



Ion Transport Property Study in Ag⁺ Ion Conducting Solid Polymer Electrolyte(SPE) Films:[(1-X) PEO: X AgCOOCH₃]

Tripti Bala Sahu, Manju Sahu, Shrabani Karan, Priyanka Kesharwani,
Y.K. Mahipal and R.C. Agrawal*

Solid State Ionics Research Laboratory
School of Studies in Physics & Astrophysics
Pt. Ravishankar Shukla University, Raipur, CG, India

Abstract— Solid Polymer Electrolyte (SPE) films, based on poly (ethylene oxide) PEO complexed with Silver Acetate (AgCOOCH₃) in different salt concentrations (x)= 0,3,5,7,10,15,20,25,30 wt.(%), have been prepared using hot - press cast. Salt- concentration dependent conductivity study identified SPE film: [93PEO: 7AgCOOCH₃] as Optimum Conducting Composition (OCC) with room temperature conductivity (σ_{rt}) $\sim 1.13 \times 10^{-7}$ S/cm, which is approximately two orders of magnitude higher than that of pure PEO ($\sigma_{rt} \sim 3.20 \times 10^{-9}$ S/cm). The complexation of salt in polymeric host has been confirmed by XRD/FTIR/SEM/DSC studies. Ion transport property has been characterized in terms of ionic conductivity (σ), total ionic (t_{ion}) / cation (t_+) transport numbers. Temperature dependent conductivity has also been measured to understand ion transport mechanism and to compute activation energy (E_a) by least square linear fitting of 'log σ - 1/T' Arrhenius plot.

Keywords— Solid Polymer Electrolyte (SPE), Hot-press Casting Procedure, Ionic/Cationic Transference Number, All-Solid-State Polymer Batteries.

1. INTRODUCTION

Dry Polymer Electrolytes such as Solid Polymer Electrolytes (SPEs) and Composite Polymer Electrolytes (CPEs) in thin flexible film form and based on high mol.wt polar polymer viz. (Poly Ethylene Oxide) PEO complexed with variety of ionic salts containing larger size anions, have recognized in recent past as promising candidates to develop All-Solid-State electrochemical power sources viz. batteries, fuel cells, supercaps etc.[1-13]. In fact, ion Conduction in polymer electrolytes was reported for the first time in 1973 by Fenton et.al. [14]. Much later, Armand et.al. [15] in 1979 demonstrated the first practical battery based on SPE film :PEO complexed with Li⁺-ion salt. A large number of dry polymer electrolyte systems involving different mobile ion species viz. H⁺, Li⁺, Ag⁺, Cu⁺, Na⁺, K⁺, Mg²⁺, Zn²⁺, Cu²⁺ etc. has been investigated since then and their cell performances have been tested worldwide by fabricating All-Solid-State batteries in all possible shapes/sizes [12, 16-19]. These batteries are manufactured at a large commercial scale in the present time. Majority of them use Li⁺-ion polymer electrolytes and lithium electrodes. However, these batteries have been reported to encounter some serious safety issues in the recent past mainly due to use of lithium chemicals. Hence, based on the high priorities safety concerns of the batteries while in use, it is felt urgently now-a-days to explore some non-lithium chemical based polymer electrolytes for battery applications. The present paper reports the investigations

on a non-lithium chemical based Solid-Polymer-Electrolyte system for possible use in All-Solid-State battery. We report the synthesis of Ag⁺-ion conducting SPE films: [(1-x)PEO: x AgCOOCH₃] of different salt concentration (x) using a novel hot-press casting technique. SPE film exhibiting optimum room temperature conductivity was identified and has been referred to as Optimum Conducting Composition (OCC) SPE film. The materials and ion transport properties of SPE OCC film have been characterized to check its possible use in All-Solid-State batteries. Characterization of ion transport properties of SPE OCC film has been done in terms of basic ionic parameters viz. conductivity (σ), ion transference numbers (total ionic ' t_{ion} ' and cationic ' t_+ '). These ionic parameters have been experimentally evaluated using different ac/dc techniques. Materials characterization and hence, confirmation of complexation of salt in PEO has been done by X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR) techniques. Thermal properties have also been studied using Differential Scanning Calorimetry (DSC). The degree of crystallinity in the film samples has been evaluated from DSC responses.

2. EXPERIMENTAL

2.1 Ion Transport Studies

SPE films: [(1-x) PEO: x AgCOOCH₃] in varying salt concentrations viz. x = 1, 3,5,7,10,15, 20, 25, 30 wt (%), have been synthesized by hot -press cast technique using AR grade precursor chemicals: poly (ethylene oxide) PEO (6x10⁵ Mw, purity > 99% Aldrich, USA), AgCOOCH₃ (99

* Corresponding Author: rakesh_c_agrawal@yahoo.co.in

%, Aldrich, USA). Dry powder of constituent chemicals in appropriate wt.(%) ratio was mixed physically for about~ 30- 60 minutes. The homogeneously mixed powder was then heated close to the melting/softening point of PEO i.e. ~ 70°C, with mixing continued for ~ 30-40 minutes. As a result, a soft lump/slurry was obtained which was then pressed (~ 1-2 ton /cm²) between two Stainless Steel (SS) cold blocks to form SPE film of uniform thickness ~ 100-150 μm. The salt concentration dependent conductivity study at room temperature (27°C) revealed SPE film composition: [93PEO: 7AgCOOCH₃] exhibiting optimum conductivity (σ_{rt}). This has been referred to as SPE OCC film, as mentioned. Characterization of ion transport property was done in terms of basic ionic parameters viz. conductivity (σ), total ionic (t_{ion}) and cationic (t₊) transference numbers. Conductivity measurement was done by placing SPE film in between two SS- electrode and a fixed frequency (5 kHz) using an LCR- meter (HIOKI IM 3533). Total ionic transference number (t_{ion}) was determined by dc polarization Transient Ionic Current (TIC) Technique [20, 21] by placing SPE OCC film between two blocking electrodes. To determine cation (Ag⁺) transport number (t₊), SPE OCC film was placed in between non-blocking Ag electrodes. A combined ac/ dc technique, developed by Evans et.al. [22], was used and t₊ was evaluated with the help of following formula:

$$t_+ = I_S (\Delta V - I_0 R_0) / I_0 (\Delta V - I_S R_S) \quad (1)$$

where, I₀/I_S and R₀/R_S are the initial/final current and resistance values respectively before/after polarization, ΔV (□ 1) is a fixed polarization voltage.

2.2 Materials Characterization Studies

The structural, spectroscopic, morphological, and thermal properties of the film material have been characterized respectively using viz. XRD (D₂ Phaser Model: 08 discover, Bruker, CuKα radiation: λ = 1.54 Å), FTIR (IR Affinity-1, Shimadzu Japan), SEM (ZEISS EVO MA 14) and DSC (STAR[®], SW 13.00, METTLER) techniques. Also, from DSC thermal responses, degree of crystallinity (X_c) has been evaluated with the help of the following equation [23, 24]:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (2)$$

where ΔH_m is the heat enthalpy of pure PEO and salt complexed PEO obtained from the area of respective endothermic peaks, ΔH_m⁰ (~ 213.7 Jg⁻¹) is the theoretical value of heat enthalpy for pure PEO with 100% crystalline phase.

3. RESULTS AND DISCUSSION

3.1 Ion Transport Studies

3.1.1 Salt Concentration Dependent Conductivity Study

Salt concentration (x) dependent conductivity (σ_{rt}) variation for different hot-press cast SPE membranes: [(1-x)PEO: (x)AgCOOCH₃] is shown in Fig.1. The conductivity increased abruptly on an initial addition of salt by x= 3 wt.(%). σ_{rt} remained almost unaltered afterward upto x= 30 wt.(%) salt except for a moderate size σ-peak appeared at x= 7 wt.(%) salt. SPE film: [93PEO: 7AgCOOCH₃], referred to as SPE (OCC) film, exhibited σ_{rt} ~ 1.13 x 10⁻⁷ S/cm which is approximately two orders of magnitude higher than that of pure PEO host (σ_{rt} ~ 3.20 x 10⁻⁹ S/cm).

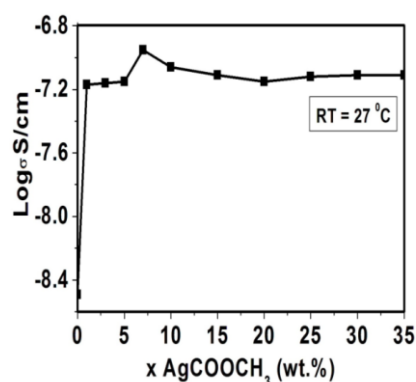


Fig. 1: σ_{rt} as a function of salt concentration (x) for hot press SPE films: [(1-x) PEO: xAgCOOCH₃].

The reasons for σ_{rt} enhancement in SPE OCC film can be attributed, as usual, to dissociation of salt into cations and anions by polymeric host and thereby resulting into an increase in degree of amorphous phase in polymeric host after complexation of salt.

3.1.2 Temperature Dependent Conductivity Study

The conductivity increased gradually as temperature increased, followed by an abrupt jump at around ~60-65°C, which corresponds to the well known semi crystalline-amorphous phase transition of PEO. 'Log σ - 1/T' plot below this transition temperature can be expressed by following Arrhenius equation representing a straight line:

$$\text{Log } \sigma = \text{Log } \sigma_0 - E_a / kT \quad (3)$$

where 'σ₀' is the pre-exponential factor, 'k' is Boltzmann constant and 'E_a' is the activation energy which was computed using linear least square fitting of 'log σ-1/T' plot of Fig. 2 below ~ 60°C and found to be ~ 0.14 eV.

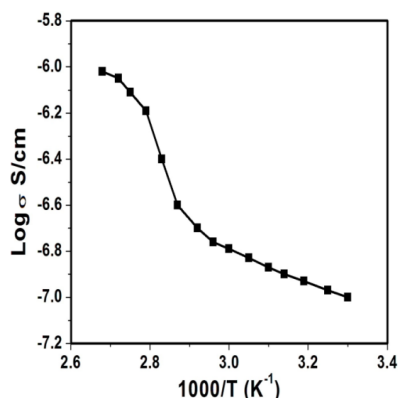


Fig. 2: ‘Log $\sigma - 1/T$ ’ plot for hot-press SPE OCC film [93 PEO: 7 AgCOOCH₃].

3.1.3 Ionic/Cationic Transference Number Studies

It is well known that in polymer electrolytes both cations and anions move. Hence, the total ionic transference number (t_{ion}) was determined using d.c. polarization TIC technique, as mentioned in Section 2. Fig. 3 shows ‘Current-Time’ TIC plot for SPE OCC film and found to be ~ 0.97 when polarized for ~ 2 hours. This value is very close to unity hence, indicative of the fact that the film material is predominantly ionic. The cationic (Ag^+) transference number (t_+), which is more relevant for good battery performance, was evaluated separately by a combined ac/dc technique, as mentioned in section 2. t_+ was found to be ~ 0.22 which is significantly low. However, both σ_{rt} as well as t_+ can be substantially increased by dispersing micro/nano filler particles of an active/passive insulating material [11] as Π^{nd} -phase dispersed into SPE which acts as I^{st} -phase host and to form micro/nano Composite Polymer Electrolytes (CPEs). Alternatively, an additional σ_{rt} increase could be achieved by introducing nano-ionic effect in dry polymer electrolyte system through high energy ball milling of powder mixtures prior to casting SPE/CPE films [25]. These works are currently being pursued in the present laboratory. Table 1 list the value of σ_{rt} (for pure PEO and SPE OCC film) along with t_{ion} , t_+ , E_a values.

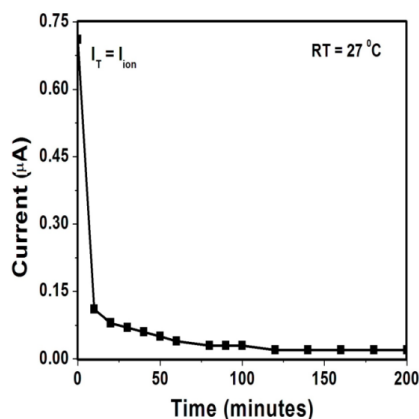


Fig. 3: ‘Current - Time’ TIC plot for hot-press SPE OCC film [93 PEO: 7 AgCOOCH₃].

Table 1: σ_{rt} of pure PEO and SPE OCC film: [93PEO: 7 AgCOOCH₃] along with t_{ion} , t_+ , E_a values.

Film	σ_{rt} (S/cm)	t_{ion}	t_+	E_a (eV)
Pure PEO	3.2×10^{-9}	-	-	-
SPE OCC Film (hot-press)	1.13×10^{-7}	0.97	0.22	0.14

3.2 Materials Property Studies

XRD Study— Fig.4 illustrates XRD patterns for pure PEO, complexing salt AgCOOCH₃ and SPE OCC film: [93PEO: 7AgCOOCH₃]. On comparing the three XRD results, it can be clearly noticed that the intensity of two main peaks of PEO at $2\theta \sim 19.5^\circ$ and 24° and the main peak related to complexing salt has been substantially suppressed. This clearly indicates the complexation/dissolution of salt in polymeric host as well as decrease in degree of crystallinity and/or increase in degree of amorphosity in PEO.

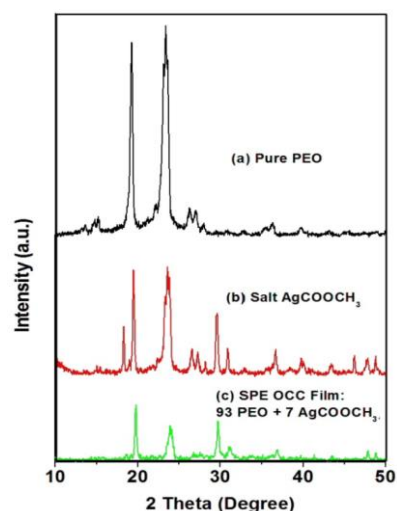


Fig. 4: XRD pattern for: (a) pure PEO, (b) AgCOOCH₃ salt, (c) SPE OCC film: [93 PEO: 7AgCOOCH₃].

SEM Study — SEM surface images for pure PEO and SPE OCC film: [93PEO: 7AgCOOCH₃] were shown in Fig. 5. The surface morphology for both films appeared quite smooth except for the presence of some wrinkles which is probably due to stress field developed during hot-pressing and/or drying of the film.

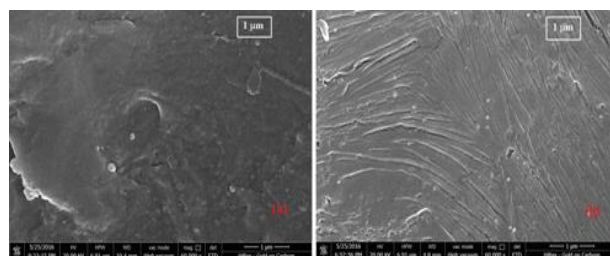


Fig. 5: Surface morphology of (a) pure PEO, (b) SPE OCC film: [93 PEO: 7AgCOOCH₃].

FTIR Study— This has been rechecked again with the help of FTIR studies. Fig.6 shows FTIR spectra of pure PEO, AgCOOCH₃ salt and SPE OCC film. The characteristic vibrational bands at ~ 2238 cm⁻¹, ~2163 cm⁻¹, ~1963 cm⁻¹ of pure PEO, peaks at ~525-530 cm⁻¹ & ~1200 cm⁻¹ related to C-O-C bending and stretching mode respectively and the bands at ~750-950, ~1820, ~2900-3000, ~1475, ~845 cm⁻¹ corresponding to symmetrical / asymmetrical stretching/vibration of CH₂ group, CH₂ bending, CH₂ rocking etc. of PEO, appeared to be suppressed after complexation of salt in polymeric host. Also, slight variations in the shapes occurred. All these changes in the spectral response of SPE OCC film further confirmed the complexation of salt in the polymer.

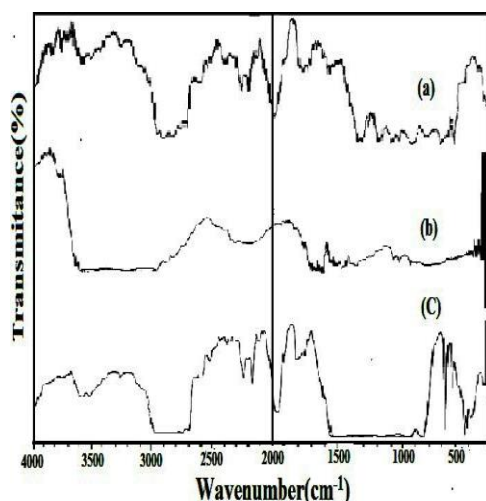


Fig. 6: FTIR for (a) pure PEO, (b) AgCOOCH₃ salt (c) SPE OCC film: [93 PEO: 7AgCOOCH₃].

DSC Study— Fig.7 shows DSC thermograms for pure PEO and SPE OCC film: [93 PEO: 7AgCOOCH₃]. The sharp endothermic peak at (T_m) ~71.09 °C shows in curve 'a'. This temperature belongs to the characteristic transition of pure PEO from mixed semicrystalline - amorphous to complete amorphous phase. It can be clearly noted that as a consequence of complexation of salt, the peak position sifted slightly towards lower temperature region 68.05 °C (curve b). The peak area has also been reduced significantly and shift in peak position is often considered as confirmation of complexation of salt and the reduction in peak area relates to decrease in degree of crystallinity in PEO. The relative percentage of crystallinity (X_c) of PEO as well as SPE host have been evaluated with the help of equation (2), mentioned in Subsection 2.2 and listed in Table 2 along with T_m and ΔH_m values. Decrease in degree of crystallinity and / or increase in degree of amorphosity of PEO which also supported our XRD/ FTIR results discussed in Subsection 3.2.

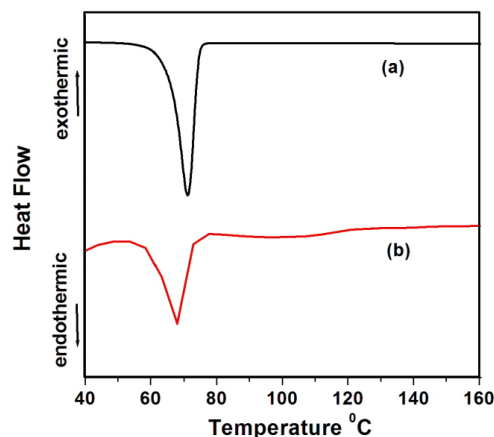


Fig. 7: DSC for (a) pure PEO, (b) SPE OCC film: [93PEO: 7AgCOOCH₃].

Table 2: Values of T_m, ΔH_m and X_c for pure PEO and SPE OCC Film: [93PEO: 7AgCOOCH₃].

Film Sample	T _m (°C)	ΔH _m (J/gm)	X _c (%)
Pure PEO	71.09	175.15	81.9
SPE OCC : [93PEO: 7AgCOOCH ₃]	68.05	119.10	55.73

4. CONCLUSION

A non-lithium chemical based Solid Polymer Electrolyte (SPE) film: [93 PEO: 7AgCOOCH₃] has been synthesized using hot press casting technique. Materials/ion transport properties have been characterized to evaluate its usefulness in the fabrication of All- Solid-State batteries. This SPE film exhibited room temperature conductivity (σ_r) ~ 1.13 x 10⁻⁷ S/cm, the total ionic transference number (t_{ion}) ~ 0.97 and t₊ ~ 0.22. σ_r and t₊ values are quite low as regards to its use in a good performing battery. However, t₊ as well as σ_r can be improved significantly by way of dispersing micro/nano filler particles in SPE host and/or introducing nano-ionic effect through high energy ball milling of dry powder mixture of constituents prior to casting the polymer electrolytes film.

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