# PREPARATION, CHARACTERIZATION AND BATTERY APPLICATIONS OF PROTON CONDUCTING POLYMER ELECTROLYTES

Synopsis submitted in fulfillment of the requirements for the degree of

# **DOCTOR OF PHILOSOPHY**

By

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February, 2013

## SYNOPSIS

Ion conducting solids are the materials which exhibit high ionic conductivity, typically in the range of ~  $10^{-5}$  -  $10^{-1}$  S cm<sup>-1</sup>, and negligible electronic conductivity [1]. These solids are also known as solid electrolytes, or fast ion conductors. The development of solid electrolytes has been driven by their tremendous technological applications in the areas of energy storage, energy conversion and in the field of environment monitoring. These materials are used as electrolytes and electrode separators in various electrochemical devices like, fuel cells, batteries, super capacitors, sensors, etc. By virtue of being a solid, solid electrolytes possess numerous advantages over liquid electrolytes like, absence of liquid containment and leakage problem, ability to operate with highly reactive electrodes over a wide range of temperature, and the possibility of miniaturization [2].

The ion transport in solid electrolytes is governed by some structural and nonstructural properties like, crystal structure, lattice arrangement, mobile ion concentration, size of the mobile ions, ionic polarizability, ion-ion interaction, ion interaction with the supporting matrix, number and the accessibility of occupancy sites, ion conduction pathway etc [3]. On the basis of their microstructure and the physical properties, the solid electrolytes are classified into four major categories:

- 1. Framework crystalline solid electrolytes
- 2. Amorphous-glassy solid electrolytes
- 3. Composite solid electrolytes
- 4. Polymer electrolytes

Out of the above four categories, polymer electrolytes are one of the most widely studied solid electrolytes. The film formability with desirable mechanical, thermal and electrochemical stability makes polymer electrolytes more attractive than the conventional liquid electrolytes and the brittle crystalline/polycrystalline, composite, and glassy solid electrolytes. Innumerable amount of work has been done on polymer electrolytes in the last few years which are excellently covered in several reviews [4-12]. The polymer electrolytes are further classified as (a) Conventional dry solid polymer electrolytes, (b) Plasticized solid polymer electrolytes, (c) Rubbery electrolytes, (d) Polyelectrolytes, (e) Gel polymer electrolytes, and (f) Composite polymer electrolytes.

The *conventional dry solid polymer electrolytes* (SPE) are basically the polymer-salt complexes prepared by dissolving suitable ion donating salts/acids into high molecular

weight polymers which act as a host. Examples of such host polymers are polyethylene oxide (PEO), polypropylene oxide (PPO), polyvinyl pyrrolidone (PVP) etc. The ion transport in these polymer electrolytes is governed by local relaxation as well as segmental motion of the polymer chains which are more favored by high degree of amorphicity of the host polymers [13, 14]. But, many host polymers are partially crystalline in nature which is an unfavorable property for achieving high ionic conductivity. Plasticization is one of the most adopted approaches used to suppress the crystallinity of polymer electrolytes. In the plasticization, a substantial amount of a liquid plasticizer, namely, low molecular weight poly(ethylene glycol) (PEG) and/or aprotic organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), diethylene carbonate (DEC), dimethylsulfoxide (DMSO), etc is added to the dry SPE matrix. These polymer electrolytes fall in the category of plasticized solid polymer electrolytes. The addition of the liquid phases in the SPEs leads to the decrease in the crystallinity and the glass transition temperature of the host polymer and promote the segmental motion of the polymer chains, which, in turn, results into the higher ionic conductivity of the plasticized polymer electrolytes at ambient conditions. The high dielectric constants of the organic plasticizers like EC and PC also help in dissociation of ion aggregates, i.e. create more free ions, which further results into the higher electrical conductivity of the plasticized polymer electrolytes [15, 16]. Rubbery *electrolytes* are "polymer-in-salt" electrolyte systems, which are prepared by addition of small amount of high molecular weight polymers into a relatively larger amount of salts. The low amount of polymer leads to the formation of rubbery material with low glass transition temperature [17]. Polyelectrolyte is another category of polymer electrolytes in which polymers possess ion generating groups attached to their main chain. The most important and well known product of this class is Nafion. The Nafion membranes produced by DuPont are currently in use in portable fuel cell applications [18]. These membranes exhibit high proton conductivity, good chemical stability and mechanical integrity. Another category of polymer electrolytes is "Gel polymer electrolytes (GPEs)". Gels, in general, are defined as the solids with continuous liquid phase enclosed into a continuous solid skeleton. In GPEs, liquid phases are normally the organic liquid electrolytes, which are obtained by dissolving ion donating salts into the organic solvents/ plasticizers, entrapped into the solid polymer network which provides dimensional stability to gel electrolytes [19]. It is observed that the larger amount of liquid electrolyte present in the polymer matrix gives rise to better ionic conductivity but diminishes the mechanical integrity of GPEs. Therefore, in order to improve the mechanical integrity, GPEs are dispersed with micro- and nano-sized ceramic fillers like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, BaTiO<sub>3</sub> etc. It is found that the dispersion of ceramic fillers not only improves mechanical strength but also improves the electrical conductivity of the GPE systems [20-24]. This category of polymer electrolytes is named as *Composite polymer electrolytes*. The dispersion of ceramic fillers has proved its worth in almost all the classes of polymer electrolytes which are often named as, composite dry SPEs, composite plasticized SPEs, composite polyelectrolyte, and composite GPEs. Polymer electrolytes support variety of ions, like Li<sup>+</sup>, H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Cu<sup>++</sup> etc, for transport. A large number of such polymer electrolytes have been developed in view of their various applications.

The proton (H<sup>+</sup>) conducting polymer electrolytes have their possible applications in the various electrochemical devices like, fuel cells, batteries, supercapacitors, sensors, etc [25-31], however, they have largely been studied for their applications focused towards the development of low and moderate temperature fuel cells. Proton batteries are one of the other possible applications where polymer electrolytes can be used. But this application has not yet received considerable attention. The scarce reports appearing in the literature on the proton batteries [26-29] indicate that these batteries may be considered as yet another potential alternative to the lithium ion batteries primarily because of small ionic radii of H<sup>+</sup> ions, like Li<sup>+</sup> ions, which makes them suitable for better intercalation into the layered structure of cathodes. The low cost of electrode and electrolyte materials used for proton batteries, and also no safety issues associated with them, are some of the important merits which support more research in this area.

The aim of the present work is directed towards preparation and characterization of proton  $(H^+)$  conducting polymer electrolyte membranes and their applications in proton batteries. The following polymer electrolyte systems have been prepared and studied in the present thesis:

- 1.  $PEO + NH_4PF_6$
- 2. PMMA/PVdF-HFP + NH<sub>4</sub>SCN
- 3. PMMA/PVdF-HFP/SiO<sub>2</sub> + NH<sub>4</sub>SCN
- 4. PVP/PVdF-HFP + BMImHSO<sub>4</sub>

The thesis is divided into eight chapters which are organized as under:

*Chapter 1* gives general introduction of various types of solid electrolytes. As the polymer electrolytes form the subject matter of the thesis, this chapter covers polymer based solid electrolytes in greater detail. It reviews different classes of polymer

electrolytes, and discusses various models/theories dealing with the ion conduction mechanism in various types of polymer electrolytes. A section of this chapter is also devoted to the current trends in proton conducting polymer electrolytes specific to various electrochemical applications.

*Chapter 2* describes the method of preparation of proton conducting polymer electrolyte membranes, and covers a comprehensive discussion of different experimental techniques used for the characterization in the present work. The characterization techniques include, Fourier transform infra-red (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Differential scanning calorimetry (DSC), ac impedance spectroscopy, dc polarization technique, and Cyclic voltammetry. The chapter also describes the fabrication of proton batteries.

**Chapter 3** discusses the characterization results of PEO +  $NH_4PF_6$  SPE system. The studies have been extended to PEO +  $NH_4PF_6$  system plasticized with EC, EC/PC, and polysorbate 80. The complexation between PEO and NH<sub>4</sub>PF<sub>6</sub> and the effect of plasticizers on PEO +  $NH_4PF_6$  complex has been studied by FTIR spectroscopy. The results of FTIR confirm the complexation between the polymer and the salt. The addition of plasticizers in the polymer-salt complex has resulted into the formation of new coordination bonds between the dissociated ammonium ions and the ether oxygen of PEO. The crystallinity of the host polymer in the SPE has decreased on the plasticization as observed by XRD studies. The surface texture of the electrolytes films has been examined by SEM. Formation of a new salt-rich crystalline phase at higher salt concentrations in the complex and also lowering of melting point on addition of plasticizers in the SPE have been obtained by DSC studies. The ionic conductivity of the electrolyte membranes has been measured using impedance spectroscopy. The highest room temperature conductivity of the unplasticized polymer electrolyte is found to be 2.5 x  $10^{-7}$  S cm<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>/EO = 0.037 which increases to  $1.52 \times 10^{-5} \text{ S cm}^{-1}$  and  $1.03 \times 10^{-5} \text{ S cm}^{-1}$  in the EC and EC/PC plasticized complexes respectively. The maximum ionic conductivity of the polysorbate 80 plasticized complex is found as ~  $10^{-5}$  S cm<sup>-1</sup>. The temperature dependence of ionic conductivity of the plasticized and unplasticized complexes shows an Arrhenius type of thermally activated process of conduction, typical of the semicrystalline polymer electrolytes. The ion transport mechanism in the polymer electrolytes has been investigated using dielectric measurements. The ionic transference number of the electrolyte, as measured by dc polarization method, has been found to be ~1, which shows that current is contributed mainly by ionic species in the prepared SPE. The proton conduction in the electrolyte has been confirmed by cyclic voltammetry and the impedance spectroscopy measurements. The electrochemical stability window (ESW) of the unplasticized and plasticized complexes has been found to be same  $\sim 4.6$  V.

Chapter 4 discusses the experimental results of a proton conducting GPE system comprising a liquid electrolyte (LE) solution of ammonium thiocynate (NH<sub>4</sub>SCN) in a mixture of ethylene carbonate (EC)/ propylene carbonate (PC) immobilized in the blend of poly(methyl methacrylate) (PMMA)/poly(vinylidinefluoride-hexafluoropropyline) (PVdF-HFP). The results have been compared with the gel electrolyte systems obtained by immobilizing the above liquid electrolyte in PMMA and PVdF-HFP separately. The effect of polymer blending on the structural, thermal, and electrical properties of the GPE has been investigated. The FTIR results show steric interaction between blend forming components PVdF-HFP and PMMA. FTIR results also indicate the conformational changes taking place in the blend GPE when added with the liquid electrolyte. The X-ray diffraction (XRD) patterns obtained for the blended and unblended gel electrolyte membranes confirm the substantial increase in the amorphicity of the blend GPE. SEM studies show the porous nature of the prepared blend GPE system. The DSC results show that participating polymers form an immiscible blend. The maximum ionic conductivity of the blend GPE at room temperature is found as  $1.9 \times 10^{-3} \text{ S cm}^{-1}$ . The temperature dependence of the ionic conductivity of the electrolyte system has been found consistent with the Vogel-Tammen-Fulcher (VTF) behavior. The proton conduction the GPE system has been confirmed by cyclic voltammetry and the impedance spectroscopy measurements. The ESW of the GPE membranes has been found to be  $\sim 3.2$  V.

**Chapter 5** reports the structural, thermal and electrical properties of a proton conducting nanocomposite GPE system,  $[35\{25PMMA + 75 PVdF-HFP) + x SiO_2\} + 65\{1 M NH_4SCN in EC/ PC\}]$ . The free standing films of the nanocomposite GPE have been prepared by solution cast technique. An ion-filler-polymer interaction in the GPE has been observed by FTIR. The XRD results show an increase in the amorphicity of the GPE on the dispersion of nano fillers. As observed by SEM studies, the dispersion of small amount of nano-sized SiO<sub>2</sub> leads to a more compact surface morphology of GPE films but higher filler concentrations leads to the segregation of the silica in the form of bigger particles from the polymer electrolyte network. The composition dependence of the ionic conductivity of the nanocomposite blend GPE has been found to show two maxima, which is typical of the composite polymer electrolyte systems. The highest room temperature conductivity of the composite GPE is found as  $4.3 \times 10^{-3} \text{ S cm}^{-1}$ . The temperature dependence of conductivity of nanocomposite blend GPE follows VTF behavior which is corroborated to the nature of highly amorphous and electrolyte-rich gel membrane. The ion dominant charge transport in the electrolyte system has been confirmed by dc polarization method. The proton conduction in the composite GPE has been confirmed by cyclic voltammetry and the impedance spectroscopy measurements. The ESW of the nanocomposite blend GPE membranes has been found to be ~ 3.2 V.

Chapter 6 elaborates the experimental results of a proton conducting blend GPE system consisting of an ionic liquid, (PCIL) 1-butyl-3-methylimidazolium hydrogen sulphate (BMImHSO<sub>4</sub>), immobilized in a blend of PVdF-HFP/ PVP. The membranes of the electrolyte system were prepared by solution cast technique using dimethylformamide (DMF) as a common solvent. The structural studies of the membranes have been carried out by FTIR, XRD, and SEM. FTIR results suggest the formation of hydrogen bonds between the certain polar groups of the participating polymers. SEM images of the surface of the membranes show porous structure of the GPE. The XRD results show a highly amorphous nature of the GPE system. The DSC analysis shows that immobilization of IL in the polymer blend matrix results into the reduction of melting of the matrix. The highest conductivity of the GPE has been obtained as  $3.9 \times 10^{-3}$  S cm<sup>-1</sup> at ambient temperature for the membrane with 70 wt% IL. The ion conduction in the prepared blend GPE has been explained on the basis of a "two phase model" as described by Wang and Tang [32]. The temperature dependence of the ionic conductivity of the prepared GPE has been found to follow Arrhenius-type thermally activated process for the membranes with 50 wt% IL; however, shows VTF behavior for the membranes with higher concentrations of IL. The proton conduction in blend GPE has been established by cyclic voltammetry and the impedance spectroscopy measurements. As obtained by cyclic voltammogram, the electrolyte membranes show electrochemical stability in the potential range, -2.1 V to +1.86 V which gives the electrochemical stability window of ~ 3.96 V.

**Chapter 7** discusses the characterization results of proton batteries fabricated using the membranes of the highest conducting compositions of the electrolyte systems discussed in chapters 3-6. A mixture of zinc dust (Zn) and zinc sulphate (ZnSO<sub>4</sub>.7H<sub>2</sub>O) was used as an anode material while a mixture of lead oxide (PbO<sub>2</sub>), vanadium pentaoxide (V<sub>2</sub>O<sub>5</sub>), graphite, and polymer electrolyte (PE) was used as a cathode material. The battery was

fabricated by sandwiching the polymer electrolyte films between thin pellets (thickness ~0.70 mm) of the anode and cathode materials. The fabricated batteries have been characterized by measuring the open circuit voltage (OCV), discharge characteristics, and charge-discharge measurement. All the cells have been found to remain stable in the open circuit conditions after an initial drop in OCV, which occurs understandably due to the electrode polarization effect. The cells have been found to be suitable for low current drain applications; as the quick discharge has been observed at higher current drains in all the cells. Various cell performance parameters have been calculated from the plateau region of the discharge curves, which shows that the cell containing IL based GPE membrane, performs better than the other cells. The highest energy density obtained is ~35.2 Whkg<sup>-1</sup> for the cell having IL containing GPE membrane as electrolyte. The cells with GPE have also been subjected to charge-discharge test. The cells have been found to show rechargeability up to 3 cycles and thereafter, a sharp capacity fading is observed during next charge-discharge cycles.

Chapter 8 summarizes all the results reported in the thesis.

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## **PUBLICATIONS FROM THE THESIS WORK**

#### **Papers in International Journals**

- [1] Mishra K., Rai D. K., "Effect of plasticizers on ion transport properties of PEO + NH<sub>4</sub>PF<sub>6</sub> polymer electrolyte system - dielectric studies", Appl. Mech. Mater., vol. 110-116, pp. 278-284, 2012.
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- [5] **Mishra K.**, Hashmi S. A., Rai D. K., "*Performance studies on proton battery fabricated with a protic ionic liquid based gel polymer electrolyte*" (Communicated).
- [6] **Mishra K.**, Rai D. K., "Studies on a proton conducting polymer blend gel electrolyte system for electrochemical applications" (Communicated).

#### Papers in Conference proceedings

[1] Mishra K., Hashmi S. A., Rai D. K., "Structural and Ion Conduction Studies of PEO-NH<sub>4</sub>PF<sub>6</sub> Polymer electrolyte System Plasticized with Polysorbate 80", Electroactive polymers: Materials & Devices, Vol. IV, pp. 306-312, 2011.

#### **Presentations in International Conferences**

- [1] Mishra K., Hashmi S. A., Rai D. K., "Structural and ion conduction studies of PEO-NH<sub>4</sub>PF<sub>6</sub> polymer electrolyte system plasticized with Polysorbate 80", Fourth International conference on Electroactive polymers: Materials and Devices, November 21-26, 2010, Surajkund, India.
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### **Presentations in National Conferences**

- Mishra K., Hashmi S. A., Rai D. K., "Structural and ion transport studies of PEO + NH<sub>4</sub>PF<sub>6</sub> polymer electrolyte system", 8<sup>th</sup> National Conference on Solid State Ionics: Materials for Novel devices, December 7-9, 2009, Dr. Hari Singh Gaur University (Central University), Sagar, India.
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