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Ion transport property studies of a new Ag^+ ion conducting blended solid polymer electrolytes

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Abstract

Ion transport property studies of a new Ag^+ ion conducting blended solid polymer electrolytes (BSPEs): (1-x) [70PEO:30AgCl] + x PVP where $0 \leq x \leq 15$ wt.%, are reported. The present BSPE films have been synthesized using a recently developed hot-press method. The maximum ionic conductivity ($\sigma \sim 1.7 \times 10^{-5}$ $S.cm^{-1}$) has been obtained at the composition: [97(70PEO:30AgCl) + 3PVP] and this has been referred to as optimum conducting composition (OCC). Material characterizations have been done by x-ray diffraction (XRD) analysis. Ion transport properties have been explained with the help of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}).

Keywords: Blended solid polymer electrolytes, XRD, ionic conductivity, ionic transference number.

INTRODUCTION

Ion-conducting solid polymer electrolyte (SPE) systems, attracted widespread attention as the most appropriate choice to fabricate all-solid-state electrochemical devices viz. batteries, sensors, fuel cells etc. The main advantages of SPEs are their high ionic conductivity, high mechanical strength, ease of fabrication of thin film form etc. [1-5]. Polymer blending is one of the methods used to enhance the ionic conductivity in polymeric electrolyte membranes [6-9]. However, it has found poor mechanical properties in SPE at a high degree of polymeric blending [8]. Polyethylene oxide (PEO) can be complexed with a 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 [8]. Several researches on silver-ion polymer electrolytes have been reported, such as polyethene oxide (PEO) and polyvinyl alcohol (PVA) based polymer salt complexes comprising $AgCF_3SO_3$, $AgNO_3$, AgI, Ag_2O etc. [8].

Polyvinyl pyrrolidone (PVP) is a cross-linked and amorphous polymer that blends with PEO to reduce crystallinity. Also, PVP has desirable characteristics such as excellent thermal, and mechanical stability. Blending PVP with PEO can improve its electrochemical activity, mechanical strength, thermal stability, and chemical, whereas the PEO enhances the flexibility of PVP structures [10].

Polymer electrolytes are prepared, in general, by conventional solution-cast and sol-gel techniques but recently a novel hot-press technique has been developed which shows several advantages over the conventional techniques [11-14].

To understand the ion conduction mechanism, the present investigation reports the ion transport property studies on hot-press synthesized Ag^+ ion conducting blended solid polymer electrolytes (BSPEs): (1-x) [70PEO:30AgCl] + x PVP where $0 \leq x \leq 15$ in wt.%.

EXPERIMENTAL

For synthesis of blended solid polymer electrolytes (BSPEs): (1-x) [70PEO:30AgCl] + x PVP where $0 \leq x \leq 15$ in wt.%, as supplied precursor chemicals: polyethene oxide (PEO) (10^5 Mw, Aldrich, USA), AgCl (purity > 98%, Merck, India) and polyvinylpyrrolidone (PVP) (purity > 98%, Merck, India) have been used. The composition (70PEO:30AgCl) with conductivity 6.02×10^{-7} $S.cm^{-1}$ has been investigated in previous communication [15] and this has been used as a first-phase host polymer or SPE host for the present polymer blending. The dry powders of SPE host and PVP chemicals in appropriate wt.% ratios were homogeneously mixed for ~ 30 min at room temperature and then heated separately at ~ 70 ^{0}C (close to the melting point of PEO) for ~ 30 min with mixing continued resulting in soft lump/ slurry. The slurry, so obtained, was pressed (~ 1.25 ton/cm^2) between two SS-cold blocks which gave rise to a uniform film of thickness ~ 0.018 cm. Materials characterization has been done with the help of x-ray diffraction (XRD) (model: Shimadzu) technique. Ion transport characterization have been explained with the help of basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n) and ionic transference number (t_{ion}) measurements. The details related to the characterization procedure have been given in our earlier communications [14-16]. The activation energy (E_a) values involved in the thermally activated conductivity processes have been computed from the temperature-dependent ionic conductivity measurements.

RESULTS AND DISCUSSION

Figure 1 shows the room temperature conductivity variation of solid polymer electrolytes (SPEs): [PEO:AgCl]. A maximum conductivity was observed at 30 wt.% of AgCl i.e. the composition: (70PEO:30AgCl) with conductivity 6.0×10^{-7} $S.cm^{-1}$ [15] and this have been used as a host polymer for the synthesis of the present blended solid polymer electrolytes (BSPEs). Figure 2 shows the conductivity plot of hot-pressed BSPEs: (1-x) [70PEO:30AgCl] + x PVP, where $0 \leq x \leq 15$ in wt.%. One can note from the figure that the conductivity increased rapidly as the PVP ratio increased up to 3 wt. (%), then decreased on further addition of the PVP. One-order conductivity enhancement ($\sigma \sim 1.7 \times 10^{-5}$ $S.cm^{-1}$) was achieved at room temperature for PEO host complexes with 3 wt% of PVP. This blended SPE film composition: 97 [70PEO:30AgCl] + 3 PVP has been referred to as Optimum Conducting Composition (OCC).

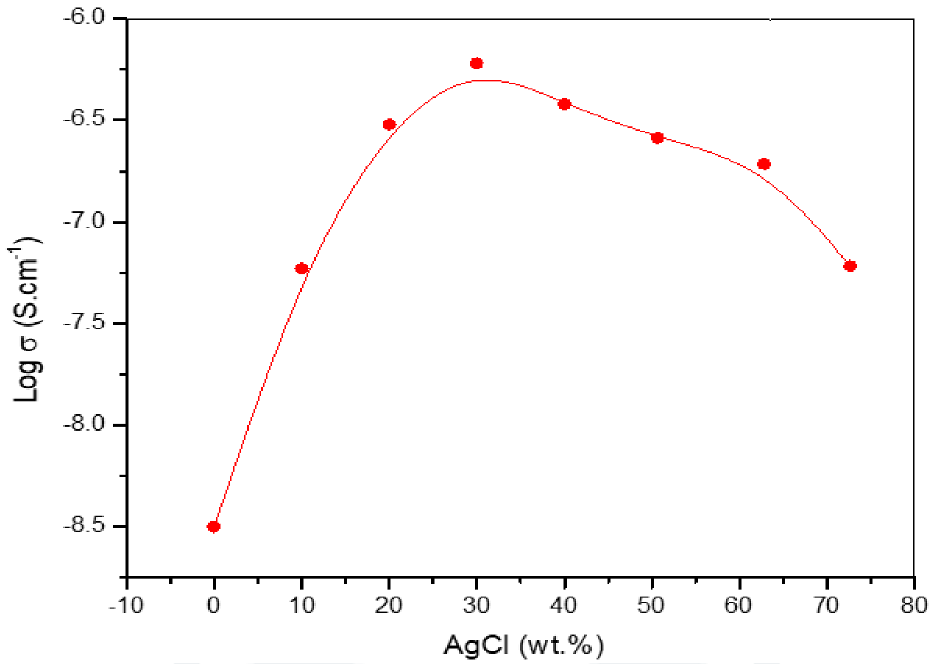

Figure 1. Conductivity variation of solid polymer electrolytes: (PEO:AgCl) at room temperature [15].

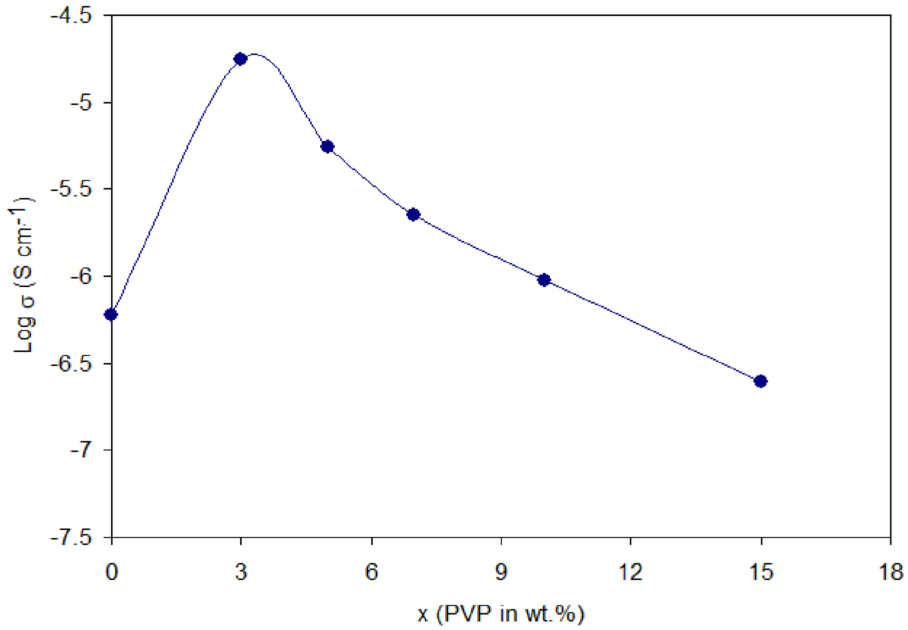

Figure 2. 'Log σ vs x' plot for hot-pressed BSPEs: (1-x) (70PEO:30AgCl) + x PVP, where $0 \leq x \leq 15$ in wt.%.

To explain the conductivity enhancement in the BSPE OCC ionic mobility (μ) and mobile ion concentration studies have been carried out at room temperature. Table 1 shows some important ionic parameters of pure polymer: PEO, SPE host: [70PEO:30AgCl] and BSPE OCC: 97 [70PEO:30AgCl] + 3PVP. It is clear from the table that the overall increase in conductivity in BSPE is due to the increase in both 'μ' & 'n'. One can note that the in μ is due to the increase in the degree of amorphicity in the polymeric electrolyte host and the increase of n is due to the dissociation of a greater number of Ag^+-ions from the salt.

Figure 3 shows the XRD patterns of pure salt PEO and SPE host: (70PEO:30AgCl) and BSPE OCC: 97(70PEO:30AgCl) + 3 PVP. The XRD of PEO contains two main peaks at 23.15° and 18°, corresponding to 112 and 120 planes, respectively designating its semicrystalline nature [17]. Also, low intense peaks at 14.7°, 26.79° and 35.95° were observed. It can be seen from the figure that characteristic peaks of pure PEO appeared between 2θ = 15-30° is decreased after the addition of salt AgCl as well as PVP. The characteristic peaks of pure PEO became relatively less prominent/ feeble and disappeared after polymer-salt complexation. A new characteristic peak of PVP has been observed at 20^o in the BSPE OCC and it is strong evidence of confirmation of blending of host polymer with PVP. The XRD spectrum of the blend film shows well-defined two diffraction peaks, which confirms the semi-crystalline nature of the blend.

The ionic transference number (t_{ion}) of BSPE OCC: 97(70PEO:30AgCl) + 3 PVP was determined at room temperature using the transient ionic current (TIC) technique, as mentioned. Figure 4 shows the current versus time plot for BSPE OCC. t_{ion} ~ 0.95, was obtained which indicates that 95% of Ag^+ ions are mobile in the system and only a negligible contribution of anions. These are our preliminary results and further investigation is in progress.

Table 1. Some important ion transport parameters of pure PEO, SPE host: (70PEO:30AgCl) [16] and BSPE OCC: 97(70PEO:30AgCl) + 3 PVP.

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 host: (70PEO:30AgCl)	6.0×10^{-7}	5.2×10^{-3}	3.5×10^{14}	0.95	0.49
BSPE OCC: 97(70PEO:30AgCl) + 3 PVP	1.7×10^{-5}	1.0×10^{-2}	4.9×10^{15}	0.95	0.36

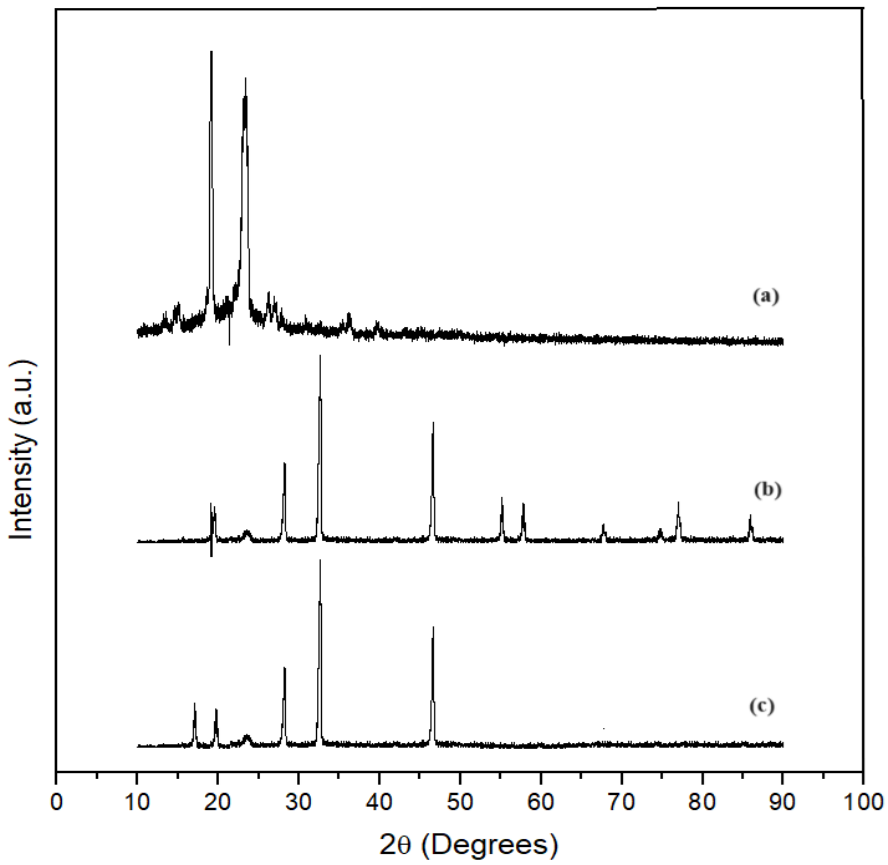

Figure 3. XRD Patterns: (a) pure PEO, (b) SPE host: (70PEO:30AgCl) and (c) BSPE OCC: 97(70PEO:30AgCl) + 3PVP.

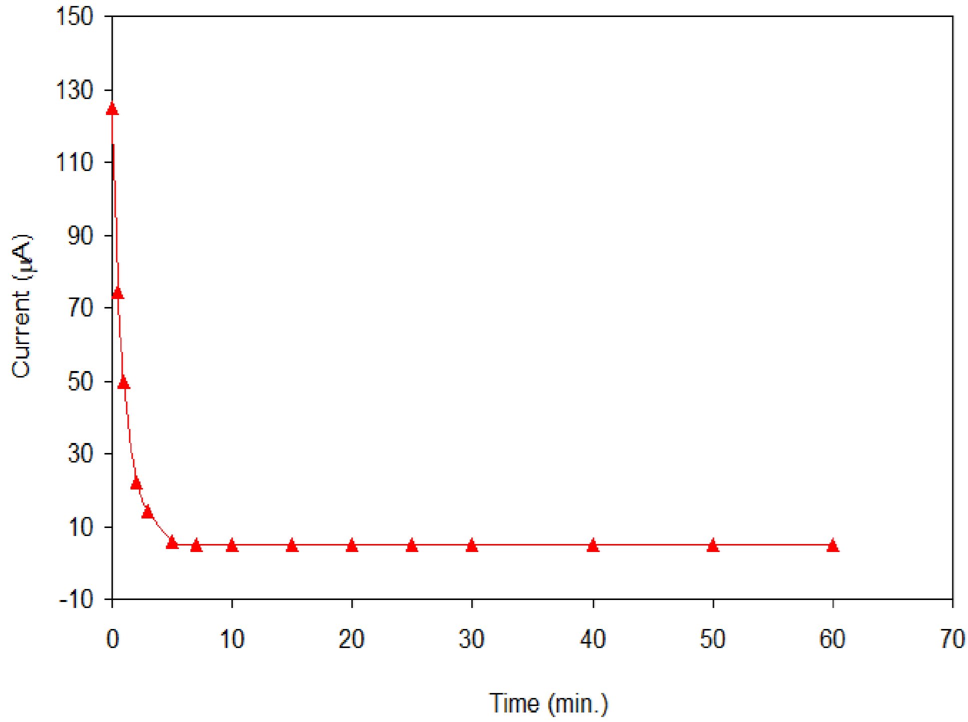

Figure 4. 'Current vs time plot' for hot-pressed BSPE OCC: 97(70PEO:30AgCl) + 3 PVP.

4. Conclusions

Ion transport studies of a newly hot-press synthesized Ag^+ ion conducting blended solid polymer electrolytes (BSPEs): (1-x) (70PEO:30AgCl) + x PVP, where $0\leq x\leq 15$ in wt.%. has been successfully explained. The ionic conductivity measurements have been carried out at different temperatures. The conductivity enhancement at 3 wt% of PVP is due to the increase in both ionic mobility (μ) and mobile ion concentration (n). The ionic transference number measurements indicated the newly synthesized blended solid polymer electrolyte is an ionic system. The charge transport is due to Ag^+ ions and only a negligible contribution of anions (Cl^-).

Declaration of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

References

1. Gray FM. Polymer Electrolytes: Fundamentals and Technological Applications, New York: VCH Publishers; 1991.
2. Agrawal RC, Chandra A. Ion transport and electrochemical cell performance studies on hot-press-synthesized Ag^+ ion conducting electroactive polymeric membranes: (1-x) PEO: x [0.7(0.75AgI:0.25 AgCl):0.3 MI]. J Phys D Appl Phys. 2007; 40: 7024-7031.
3. Agrawal RC, Pandey GP. Solid Polymer Electrolytes: Materials Designing and All-solid-state Battery Applications: An Overview. J Phys D Appl Phys. 2008; 41: 223001.

4. Lin D, Liu W, Liu Y, Lee HR, Hsu PC, Liu K, Cui Y. High Ionic Conductivity of Composite Solid Polymer Electrolyte via In Situ Synthesis of Monodispersed SiO_2 Nanospheres in Poly(ethylene oxide). Nano Lett. 2016; 16: 459-465.
5. Ngai KS, Ramesh S, Ramesh K, Jaun JC. A review of polymer electrolytes: fundamental, approaches and applications. Ionics. 2016; 22: 12591279.
6. Choi NS, Lee Y, Park J, Ko JM. Preparation and electrochemcial characteristics of plasticized polymer electrolytes based upon a P (VdF-co-HFP)/PVAc blend. Electrochim. Acta. 2001; 46: 1581-1586.
7. Chandra A. Hot-pressed PEO-PVP blended solid polymer electrolytes: Ion transport and battery application. Polymer Bulletin. 2016; 73: 2707-2718.
8. Brza MA, Aziz SB. The study of ion transport parameters using two models in plasticized sodium ion conducting polymer blend electrolytes. Polymer Bulletin. 2023; 81: 3021-3042.
9. Paren BA, Nguyen N, Balance V, Hallianan DT, Kennemur JG, Winey KI. Superionic Li-ion transport in a single-ion conducting polymer blend electrolyte. Macromolecules. 2022; 55: 4692-4702
10. Choudhary S. Structural, optical, dielectric and electrical properties of (PEO–PVP)–ZnO nanocomposites. J Phys Chem Solid. 2018; 121: 196-209.
11. Appetecchi GB, Croce F, Hasson J, Scrosati B, Salomon M, Cassel F. Hot-pressed, Dry, Composite, PEO-based Electrolyte Membranes: I. Ionic Conductivity Characterization. J Power Sources. 2003; 114: 105-112.
12. Agrawal RC, Chandra A, Bhatt A, Mahipal YK. Investigations on ion transport property and battery discharge characteristics studies on hot-pressed Ag^+ ion conducting nano-composite polymer electrolytes: (1-x) [90PEO:10AgNO$_3$] : x SiO_2. New J Phys. 2008; 10: 043023.
13. Pandey GP, Hashmi SA, Agrawal RC. Hot-press synthesized polyethylene oxide based proton conducting nanocomposite polymer electrolyte dispersed with SiO_2 nanoparticles. Solid State Ionics. 2008; 179: 543-549.
14. Chandra A. Preparation and characterization of hot-pressed solid polymer electrolytes: (1-x) PEO: x NaBr. Indian J Pure Appl Phys. 2016: 54: 583-588.
15. Chandra A, Chandra A, Dhundhel RS, Jain A, Thakur K, Thakur SS, Basak S, Khan MZ, Bhatt A. Silver ion conducting solid polymer electrolytes: Synthesis and ion transport studies. Indian J. Pure & Applied Physics. 2020: 58: 686-690.
16. Chandra A, Chandra A, Dhundhel RS. Electrolytes for sodium ion batteries: a short review. Indian J Pure Appl Phys. 2020; 58: 113-119.
17. Rajeh A, Morsi M, Elashmawi I. Enhancement of spectroscopic, thermal, electrical and morphological properties of polyethylene oxide/carboxymethyl cellulose blends: Combined FT-IR/DFT. Vacuum. 2019; 159: 430-440.