes. Again these materials suffer from poor mechanical stability and presence of volatile solvent. To overcome such problems, various physical and chemical modification techniques have been adopted in the past decades. The polymer blending is one of them. Basically, the polymer blend is a mixture of two or more polymers, one that absorbs the electrolyte active species while another remains as an un-dissolved and inert second phase providing toughness to the polymer electrolyte films.

Nowadays, one another class of materials are used for the synthesis of polymer gel electrolytes, namely ionic liquid (IL) based polymer gel electrolytes. The ionic liquids are made up of larger organic cations and inorganic or organic anions of various sizes. The presence of self dissociated cations and anions, leads to the high ionic conductivity in ILs. These materials have various advantageous properties like negligible vapour pressure, inflammability, high electrochemical window, wider thermal and chemical stability, wider liquidous phase and recyclability, which makes it a potential candidate as an electrolyte material for the fabrication of different types of electrochemical devices.

In past few decades, large number of lithium ion conducting polymer electrolytes was used for the fabrication of electrochemical devices, especially in rechargeable battery. At the same time, it is well known fact that the lithium based devices have some major drawbacks such as quite expensive, sensitive with humidity, explosive in nature and other related problems. In order to overcome these drawbacks, different salts based on sodium, magnesium and
zinc ion conducting polymer electrolyte provides a better substitute for lithium ion due to its non-toxicity, cheaper than lithium, natural abundance, environmental friendly nature, high electrochemical reduction potential, comparable ionic radii, high specific energy, more safer than lithium and can be handled safely in oxygen & humid atmospheres.

Worldwide efforts are continued to synthesize different types of polymer electrolytes, but still there is a need to optimize its various parameters such as electrical conductivity, low internal resistance, wider potential window etc., for their use in different electrochemical devices like batteries, supercapacitors, fuel cells as a commercial products.

The experimental work reported in the present thesis is devoted towards the studies on sodium ion based polymer blend electrolytes and the ionic liquid based polymer gel electrolytes containing magnesium salts, as an alternative to lithium ion based polymer electrolyte.

**OBJECTIVES OF THE PRESENT STUDIES**
The main objectives of the present studies are described as follows:

1. To synthesize sodium ion based polymer blend electrolytes and ionic liquid based polymer gel electrolytes with magnesium salts using standard solution cast techniques.
2. To optimize the synthesized samples of polymer blend/gel electrolytes using impedance spectroscopy techniques.
3. To characterize the optimized composition of polymer blend/gel electrolytes using different electrical and electrochemical methods such as, room temperature conductivity measurements, temperature dependence conductivity measurements, dielectric studies, modulus studies, conductance spectra, polarization techniques for measurement of ionic transport number and potential window measurements.
4. To perform the structural characterization of the optimized composition of polymer blend and gel electrolytes using different microscopic techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques.
5. To perform the thermal characterization of the optimized composition of polymer blends and gel electrolytes using Differential Scanning Calorimetry (DSC) techniques.

**SUMMARY OF THE THESIS**
In order to accomplish the stated objectives, different experimental studies has been carried out and discussed in the thesis. The chapter wise summary of the thesis is summarized below:
Chapter-1: Introduction and Literature Review

Materials exhibit several properties, amongst which electrical conduction is the most prominent one, where the charge particles are transported under the influence of an applied electric field. The well known and established electrical conductors are metals & semiconductors, where the mobility of an electrons & holes under the influence of an applied electrical field is mainly responsible for the electrical conductivity. After the discovery of transistor in 1950’s, the new branch of science and technology was emerged named as “Solid State Electronics”, where the mobility of an electron is the major charge carriers. Later on sometimes during 1970 in analogy to the “Solid State Electronics”, new and emerging field of materials science and technology was evolved namely “Solid State Ionics” by Prof. T. Takahashi of Japan, wherein solids having exceptionally large ionic conductivity at room temperatures comparable to that of liquid electrolytes are discovered, having conductivity of the order of $10^{-5}$-$10^{-1}$ S cm$^{-1}$. This class of materials, where majority charge carriers are ions, were called as “Solid State Ionics” or “Superionic Solids” [Chandra (1981)].

The basic characteristic properties of superionic solids are; (i) Main charge carriers are ions (ii) Bonding in the crystal is generally ionic (iii) Low activation energy ($< 0.3$ eV) (iv) High ionic conductivity ($10^{-1}$ - $10^{-5}$ S cm$^{-1}$) (v) High ionic transference number close to unity i.e ($t_{\text{ion}} \sim 1$) and (vi) Electronic transference number is small i.e., ($t_{\text{e}} < 10^{-4}$).

On the basis of composition, phase and microstructure, superionic solids may be divided into different classes such as crystalline/polycrystalline, amorphous/glassy electrolytes, composite electrolytes and polymer electrolytes. [Chandra (1981), Bruce et al. (2011)]

In 1973, Fenton et al. developed the first ion conducting polymer electrolyte based on polyethylene oxide (PEO) which was dissolved with alkali metal salts [Fenton et al. (1973)]. Thereafter its application aspect was explored and was demonstrated for the first time by Armand et al. in 1979 [Armand et al. (1979)], where the solid polymer electrolyte was used as a separator in the Li-ion based solid state battery. After the discovery of Li-battery as a commercial product, it inspired the research community from academia as well as industrial sector to explore this new and emerging field of Solid State Ionics. Thereafter large number of polymer electrolyte materials was discovered and studied extensively using different types of mobile ions namely H$^+$, Li$^+$, Na$^+$, Ag$^+$ and Mg$^{2+}$ etc. This class of polymeric material shows various attractive properties like easy thin film formability, good processibility, light weight, flexibility, cost effective, elasticity, plasticity and transparency etc. These characteristic properties of polymeric materials provides the favourable condition for the fabrication of
various electrochemical devices such as solid state secondary battery, solar cell, supercapacitor, electrochemical display devices and sensors etc., [Gray (1991), Bruce et al. (2011)]. Since then a variety of polymer hosts like poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(vinlidene fluoride) (PVdF), poly(vinlidene fluoride-co-hexafluoropropene) (PVdF-HFP) and poly(acrylo nitrile) (PAN) was investigated in the past decades. For improving the mechanical, electrical and electrochemical properties of the polymer electrolytes, various chemical and physical approaches have been adopted by different researchers; such as, use of branched or cross linked polymers networks, addition of another polymer component to form blend, copolymers, comb branch polymer addition of micro or nano ceramic filler such as Al$_2$O$_3$, SiO$_2$, TiO$_2$ and MgO etc., in the polymer electrolyte to get composite polymer electrolytes etc.

Recently, one another methods are adopted for the synthesis of polymer electrolytes namely, ionic liquid (IL) based polymer electrolytes. Generally, ionic liquids are salts consisting of bulky, asymmetric organic cations and inorganic anions. A unique feature of ionic liquid such as high ionic conductivity ($\sim 10^{-3}$ to $10^{-2}$ S cm$^{-1}$), large range of liquid phase ($\sim$100 - 400 °C), wider electrochemical window ($\sim$ 4 - 6 V), non-volatility, non-flammability, non-toxicity and excellent environmental friendly nature make these materials ideal candidates as a non-volatile solvent in polymer gel electrolyte systems [Ohno (2005)]. Hence it provides a superior alternative as electrolyte materials for the fabrication of different electrochemical devices such as batteries, supercapacitors, solar cell, fuel cells etc.

Most of the energy storage and conversion devices reported in the literature are based on lithium ion, especially rechargeable lithium batteries. At the same time, it is well known fact that the lithium based devices have some major drawbacks such as quite expensive, high sensitive with humidity, safety limitations like explosive in nature and other related problems [Tripathi et al. (2012)]. In order to overcome these drawbacks sodium, magnesium and zinc ion based polymer electrolytes proves to be a better substitute for lithium ion [Thakur and Hashmi (2010), Kumar and Hashmi (2010), Li et al. (2013)].

Worldwide efforts are continued to synthesize different types of polymer electrolytes, but still there is a need to optimize its various parameters such as electrical conductivity, low internal resistance and wider potential window etc., for their use in different electrochemical devices like batteries, supercapacitors, fuel cells as a commercial products.

In view of the abovesaid reasons, sodium ion based polymer blend electrolytes and ionic liquid based polymer gel electrolyte having magnesium salts has been chosen for detailed experimental studies in the present thesis.
Chapter-2: Experimental Details

Materials Preparation

Sodium ion based polymer blend electrolytes and ionic liquid based polymer gel electrolytes using magnesium salts has been prepared by using "standard solution cast techniques".

Materials optimization and characterization

Impedance spectroscopy technique was used for the optimization of polymer blend/gel electrolytes. For the microscopic characterization various electrical, electrochemical and physical characterization techniques were used such as impedance spectroscopy, transference number measurement, potential window studies, X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC) studies.

Chapter-3: Experimental studies on polymer blend electrolytes

PVdF(HFP)-PMMA-NaX (X=I\(^-\), SCN\(^-\))

In this chapter, sodium ion based polymer blend electrolytes comprising of poly(vinylidenefluoride-co-hexafluoropropylene)-poly(methyl-methacrylate)-Sodium (iodide / thiocyanate) [PVdF(HFP)-PMMA-NaX (X=I\(^-\), SCN\(^-\))] has been synthesized using standard "solution cast techniques" and is being optimized by impedance spectroscopic methods. It was found that the optimized composition of polymer blend electrolyte shows room temperature ionic conductivity of the order of ~ 10\(^{-2}\) S cm\(^{-1}\). The optimized compositions of polymer blend electrolytes were further used for its electrical, electrochemical, structural and thermal characterization.

Temperature dependence behaviour of the optimized composition for both the polymer blend electrolytes has been studied and it was found that they shows Arrhenius behaviour.

In order to reveal the information about the nature and types of molecular motion as well as its ionic transport phenomena, dielectric relaxation behaviour of the polymer blend electrolytes has been studied and was discussed in the thesis in detail.

To understand the bulk properties of the polymer blend electrolytes, an electrical modulus study has been performed and was included in the report.

Electrochemical potential window of the polymer blend electrolyte has been measured using linear sweep cyclic voltammetry and was found to be about ~ 4 V, which is acceptable from device fabrication point of view.
Ionic transport number for both the polymer blend electrolyte was measured and it was found that it shows its predominant ionic nature.

X-ray diffraction studies were performed for both the polymer blend electrolytes and it was observed that both salt gets completely dissolved with the PVdF(HFP)-PMMA polymer blend at the molecular level and gives a clear indication of complexation of the salt in the polymer blend system.

To understand the surface texture and morphology of the polymer blend electrolytes, optical and scanning electron microscopy (SEM) studies were performed. The image shows the spherulitic texture and amorphous nature of the polymer blend electrolytes. It was also observed that the liquid electrolyte is entrapped in the polymer matrix and is responsible for the enhancement in the ionic conductivity of the blend system.

In order to understand the nature of bonding along with the interactions of different functional groups in the polymer blend electrolyte, FTIR spectroscopy studies were performed. Different vibration peaks corresponding to the bending, wagging, stretching, scissoring mode has been assigned and is being tabulated in the thesis. It was inferred from the studies that there exists a strong molecular interaction between ions. Shifting of frequency peak from the pure polymer and salt spectra, shows the proper interaction and complete complexation of salts in the polymer blend electrolytes.

In order to explore the thermal properties of polymer blend electrolytes for the identification of its thermal stability, glass transition temperature, melting temperature, crystallinity as well as its phase determination, DSC studies has been performed and is being reported in the thesis.

**Chapter-4: Experimental studies on ionic liquid based PVdF(HFP)-(EDiMIM)(BF₄)(PC)-Mg(ClO₄)₂ polymer gel electrolytes**

In this chapter, ionic liquid based polymer gel electrolytes using magnesium salts comprising of poly(vinylidenefluoride-co-hexa-fluoropropylene) - 1-Ethyl-2,3-dimethylimidazolium tetrafluoroborate - propylene carbonate - magnesium perchlorate [PVdF(HFP)-(EDiMIM)(BF₄) - (PC) - Mg(ClO₄)₂] has been synthesized and characterized using different experimental techniques, as summarized in the following section.

The electrical conductivity of ionic liquid based polymer gel electrolytes were measured by impedance spectroscopy techniques. The optimized composition of electrolyte system shows maximum room temperature ionic conductivity of the order of ~ 10⁻³ S cm⁻¹.

Temperature dependence behaviour of the optimized composition of ionic liquid based polymer gel electrolytes has been studied and was found that it shows Vogel-Tammen-
Fulcher (VTF) behaviour. From the plot activation energy of the optimized composition of polymer gel electrolyte were also calculated and was reported in the thesis.

In order to understand the information regarding the ion polarization, molecular motion and their dielectric relaxation behaviour, dielectric spectroscopy technique has been used. Further its electrode-electrolyte interfacial behaviour and its bulk properties were also explained with the help of modulus spectra. The detail description of dielectric (constant & loss), modulus (real & imaginary), and conductance spectra has been covered in the thesis.

Electrochemical potential window of the optimized composition of gel electrolyte has been measured using linear sweep cyclic voltammetry and was found in the range of ~ 6 V. This value is quite appealing from device fabrication point of view.

Ionic transference numbers were also calculated for the optimized electrolyte system and the result shows its predominant ionic nature.

To reveal the structure and morphology of polymer, ionic liquid, polymer-ionic liquid blend and polymer gel electrolyte, X-ray diffraction, FTIR spectroscopy and scanning electron microscopy techniques were used successfully.

X-ray diffraction pattern clearly shows the semi-crystalline nature of pure PVdF(HFP) film and after blending with the ionic liquid and liquid electrolytes solution, some peaks of host polymer PVdF(HFP) was disappeared. This clearly indicates that the ionic liquid or liquid electrolytes is most likely blended with the PVdF(HFP) at a molecular level.

Using FTIR spectra, different vibration peaks corresponding to the symmetric, bending, wagging, stretching and scissoring mode has been assigned to the polymeric systems. The Shifting of peaks in FTIR spectra of polymer gel electrolytes (with respect to pure polymer peaks and polymer-ionic liquid blend peaks) suggest the proper interaction between the constituents of the polymer gel electrolytes and its formation at a microscopic level. Details of the peak assignment were tabulated in the thesis.

Scanning electron microscopy (SEM) image of polymer-ionic liquid blend shows the interconnected and almost uniformly distributed pore structure. It also shows the homogeneously distributed pore morphology for optimized gel polymer electrolyte system, which is capable to retain the ionic liquid and liquid electrolyte solutions in them. These pore structures are capable for better ion transport through the polymer matrix.

In order to ascertain the thermal stability of the ionic liquid based polymer gel electrolytes, differential scanning calorimetric (DSC) studies were performed. It was observed that the optimized composition of polymer gel electrolytes shows its thermal stability in a wide
temperature region, which is acceptable from device fabrication point of view. Detail description was reported in the thesis.

**Chapter-5: Experimental studies on ionic liquid based PVdF(HFP)-(BDiMIM)(Cl)-PC-Mg(ClO$_4$)$_2$ polymer gel electrolytes**

In this chapter, ionic liquid based polymer gel electrolytes using magnesium salts comprising of poly(vinylidenefluoride-co-hexa-fluoropropylene) - 1-Butyl-2,3-dimethylimidazolium chloride - propylene carbonate - magnesium perchlorate [PVdF(HFP)-(BDiMIM)(Cl)-(PC)-Mg(ClO$_4$)$_2$] has been synthesized and characterized using different experimental techniques, as summarized in the following section.

The optimized composition of polymer gel electrolyte shows the room temperature ionic conductivity of $\sim 10^{-2}$ S cm$^{-1}$.

Temperature dependence behaviour of the optimized composition of ionic liquid based polymer gel electrolytes has been studied and it was found that it shows Vogel-Tamman-Fulcher (VTF) behaviour. From the plot, activation energy was also calculated and reported in the thesis.

The dielectric (constant & loss), modulus (real & imaginary) and conductance spectra studies has been performed for the optimized composition of ionic liquid based polymer gel electrolytes in order to understand the statistical thermal motion of polar groups and its relaxation behaviour, the nature and types of molecular motion as well. Detail description has been reported in the thesis.

Electrochemical potential window of the optimized composition of polymer gel electrolyte was measured using linear sweep cyclic voltammetry and was found to be about $\sim 4.0$ V, which determines the safety potential limit for electrochemical devices.

Ionic transport number was also measured and was found to be closer to that of liquid electrolyte, showing its predominant ionic behaviour.

To reveal the structure and morphology of polymer, ionic liquid, polymer-ionic liquid blend and polymer gel electrolyte; X-ray diffraction, scanning electron microscopy and FTIR spectroscopy techniques was used.

X-ray diffraction studies shows that the ionic liquid and liquid electrolytes solution gets completely dissolved in the host polymer at the molecular level. It also confirms the composite nature of the polymer gel electrolytes.

SEM image of the optimized composition of polymer gel electrolyte clearly shows that the uniformly dispersed pore dimensions are capable enough to retain liquid electrolyte solu-
tion in them and provides better connectivity through the polymeric chain in order to achieve high ionic conductivity.

FTIR spectroscopic studies were conducted to investigate the ionic liquid and liquid electrolytes interactions with the host polymer, polymer/ionic liquid blend, polymer gel electrolytes system at a microscopic level and possible conformational changes in the host polymer due to ionic liquid and liquid electrolytes entrapment. Details of the peak assignment and the formation of complete complexation in the polymer gel electrolytes were presented in the thesis report.

The thermal stability of ionic liquid-polymer blend and polymer gel electrolyte was measured by differential scanning calorimetry (DSC) techniques. It was observed that the ionic liquid based polymer gel electrolyte films are remain stable in the gel phase over a substantially wider temperature range showing its possibility as a potential candidate for its application in different electrochemical devices.

Chapter-6: Experimental studies on ionic liquid based PVdF(HFP) (EMIM)(Br)-PC-Mg(ClO₄)₂ polymer gel electrolytes

In this chapter, ionic liquid based polymer gel electrolytes using magnesium salts comprising of poly(vinylidenefluoride-co-hexa-fluoropropylene) - 1-Ethyl-3-methylimidazolium bromide - propylene carbonate - magnesium perchlorate PVdF(HFP)-(EMIM)(Br)-(PC)-Mg(ClO₄)₂ has been synthesized and characterized using different experimental techniques, as summarized in the following section.

The maximum conductivity for the optimized composition of polymer gel electrolyte was found in the range of ~ 10⁻² S cm⁻¹ at room temperature.

Temperature dependence behaviour of the optimized composition shows Vogel-Tammen-Fulcher (VTF) pattern. From the plot, activation energy was also calculated and reported in the thesis.

The dielectric (constant & loss), modulus (real & imaginary) and conductance spectra studies has been performed and was presented in the thesis for the polymer gel electrolytes in order to understand its polarization behaviour like ionic, electronic, dipolar, interfacial polarization, statistical thermal motion of polar groups and its relaxation behaviour.

Electrochemical potential window of the optimized composition of polymer gel electrolyte was also measured using linear sweep cyclic voltammetry and was found to be ~ 4.0 V.

The measurement of ionic transport number for the optimized composition of polymer gel electrolytes shows its predominant ionic nature.
X-ray diffraction (XRD), scanning electron microscopy (SEM) and FTIR spectroscopy techniques was used to understand the structure and morphology of polymeric system under present studies and was discussed in detail in the thesis.

The thermal studies have been carried out by DSC techniques to examine the temperature stability range in which the polymer gel electrolytes can be used safely in fabrication of different electrochemical devices. DSC plot and its detail description were reported in the thesis.

### Chapter-7: Conclusions and future scope of work

Combining all the above studies, it may be concluded that:

1. Sodium ion based polymer blend electrolytes and ionic liquid based polymer gel electrolytes using magnesium salts has been synthesized successfully using standard “solution cast techniques”. It was observed that the electrical conductivity of the polymeric system under present investigation was in the range of $10^{-2}$ to $10^{-3}$ S cm$^{-1}$ and is approachable to that of the liquid electrolytes.

2. The ionic transport number for all the polymer electrolyte system in the present report shows its predominant ionic character.

3. Thermal stability of the polymer blend/gel electrolyte system in the present work were performed using DSC techniques and was found that all the polymeric system is thermally stable in a wide temperature range varying from lower to higher temperature.

4. The electrochemical stability of the all the polymer blend/gel electrolytes in the present studies is found to be in the range of ~ 4.0 - 6.0 V.

5. X-ray diffraction, optical microscopy, scanning electron microscopy and FTIR spectroscopy techniques has been used successfully for the identification of complex formation, surface morphology, pore structure, molecular interaction and chain structure for all the studied polymeric systems.

6. Studies on dielectric constant and loss exhibit the space charge effect, which is contributed by the accumulation of charge carriers near the electrode-electrolyte interfaces. It also reveals the polarization and relaxation behaviour of the polymeric systems. The modulus analysis shows bulk effect and relaxation mechanism of the polymeric system.

In view of the above said results achieved in the present thesis, it can be inferred that all the optimized composition of polymer blend/gel electrolytes using sodium and magnesium salts can be used as a potential candidate as an electrolyte materials in different electrochemical devices as an alternative to lithium ions.
Future scope of work

Different types of polymer electrolyte system having good electrical, mechanical, thermal and electrochemical stability has to be explored as an alternative to lithium ions, since it is quite expensive and having safety limitations such as its explosive nature at ambient conditions, when used in different electrochemical energy storage and conversion devices like secondary rechargeable batteries, supercapacitors, solar cells, fuel cells etc.

Ionic liquid based polymeric system has to be further investigated in order to improve its electrochemical potential window, which can further improve the device performance.

REFERENCES