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Silver ion conducting solid polymer electrolytes: Synthesis and ion transport studies

Angesh Chandra[a*], Archana Chandra[a], R S Dhundhel[a], Alok Jain[a], Kiran Thakur[b], S S Thakur[c],
Subhashis Basak [d], M Z Khan [d] & Alok Bhatt[e]

[a]Shri Shankaracharya Institute of professional Management and Technology, Raipur, Chhattisgarh, 492 015, India
[b]Department of Chemistry, Govt. Pataleswar College Masturi, Bilaspur,
Chhattisgarh, 495 551, India
[c]Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Bilaspur, Chhattisgarh, India
[d]Dr. C V Raman University, Kargi Road, Kota, Bilaspur, Chhattisgarh, India
[e]Bharti College of Engineering and Technology, Durg-491 001, Chhattisgarh, India

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A new silver ion conducting Polyethylene Oxide (PEO) based solid polymer electrolyte (SPE) films: (1-x) PEO: xAgCl, where $0 \leq x \leq 70$ in wt.%, are synthesized by using a new hot-press and traditional solution-cast techniques. The electrical conductivity of the SPE increased with the concentration of salt AgCl. The optimum conducting composition (OCC): 70PEO: 30AgCl with ionic conductivity (σ) 6.0×10^{-7} Scm^{-1} have been determined at room temperature. The increase in ionic conductivity has been explained with the help of ionic mobility (μ) and mobile ion concentration (n) studies. To explain the ionic nature of the present system, ionic transference number (t_{ion}) measurement has been carried out at room temperature.

Keywords: Solid polymer electrolyte, hot-press technique, ionic conductivity, ionic mobility, ionic transference number.

Introduction

Solid polymer electrolytes with high ionic conductivity have been a subject of great interest in recent years in the area of polymer research due to theoretical interest as well as practical importance for the development of all-solid-state mini/micro electrochemical power sources *viz.* rechargeable batteries, electro chromic display devices, and fuel cells, or super capacitors and other applications[1-3]. Solid Polymer electrolyte **(**SPE) have been quite attractive because this can lead to flexible, compact, laminated solid state structure, free from leaks and available in different geometries[4]. Pure Poly ethylene oxide (PEO) polymers often exhibit poor electrical conductivity (PEO) but it dissolves in high concentrations a wide variety of salts to form polymeric electrolytes[5-7]. Recently Park *et al*. studied the differences between the performance parameters for dye-sensitized solar cells (DSCs) using liquid and poly (ethylene oxide)-based solid polymer electrolytes[7]. The conductivity of SPE film was found to depend upon the concentration and particle size of the inert phases[8-9]. In PEO polymer, cations are coordinated with the polymer chain. Physical properties can be changed by changing the chemical composition. The polymer electrolyte plays a roll of a solvent for ions that shows a liquid-like degree of freedom[10-11]. SPE films are usually prepared by the traditional 'solution cast' technique however in the recent years a completely dry procedure known as 'hot-press' technique, has been developed for casting dry polymer electrolyte films[12-15]. Polyethylene oxide (PEO) can be complexed with wide variety of ionic salts with the only requirement of selecting those having large anions and de localized charge, to assure the stability of the complex[16]. The several researches on silver-ion polymer electrolytes has been reported, such as poly ethylene oxide (PEO) and polyvinyl alcohol (PVA) based polymer salt complexes comprising $AgCF_3SO_3$, $AgNO_3$, AgI, Ag_2O etc[17-19]. The present investigation reports, synthesis and ion transport studies of a new Ag^+ ion conducting conduction solid polymer electrolytes (SPEs): (1-x) PEO: x AgCl, where $0 \leq x \leq 70$ wt.%.

Experimental

SPE films of different salt concentrations: (1-x) PEO: x AgCl, where $0 \leq x \leq 70$ wt.%, have been casted

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*Corresponding author: (E-mail: chandrassi@gmail.com) using AR grade precursor chemicals: poly (ethylene oxide) PEO [10^5 MW, Sigma Aldrich, USA], AgCl [99% purity, AR Himedia, India]. Dry powder of the PEO and AgCl in appropriate wt.% ratios was physically mixed at room temperature (for ~ 40 min.). The homogeneous mixtures were heated separately at ~70 °C (close to the melting point of PEO) for ~30 min. With continuous mixing to form soft lump/slurry and then pressed (~ 1.25 ton/cm^2) between two stainless steel (SS) blocks and a thin film of thickness ~0.017 cm was obtained. The details related to hot press casting has been discussed elsewhere in the literature[20-25]. For the sake of comparison, SPE were also prepared by using traditional solution-cast technique using methanol [*SD Fine Chem Ltd*., India] as a solvent.

The conductivity (σ) measurement was carried out at a fixed AC frequency of 5 kHz on the film samples sandwiched between SS electrodes using an LCR meter (model: HIOKI 3532-50, Japan). Materials characterization has been done with the help of X-ray diffraction (XRD) (model: Shimadzu) technique. The ionic transference number (t_{ion}) and ionic mobility (μ) have been determined by using d. c. polarization transient ionic current (TIC) techniques[26, 27]. The mobile ion concentration (n) was subsequently evaluated from σ and μ data. Activation energy (E_a) of SPE has been calculated with the help of temperature dependent conductivity studies.

Results and Discussion

Figure 1 shows the salt concentration dependent conductivity studies of SPE films (1-x) PEO: x AgCl, where $0 \le x \le 70$ wt% at room temperature prepared by both hot press and solution cast techniques. It is seen that the conductivity increased abruptly on initial addition of 10 wt. (%) salt in the PEO host initially upto x = 30 wt.% for both the hot press and solution cast films. The increase in conductivity is due to the increase in mobile ion concentration as a result of dissociation of salt in PEO and also increases the amorphicity in PEO to some extent. This may be increase the ionic mobility and hence, the ionic conductivity. The film beyond 30 wt.% of AgCl exhibit lower conductivity values. Hence, SPE film composition: (70PEO:30AgCl) exhibiting highest room temperature conductivity ($\sigma \sim 6.0 \times 10^{-7}$ Scm^{-1}), which is more than two order of magnitude higher than that of pure PEO ($\sigma \sim 3.2 \times 10^{-9}$ Scm^{-1}) and this has been identified as optimum conducting composition (OCC) of SPE film. The pattern of 'Log σ-x' variations' for SPE prepared by both the techniques appears similar, but the hot press casted film shows higher conductivity values at room temperature.

The ionic mobility (μ), mobile ion concentration (n) and the ionic transference numbers (t_{ion}) have been evaluated by d.c. polarization transient ionic current (TIC) technique. Figures 2 shows 'log $\mu - x$' plots for SPE films: $(1-x)$ PEO: x AgCl, where $0 \le x \le 70$ wt.% prepared by both the hot-press and solution-cast technique. It is clear from the figure that ionic mobility of slightly lower in case of sample prepared by the solution-cast method but mobility variations

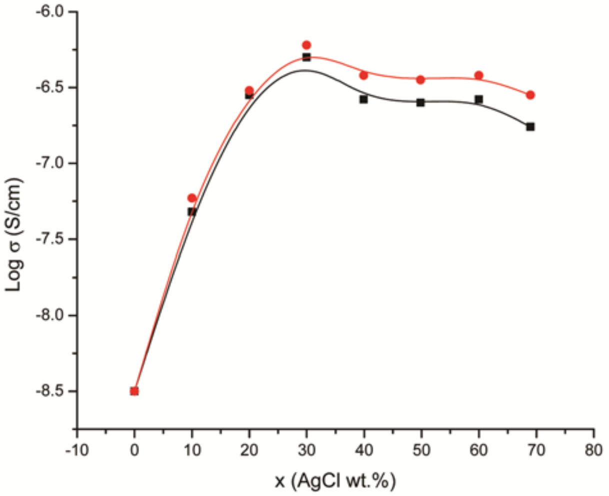


Fig. 1 — 'Log σ – x' plot for SPE films: (1-x) PEO: x AgCl, where $0 \le x \le 70$ wt.%. Film prepared by: hot-press (●) and solution-cast technique (■).

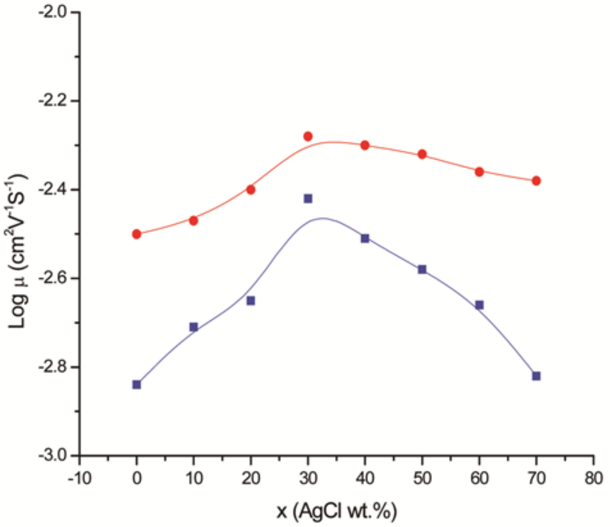


Fig. 2 — 'Log $\mu - x$' plots for SPE films: (1-x) PEO: x AgCl, where $0 \le x \le 70$ wt.%. Film prepared by: hot-press (●) and solution-cast technique (■).

are almost identical as well as comparable. The increase in ionic mobility is due to the available of more conducting paths. Fig. 3 shows ‘log *n−x’* plot for hot-pressed SPE films: (1−*x*) PEO: *x* AgCl, where 0≤ x≤70 wt.%. It is obvious from the figure that both the variations are almost analogous to ‘log *σ−x*’ plot, as shown in Fig. 1. Figures 2 & 3 clearly indicated that the overall all increase in ionic conductivity in the present SPEs is due to the increase in both ionic mobility (μ) and mobile ion concentration (n).

Figure 4 shows the XRD patterns of pure salt PEO and SPE OCC: (70PEO:30AgCl). It can be clearly seen from the figure that characteristic peaks of pure PEO appeared between 2θ = 15-30° is decreased after the addition of salt AgCl. The characteristic peaks of pure PEO became relatively less-prominent/ feeble and disappear after polymer-salt complexation. This is usually attributed to the increase in the degree of amorphicity or decrease in degree of crystallinity and it is strong evidence of confirmation of polymer-salt complexation. The proposed interaction between polyethylene oxide (PEO) and AgCl might be depicted as *Scheme I*:

The solvating heteroatom, here oxygen acts as a donor for the Ag^+ ions and Cl^- ions, generally a large dimension stabilizes the PEO-MX complex[28].

The ionic transference number (t_{ion}) of SPE OCC prepared by both the hot-press and solution-cast method have been determined by using ‘current – time’ plots, as shown in Fig. 5. $t_{ion} \sim 0.95$ obtained at

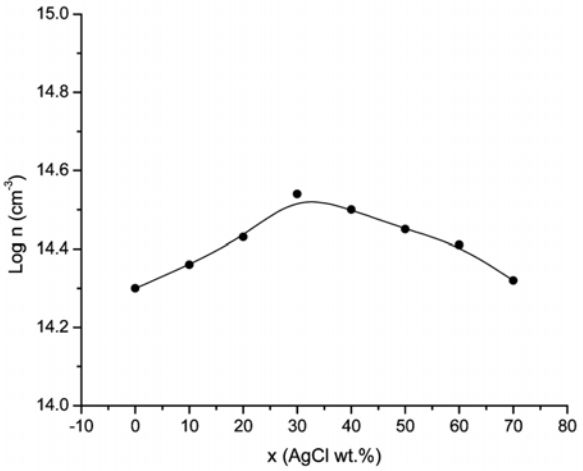
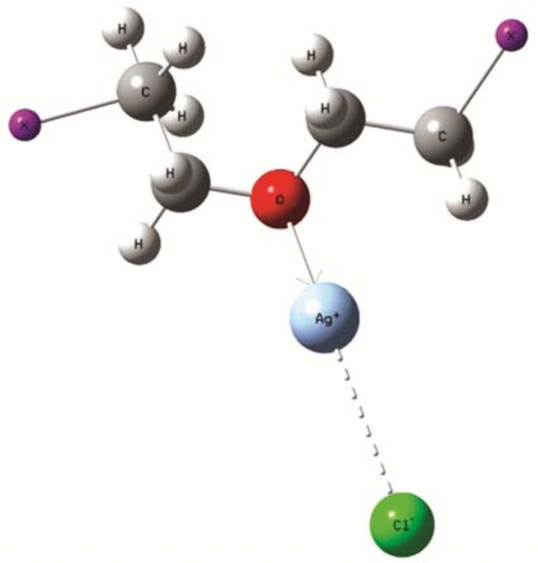


Fig. 3 — ‘Log *n – x’* plot for hot pressed SPE films: (1-x) PEO: xAgCl, where 0 ≤ x ≤ 70 wt.%.



Scheme — 1

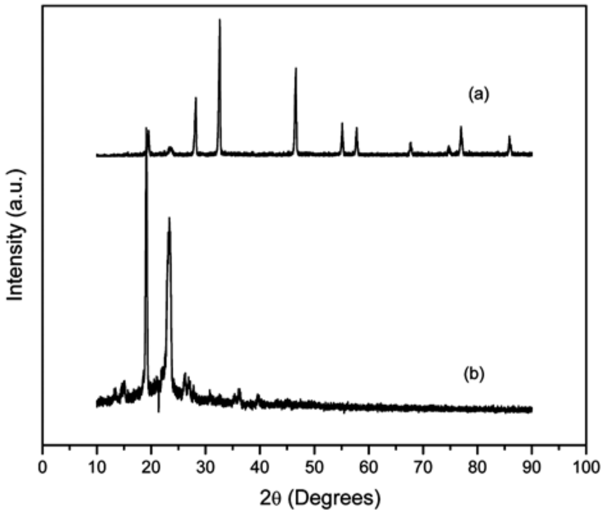


Fig. 4 — XRD Patterns: (a) hot-pressed SPE OCC: (70PEO:30AgCl) and (b) pure PEO.

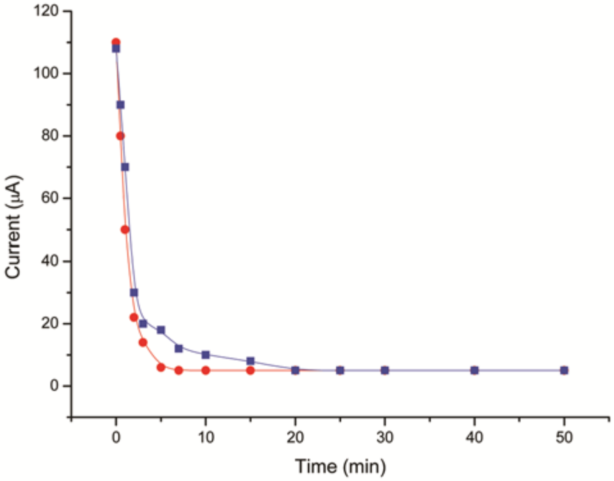


Fig. 5 — ‘Current vs time’ plots for SPE OCC: (70PEO:30AgCl). Film prepared by: hot-press (●) and solution-cast technique (■).

Table 1 — Some important ion transport parameters of pure PEO and hot-pressed SPE OCC: (70PEO:30AgCl).

System	Ionic Conductivity (Scm^{-1})	Ionic mobility ($cm^2 V^{-1} s^{-1}$)	Mobile ion concentration (cm^{-3})	Ionic transference number (t_{ion})	Activation Energy (eV)
Pure PEO	3.2×10^{-9}	-	-	-	-
SPE OCC: (70PEO: 30AgCl)	6.0×10^{-7}	5.2×10^{-3}	3.5×10^{14}	0.95	0.49

room temperature for both the samples and it is clearly indicates that SPE OCC film is purely an ion conducting system. Therefore, this can be appropriately employed as electrolyte to fabricate thin film electrochemical devices viz. batteries, sensors etc. The major ion conducting species in this SPE OCC are yet to be identified, as both cations & anions may be mobile. However, cations: Ag^+-ions, being relatively smaller in size than anion Cl^-. Therefore, Ag^+-ions are expected to be the main transporting ionic species in this SPE material. Table 1 list the room temperature values of σ, μ, n and t_{ion} for SPE OCC film for direct comparison.

To calculate the activation energy (E_a) of the present, temperature dependent ionic conductivity measurement of SPE OCC has been carried out. Fig. 6 shows the 'log σ-1/T' plot of hot-pressed SPE OCC: (70PEO:30AgCl). The conductivity increased linearly with temperature, except for an upward change in the slope at ~ 65-70 °C which corresponds to semi-crystalline to amorphous phase transition temperature of PEO. The increase in ionic conductivity with temperature can be interpreted as a hoping mechanism between coordinating sites, creation of additional conducting paths. This can also be explained with the help of various proposed theoretical models[29, 30]. The linear portion below the transition temperature can be expressed by following Arrhenius equation:

$$\sigma (T) = 2.5 \times 10^{-3} \exp (-0.49/ kT) \quad [S.cm^{-1}] \qquad \dots (1)$$

where 0.49 is the activation energy (E_a) in (eV). The low activation energy (E_a) in the present SPE system indicates that this can be used for all-solid-state device fabrications.

Conclusions

A new Ag^+ ion conducting solid polymer electrolyte (SPE) film: (70PEO:30AgCl) with room temperature ionic conductivity (σ ~ 6.0×10^{-7} Scm^{-1}) has been synthesized. This SPE film has been casted by recently developed hot press technique. It has been suggested that that this technique can be preferred over the traditional solution-cast technique. Two orders of conductivity enhancement have been achieved in the newly synthesized SPE OCC. The conductivity enhancement have been explained with the help of ionic mobility and mobile ion concentration studies and the overall increase in conductivity is due to the increase in both ionic mobility and mobile ion concentration. The lower activation energy in the present system indicates that this can be potentially used for solid state device fabrications.

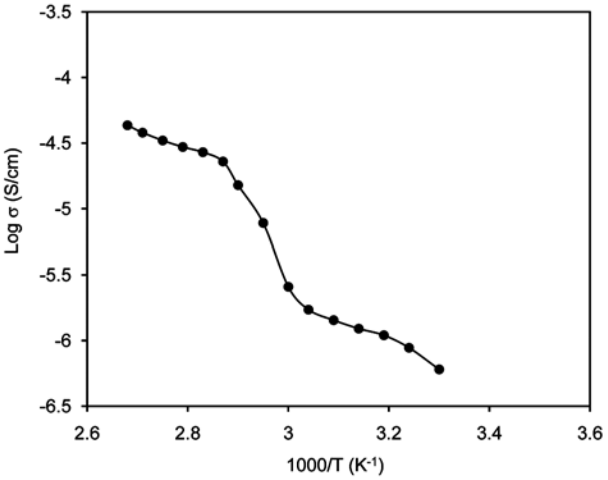


Fig. 6 — 'Log σ –1/T' plot for hot-pressed SPE OCC: (70PEO:30AgCl).

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