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Study of Ion Transport Property of Ag^+ Ion Conducting Electro Active Nanocomposite Polymer Electrolyte Thin Film Prepared by Hot Press Technique.

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Abstract: The study of ion transport property of hot-press-synthesized Ag^+ ion conducting electro active polymeric membrane (1-x) [70PEO: 30 Ag_2SO_4]: x Fe_2O_3 is the prime theme of this paper. The composition 94[70PEO:30AgCl]:6 Fe_2O_3 is identified as optimum conducting composition (OCC). The conductivity is enhanced by more than two order in nanocomposite polymer electrolyte thin film as compare to pure poly(ethylene oxide) PEO host.

Keywords: transport, synthesized, membrane, conductivity, nanocomposite.

Introduction:

The increasing energy needs of modern society have spurred extensive research and development in the areas of energy production, storage and distribution. Devices incorporating solvent-free polymer electrolytes, in particular the ‘lithium polymer battery’ (LPB), are highly desirable due to characteristics such as inherent low safety risks and their ability to be formed into thin film structures of large surface area, yielding high energy density cells that are lightweight and flexible [1]. Poly(ethylene oxide) (PEO) doped with alkali metal salts has long been favored a candidate for use as an electrolyte in solid-state rechargeable lithium batteries [2]. Most efforts aimed at lowering the operation temperatures of PEO systems to the ambient region have focused on the development of copolymerization or cross-linking strategies and the use of suitable plasticizers to create completely amorphous systems with enhanced conductivity [3-6]. Conductivity of electrolytes can be enhanced by various methods like doping ionic salt in polymeric medium [7], by blending two polymers [8], by adding polarizing agent [9], and by adding nanosize fillers to the polymer electrolytes [10]. polymer electrolytes are prepared by using variety of host polymers viz PEO(polyethylene oxide), PPO(poly propylene oxide), PEG(polyethylene glycol), PVC(polyvinyl chloride), PMMA (poly methylmetha acrylate) etc are complexed with large number of salt such as AgI,KI,AgNO3,LiBF4 etc. Further the conductivity may be increased by dispersing organic /inorganic filler of micro/nano size particles like PMMA,PVA,Al2O3,TiO2,Fe2O3 etc[11].The solid polymer electrolyte (SPE) dispersed with nanosize filler is known as Nanocomposite polymer electrolyte(NCPE).

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Material Preparation:

Ag^+ ion conducting nanocomposite polymer electrolyte (NCPE) thin film of composition (1-x) [70PEO: 30 Ag_2SO_4]: x Fe_2O_3 is prepared by dry hot press technique. For the casting of membrane precursor grade chemicals PEO poly (ethylene oxide) (10^6 Mw, Aldrich, USA) and silver sulphate Ag_2SO_4 (purity>99%, Reidel Lab Reagent) and nanoscopic Fe_2O_3 (particle size < 50 nm, Aldrich, USA) are used. Powders of constituent chemicals in appropriate (wt %) ratio is homogeneously mixed for 20 min in an agate pestle mortar at room temperature. Finely grounded mixture of different compositions is then heated separately in crucible nearly at temperature~ 70^0C (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) in which film of thickness 0.035 cm is casted.

Conductivity (σ) measurement:

Conductivity (σ) measurements are carried out on samples of different composition by keeping them between two SS-non blocking silver electrodes at fixed frequency (~ 1kHz) using LCR Bridge (ESCORT , ELC-131D, TAIWAN). For the calculation of activation energy (Ea) temperature variation study of conductivity is done. Activation energy (Ea) was determined by least square fitting of conductivity data obtained at different temperature and different composition of SPE membrane.

Salt concentration dependent room temperature conductivity (σ) of nanocomposite polymer electrolyte (NCPE) membrane (1-x) [70PEO: 30Ag_2SO_4]:xFe_2O_3 is shown in figure 1.

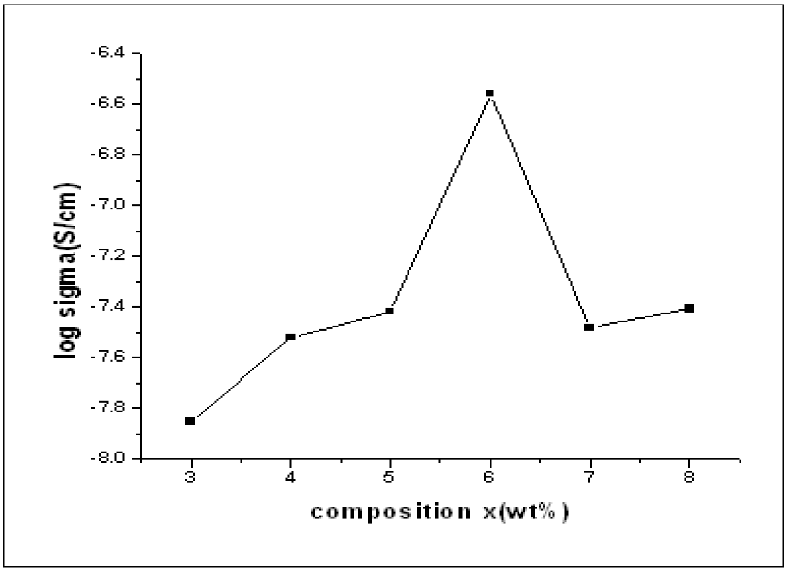

Figure1: Room temperature conductivity log σ as a function of Fe_2O_3 filler particle concentration(x) for 94[70PEO: 30Ag_2SO_4]:6Fe_2O_3.

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The conductivity of the semiconductor increases with the increase in concentration.The composition 94[70PEO: $30Ag_2SO_4$]:$6Fe_2O_3$ with moderate conductivity ($\sigma \sim 6.07\times10^{-7}$ S/cm) is identified as optimum conducting composition (OCC).

temperature variation of conductivity (σ) for NCPE (OCC) membrane is shown in figure 2. Conductivity (σ) increases linearly with temperature, except for upward change in the slope at ~700C which corresponds to semicrystalline to amorphous phase transition temperature of PEO. The linear portion below this transition can be expressed by following Arrhenius equation:

$$\sigma\,(T) = 7.07\times10^{-6} \exp\,(-0.375/kT)$$

Where the numerical part of the exponential is 0.375eV is the activation energy. Activation energy is calculated by least square fitting of the data.

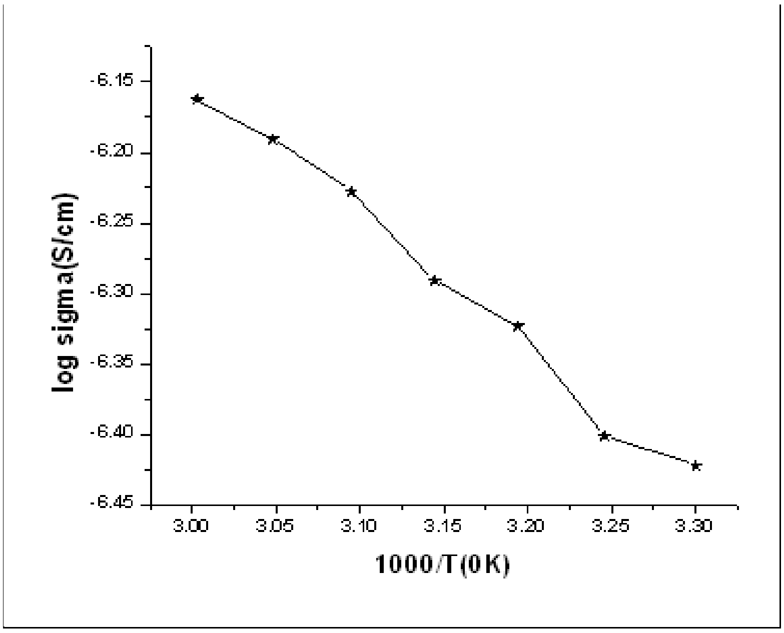

Figure2: Arrhenius plot 'Log σ- 1000/T' plot for membrane 94[70PEO: $30Ag_2SO_4$]:$6Fe_2O_3$.

Conclusion:

The nanocomposite polymer electrolyte NCPE membrane is casted by novel hot press technique. The optimum conducting composition (OCC) of NCPE membrane is identified as 94[70PEO:$30Ag_2SO_4$]:$6Fe_2O_3$. The activation energy Ea is calculated by least square fitting of the data activation energy for this composition has been found to be 0.375 eV. The reason for the enhancement of conductivity of NCPE may be possibly due to dispersion of nanoscopic fillers Fe_2O_3 ,which increases amorphousity of the membrane hence segmental motion of the polymer increases which supports fast ion conduction.

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