



# Synthesis of Ion Conducting Hot-pressed Glass Polymer Electrolytes

Angesh Chandra, Alok Bhatt, Archana Chandra

Dept. of Applied Physics, Shri Shankaracharya Institute of Professional Management & Technology, Raipur – 492015, C.G., India

Department of Applied Physics, Bharti College of Engineering & Technology, Durg – 491001, C.G., India

Dr. C.V. Raman University, Kargi Road Kota, Bilaspur, C.G., India

Email: chandrassi@gmail.com, abssi@rediffmail.com, archanachem.chandra@gmail.com

**Abstract** - A new hot-press synthesized an  $\text{Ag}^+$  ion conducting glass-polymer electrolytes (GPEs):  $(1-x)$  PEO:  $x$   $[0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)]$ , where  $0 < x < 50$  wt.%, are reported. Silver ion conducting glass and GPEs were casted using melt-quenching and hot-press techniques, respectively. The composition:  $70\text{PEO}:30[0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)]$  with conductivity  $(\sigma) \sim 8.5 \times 10^{-7} \text{ S.cm}^{-1}$  was identified as highest conducting composition from the compositional dependent conductivity study and this has been referred to as the Optimum Conducting Composition (OCC). Approximately two and half orders of conductivity enhancement have been achieved in the present GPE OCC from that of the pure polymer PEO. The ion transport behavior has been reported on the basis of experimental measurements on some basic ionic parameters viz. ionic mobility ( $\mu$ ), mobile ion concentration ( $n$ ) and ionic transference number ( $t_{\text{ion}}$ ).

**Key Words**- Hot-press technique; glass polymer electrolytes; ionic conductivity; ionic transference number.

**Broad Area**- Applied Physics.

**Sub-Area**-Polymer Science.

## I. INTRODUCTION

Solid polymer electrolytes (SPEs) including nano-composite polymer electrolytes (NCPEs) and glass polymer electrolytes (GPEs), complexed with variety of ionizable salts show tremendous technological applications [1-3]. The main materials advantages of these polymer electrolytes are their good mechanical processibility, ease of fabrication in the thin flexible film forms which make them as appropriate choices in fabricating all-solid-state thin film electrochemical devices viz. mini/ micro batteries of desirable shapes/sizes. A glass electrolyte is one of the best solid electrolytes for the solid state battery applications but it is very difficult to handle at room temperature because of its glassy phase. To overcome these problems, glass-polymer electrolytes (GPEs) have been proposed [4-6]. GPEs are easy to handle, relatively high ionic conductivity, high mechanical flexibility and shows no side reaction between glass electrolyte and polymer electrolyte. SPE/ GPE films are prepared, traditionally by a solution-cast/ sol-gel methods. However, recently a

novel hot-press technique has been developed for casting SPE/ GPE films. Hot-press technique has several procedural conveniences viz. solution free/ dry, least expansive, quicker procedure etc. than those of solution-cast method [7-9]. In the present paper, we report the synthesis of a new  $\text{Ag}^+$  ion conducting PEO-based glass polymer electrolytes (GPEs):  $(1-x)$  PEO:  $x$   $[0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)]$ , where  $0 < x < 50$  wt.%, using hot-press technique. The ion transport behavior have been studied on the basis of experimental measurements on some basic ionic parameters viz. conductivity ( $\sigma$ ), ionic mobility ( $\mu$ ), mobile ion concentration ( $n$ ), ionic transference number ( $t_{\text{ion}}$ ).

## II. EXPERIMENTAL DETAILS

Poly (ethylene oxide) PEO ( $10^5$  Mw, Aldrich, USA), AgI (purity >98%, Reidel India), AgCl (>99%, Reidel India),  $\text{Ag}_2\text{O}$  (>98%, Reidel India) &  $\text{WO}_3$  (>99%, Reidel India) has been used for synthesis of a new Glass Polymer Electrolytes (GPEs):  $(1-x)$  PEO:  $x$   $[0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)]$ , where  $0 < x < 50$  in wt.%. Firstly, the  $\text{Ag}^+$  ion conducting phosphate glass:  $0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)$  have been prepared using melt-quenching technique [10]. This ion conducting glass was used as a host salt for synthesis of GPEs. The dry powders of pure polymer PEO and salt in appropriate wt.% ratios were homogeneously mixed for ~ 30 min at room temperature then heated separately ~  $70^\circ\text{C}$  (close to the melting point of PEO) for ~ 30 min with mixing continued. It resulted into a soft lump/ slurry which was then pressed (~  $1.25 \text{ ton/cm}^2$ ) between two SS- cold blocks, giving rise to a uniform film of thickness ~ 0.013 cm. The details related to hot-press casting of other SPEs/ GPEs and conductivity ( $\sigma$ ), mobility ( $\mu$ ),  $t_{\text{ion}}$  measurements have been given elsewhere in the literature [11,12].

## III. RESULTS AND DISCUSSION

An  $\text{Ag}^+$  ion conducting glass electrolyte:  $[0.7(0.75\text{AgI}:0.25\text{AgCl}):0.3(\text{Ag}_2\text{O}:\text{WO}_3)]$  in mol. wt. %, have been synthesized by melt-quenching technique, as reported elsewhere [10]. This ion conducting glass

electrolyte has been used for the synthesis of the present GPEs: (1-x) PEO: x [0.7(0.75AgI: 0.25AgCl): 0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)], where 0 < x < 50 in wt.%. Figure 1 shows the room temperature conductivity ( $\sigma$ ) variation with different salt concentration for hot-pressed GPEs. The conductivity ( $\sigma$ ) increased abruptly ( $\sim 10^2$  times) after the addition of salt in the host polymer. However, a moderate sized  $\sigma$ -maxima appeared at x = 30 wt.% and then decreases on further addition of salts. The GPE films beyond 50 wt.% salt concentration were brittle and appeared physically less stable. GPE film: 70PEO: 30[0.7(0.75AgI:0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)], with room temperature conductivity ( $\sigma \sim 8.5 \times 10^{-7}$  S/cm), exhibited optimum conductivity and this has been referred to as Optimum Conducting Composition (OCC). The two and half orders of conductivity enhancement in the present GPE OCC have been achieved at room temperature. The ionic conductivity increase in the present GPE OCC is due to increase in degree of amorphicity and this can also be explained by ionic mobility ( $\mu$ ) and mobile ion concentration (n) measurements. Figure 2 shows 'log  $\mu - x$ ' and 'log n - x' plots for GPEs: (1-x) PEO: x [0.7(0.75AgI:0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)]. It is obvious from the figure that both the variations are almost analogous to 'log  $\sigma - x$ ' and the highest values of  $\mu$  and n were obtained at x = 30 wt.% at room temperature. These results clearly indicated the fact that the increase in room temperature conductivity of GPE OCC is due to the increase in both ' $\mu$ ' & 'n'.

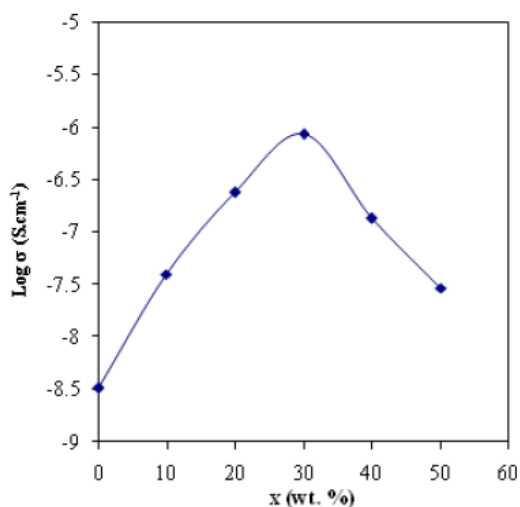


Figure 1. 'Log  $\sigma - x$ ' plot for GPEs: (1-x) PEO: x [0.7(0.75AgI: 0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)].

The ionic transference numbers ( $t_{ion}$ ) of pure glass electrolyte and GPE OCC have been evaluated using dc polarization technique. The variation of current with time is shown in Figure 3.  $t_{ion}$  was calculated using the following well-known equation:

$$t_{ion} = 1 - [I_e / I_T] \quad (1)$$

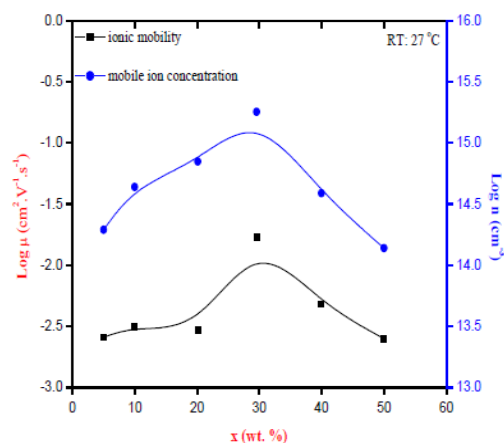


Figure 2. 'Log  $\mu - x$ ' and 'Log n - x' plots for glass polymer electrolytes: (1-x) PEO: x [0.7(0.75AgI: 0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)].

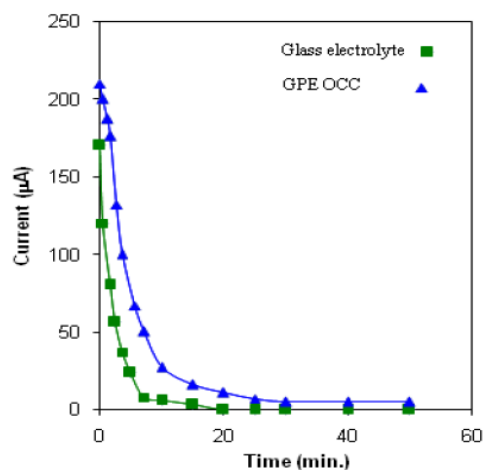


Figure 3. 'Current vs time' plots for the pure glass electrolyte: [0.7(0.75AgI: 0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)] and GPE OCC: 70 PEO: 30 [0.7(0.75AgI: 0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)].

where  $I_e$  is the electronic current and  $I_T$  is the total current.  $t_{ion} \sim 1$  and 0.95 obtained for pure glass electrolyte and GPE OCC respectively. It is indicative that the majority of charge carriers ( $\sim 95\%$ ) are cations  $Ag^+$  and only a negligible contribution of anions in GPE and hence this can be potentially used for fabrication of ion conducting devices.

Table 1 shows the ionic conductivity ( $\sigma$ ) and ionic transference number ( $t_{ion}$ ) of pure PEO, glass electrolyte and GPE OCC for direct comparison. Figure 4 shows 'log  $\sigma - 1/T$ ' variation for GPE OCC: 70 PEO: 30 [0.7(0.75AgI: 0.25AgCl): 0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)]. The plot exhibits a linear increase in conductivity as temperature increased including a  $\sigma$ -jump (indicated by an arrow) at  $\sim 65 - 70$  °C. This temperature corresponds to semicrystalline-amorphous phase transition of the host polymer PEO. The linear portion below this transition can be expressed by following Arrhenius equation:

$$\sigma(T) = 4.30 \times 10^{-3} \exp(-0.234/kT) \quad (2)$$

where 0.234 (eV) is the activation energy ( $E_a$ ) computed by least square linear fitting of the data.

**Table 1. Room temperature ionic conductivity ( $\sigma$ ) and ionic transference number ( $t_{ion}$ ) of pure PEO, glass electrolyte and GPE OCC.**

Electrolytes	$\sigma$ (S.cm <sup>-1</sup> )	$t_{ion}$
Pure polymer: PEO	$2.5 \times 10^{-9}$	---
Glass electrolyte: [0.7(0.75AgI: 0.25AgCl): 0.3(Ag <sub>2</sub> O:WO <sub>3</sub> )]	$4.0 \times 10^{-3}$	1
GPE OCC: 70PEO: 30[0.7(0.75AgI:0.25AgCl):0.3(Ag <sub>2</sub> O:WO <sub>3</sub> )]	$8.5 \times 10^{-7}$	0.95

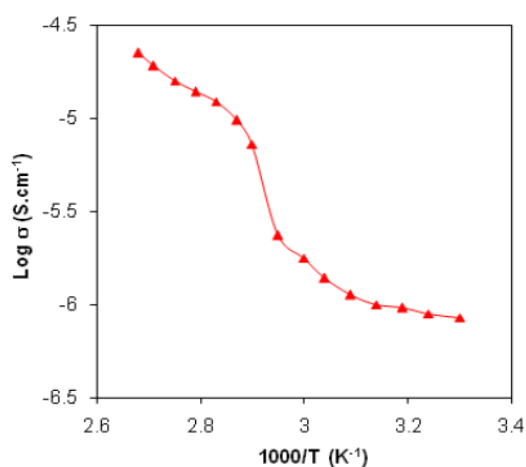


Figure 4. ‘Log  $\sigma - 1/T$ ’ plot for GPE OCC: 70 PEO: 30 [0.7(0.75AgI: 0.25AgCl): 0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)].

#### IV. CONCLUSIONS

A new ion conducting glass-polymer electrolyte (GPE): 70PEO: 30[0.7(0.75AgI:0.25AgCl):0.3(Ag<sub>2</sub>O:WO<sub>3</sub>)] has been synthesized using a hot-press technique instead of the solution cast method. A conductivity enhancement of more than two and half orders of magnitude than that of the pure polymeric host PEO was achieved. The characterization of ion transport behavior has been done in term of the basic ionic parameters:  $\sigma$ ,  $\mu$ ,  $n$ ,  $t_{ion}$  determined using different experimental techniques. The low activation energy in newly synthesized GPE OCC indicates that it can be potential used for solid state device applications.

#### ACKNOWLEDGMENT

One of the author (Angesh Chandra) sincere thanks to DST SERB, New Delhi for providing financial support through the ‘SERB DST Young Scientist Research Project’ (No. SR/FTP/PS-23/2009).

#### REFERENCES

[1] M. B. Armand, Polymer Electrolyte Reviews, Amsterdam: London, 1987.

[2] S. Chandra, Superionic Solids- Principle and Applications, North Holland: Amsterdam, 1981.

[3] R. C. Argawal, and G.P. Pandey, Solid polymer electrolytes: Materials designing and all-solid-state battery applications: An overview, J. Phys. D: Appl. Phys., vol. 41, pp. 223001, 2008.

[4] B. Kumar, J. D. Schaffer, M. Nookala, and L. G. Scanlon, An electrochemical study of PEO:LiBF<sub>4</sub>-glass composite electrolytes, J. Power Sources, vol. 47, pp. 63-78, 1994.

[5] X. W. Zhang, C. Wang, A. J. Appleby, and F. E. Little, Characteristics of lithium-ion-conducting composite polymer-glass secondary cell electrolytes, J. Power Sources, vol. 112, pp. 209-215, 2002.

[6] A. Chandra, Synthesis and ion transport characterization of hot-pressed Ag<sup>+</sup> ion conducting glass-polymer electrolytes, Indian J. Phys., vol. 87, pp. 643-649, 2013.

[7] G. B. Appetecchi, F. Croce, J. Hassoun, B. Scrosati, M. Salomon, and F. Cassel, Hot-pressed, dry, composite, PEO-based electrolyte membranes: I. Ionic conductivity characterization, J. Power Sources, vol. 114, pp. 105-112, 2003.

[8] A. Chandra, and A. Chandra, Hot-pressed polymer electrolytes: Synthesis & characterization, Germany: Lambert Academic Publication, 2010.

[9] R. C. Agrawal, Y. K. Mahipal, and R. Ashrafi, Materials and ion transport property studies on hot-pressed solid polymer electrolyte membranes: [(1-x)PEO:xKIO<sub>3</sub>], Solid State Ionics, vol. 92, pp. 6-8, 2011.

[10] R. C. Agrawal, M. L. Verma, A. Bhatt, and R. Kumar, Investigation on silver tungstated glass: x [0.72AgI:0.25AgCl]: (1-x) (Ag<sub>2</sub>O:WO<sub>3</sub>) - A new Ag<sup>+</sup> ion conducting solid electrolyte system, Proc. 7<sup>th</sup> Int. Symposium on Advances in electrochemical science and technology, Chennai, pp. D170-D173, 2002.

[11] A. Chandra, Hot-pressed Ag<sup>+</sup> ion conducting glass-polymer electrolytes: Synthesis and battery application, Portugaliae Electrochimica Acta, vol. 30, pp. 261-266, 2012.

[12] A. Chandra, A. Chandra, and K. Thakur, Synthesis, characterization and device application of hot-pressed solid polymer electrolytes: (1-x) PEO: x NaHCO<sub>3</sub>, Polym. Bull., vol. 71, pp. 181-192, 2014.

