



Study of Thin Film of Solid Polymer Electrolyte (SPE) Prepared by Hot Press Technique

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Abstract:

Solid polymeric electrolyte material is important for industrial as well as for preparing energy storage devices. In present work Solid polymer Electrolyte (SPE) is made by using PEO as host polymer and AgCl as salt in appropriate weight% ratio of the composition $[(1-X) \text{ PEO} : X \text{ AgCl}]$ Where $X = 5, 10, 15, 20, 25, 30, 35, 40, 45$ etc. by novel Hot press technique. The composition $[70 \text{ PEO} : 30 \text{ AgCl}]$ is identified as optimum conducting composition (OCC) for SPE membrane. The ion transport behavior in SPE (OCC) has been discussed on the basis of conductivity (σ). The conductivity as a function of temperature has been studied to compute activation energy by least square fitting of " $\log \sigma - 1/T$ " Arrhenius plot.

Keywords: optimum conducting composition, hot press technique, polymer electrolyte.

1. Introduction:

Superionic solids are class of superconductor showing high ionic conductivity. Composite electrolyte systems are the new class of fast ion conductors or super ionic solids. Super ionic are solids which contains high degree of ionic conductivity and low degree of electronic conductivity. Most of the research in solid state ionic deals with conducting solid polymer electrolytes because of their potential applications in various electrochemical devices, solid state batteries, memory devices, chemical sensors, etc because of their safety performance, ease of handling, long life high processibility [1-2]. In physical modification methods morphology and phase structure of polymer electrolytes can be changed by incorporating a suitable plasticizer or organic/inorganic filler which either introduces flexibility in polymeric chain or creates amorphous cell with defectation around dispersed grains. The addition of small organic/inorganic or inert fillers decreases the crystallinity and enhances amorphousity of system [3]. Composite electrolytes are prepared according to the various procedures. This procedure varied depending upon types of fillers and the form of polymeric material [4]. A lot of work has been done with various polymers and salts to attain different desired properties for better performance of electrochemical devices. Ion conducting behavior of polymer electrolytes is such a property which has been intensively and extensively studied for device application[6].



Traditional solid polymer electrolyte (SPE) films are prepared by usual solution cast method which requires common solvent to dissolve both polymer and salt. Recently a new technique is developed which is solvent free and dry technique called hot press technique. This technique is quicker as well as cost effective technique [5]. The present paper reports the casting of Ag^+ ion conducting SPE membrane [(1-x) PEO: AgCl] by novel hot press technique.

2 Experimental techniques:

2.1 Material preparations:

For preparing Ag^+ ion conducting solid polymer electrolyte (SPE) membrane [(1-x) PEO: x AgCl] solvent free / dry hot press technique is used. For preparing thin film [(1-x) PEO: X AgCl] where $x=5,10,15,20,25,30,35,40,45$ etc in weight% ratio, PEO poly(ethylene oxide) (10^6 Mw, Aldrich, USA) and silver chloride AgCl (purity>99%, Reidel Lab Reagent) are used. Powders of the chemical in appropriate weight % ratio is homogeneously mixed for 30 min in an agate pestle mortar at room temperature. Finely grounded mixture of different compositions is then heated separately in crucible nearly at temperature~ 70°C (close to melting point of PEO) with continuously mixing for 20 minutes. The soft slurry so obtained is then pressed between two cold SS- blocks (~ 1.25 tons/ cm^2) which give rise to film of uniform thickness 0.035 cm.

2.2 Conductivity (σ) measurement:

Conductivity (σ) is measured by keeping thin film of the sample between two SS-non blocking silver electrodes at fixed frequency ($\sim 1\text{kHz}$) using LCR Bridge (ESCORT , ELC-131D, TAIWAN). For the calculation of activation energy (E_a) temperature variation study of conductivity is done. Activation energy (E_a) was determined by least square fitting of conductivity data obtained at different temperature and different composition of SPE thin film.

3. Result & discussion:

3.1 Measurement of Ionic conductivity (σ) based on salt concentration and temperature:

The salt concentration dependent room temperature conductivity (σ) of solid polymer electrolyte (SPE) membrane [(1-x) PEO: x AgCl] where x is taken as 5, 10,15,20,25,30,35,40 in weight % ratio is shown in figure1.

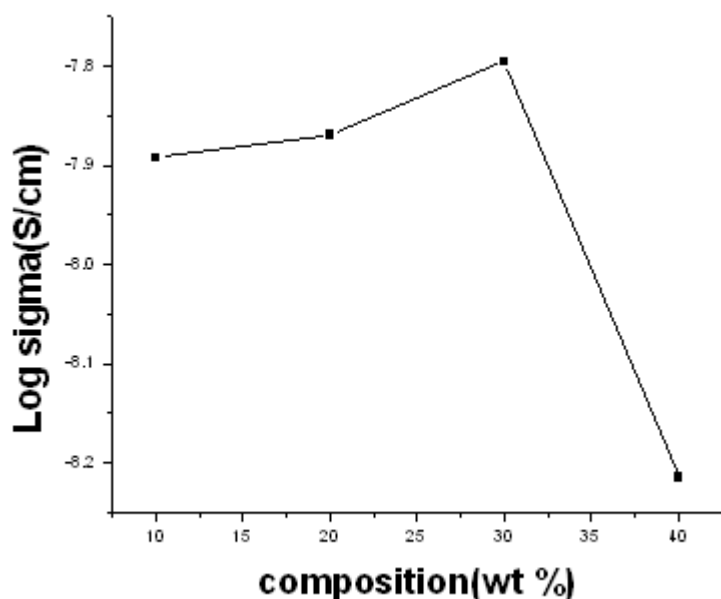


Figure1: Room temperature conductivity Log σ as a function of salt concentration(x) in wt % ratio for hot pressed synthesized SPE membrane [70PEO:30AgCl]

From the figure it is clear that ionic conductivity increases gradually with the increase in salt concentration (x) in wt % ratio it attains maximum value for x=30(wt %) of salt concentration and then starts decreasing with further increase in salt concentration. The maximum conductivity (σ) obtained for x= 30 wt % of salt concentration is optimum conducting composition (OCC) of the SPE membrane. The SPE membrane of composition [70PEO:30AgCl] with room temperature conductivity of ($\sigma = 1.6 \times 10^{-8}$ S/cm) with (σ) enhancement of approximately one order of magnitude can be seen as compare pure PEO (polymeric host).

Figure2 depicts the temperature dependence of Ionic conductivity ($\log \sigma - 1000/T$) of SPE membrane. The behavior is typical Arrhenius behavior described by

$$\sigma(T) = \sigma_0 \exp(-E_a/kT)$$

Where σ_0 is pre exponential factor and E_a is activation energy

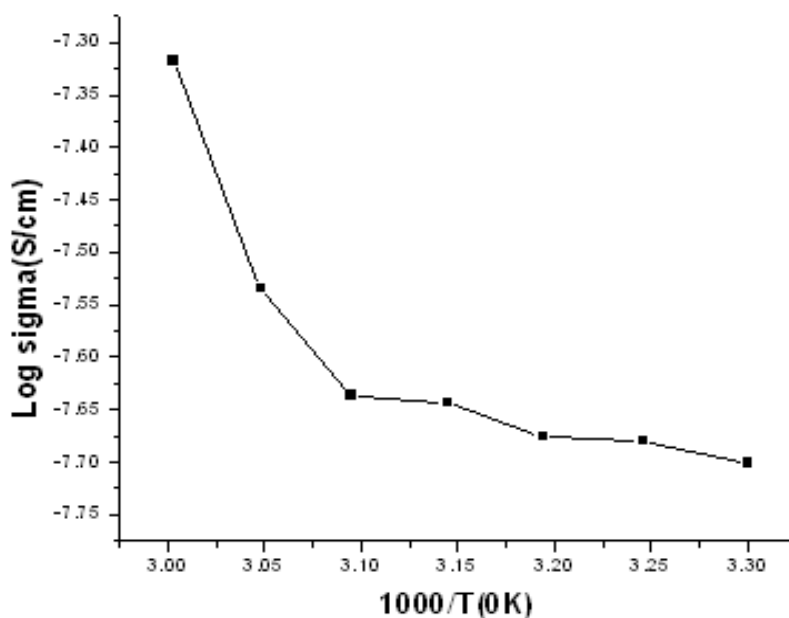
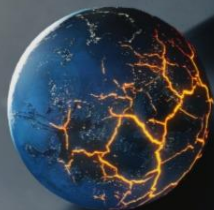


Figure 2: Arrhenius plot for “Log σ -1000/T” plot for SPE membrane (OCC) [70PEO:30AgCl]

From the figure it is clear that there is sudden jump at ($\sim 70^{\circ}\text{C}$) of conductivity which corresponds to semi crystalline to amorphous phase transition of PEO. The linear portion below this temperature may be expressed by Arrhenius equation:

SPE host membrane: $\sigma(T) = 0.494 \times 10^{-4} \exp(-0.814/kT)$ (1)

Where activation energy (E_a) = 0.814 eV for the SPE (OCC) membrane is calculated by least square fitting of the data of conductivity.

4. Conclusion:

A new Ag^+ ion conducting SPE membrane [70PEO:30AgCl] has been synthesized by novel hot press technique. The optimum conducting composition (OCC) [70PEO:30AgCl] is determined by compositional variation of conductivity. The ion conduction mechanism is explained on the basis of transport parameters viz ionic conductivity (σ), ionic transference number ($t_{\text{ion}} \sim 0.95$) which indicates that SPE membrane is predominantly ion conducting. The activation energy ($E_a \sim 0.817$ eV) of SPE (OCC) is computed by least square linear fitting of data of conductivity with respect to temperature.



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