

Ionic drift velocity measurement on hot-pressed Ag⁺ ion conducting glass-polymer electrolytes

ANGESH CHANDRA

Solid State Physics Research Laboratory, Department of Applied Physics,
Shri Shankaracharya Institute of Professional Management & Technology, Raipur 492 015, India

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Abstract. Ionic drift velocity (v_d) measurements of a new Ag⁺ ion conducting glass-polymer electrolytes (GPEs): $(1-x)$ PEO : x [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)], where $0 < x < 50$ wt%, were reported. GPEs were casted using the hot-press techniques developed in recent times. The composition: 70PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)] with conductivity (σ) $\sim 7.7 \times 10^{-7}$ S cm⁻¹ was identified as highest conducting composition from the compositional-dependent conductivity studies. The ionic mobility (μ), mobile ion concentration (n), ionic transference number (t_{ion}) and ionic drift velocity (v_d) of GPEs were determined at different temperatures with the help of the d.c. polarization technique and other well-known important relations.

Keywords. Glass-polymer electrolytes; hot-press technique; ionic transference number; ionic drift velocity.

1. Introduction

Among the known superionic solids, solid polymer electrolytes (SPEs), which include conventional as well as micro/nanocomposites and gels, have attracted widespread attention as the most appropriate choice to fabricate flexible, light-weighted, compact and laminated all-solid-state batteries.^{1–5} The first ion conducting SPE: poly(ethylene oxide) PEO : Li⁺-salt complex was discovered in 1973.¹ Since then, large numbers of polymer electrolyte materials involving variety of mobile ions, viz., H⁺, Li⁺, Ag⁺, K⁺, Na⁺, etc., as principal charge carriers, have been reported in the last nearly three and half decades. The higher molecular weight PEO has been commonly employed as polymeric host for salt complexation as it possesses exceptional ability to dissolve high concentrations of variety of salts.⁶

The ion conducting glassy superionic solid 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. In the recent years, to overcome these problems, glass-polymer electrolytes (GPEs) have been proposed.^{7–9} The ion conducting GPEs show several advantages such as high mechanical flexibility, high ionic conductivity and stability. Polymer electrolytes are prepared, in general, by complexing/dissolving variety of ionic salts in different kinds of polymeric hosts adopting the usual solution-cast route. In recent times, a novel hot-press (extrusion) method has been developed for casting polymer electrolyte membranes.^{10–17} This technique is relatively more rapid, least expensive and solvent-free procedure as compared with the conventional solution-cast method.

To understand the ion conduction phenomenon and ionic behaviour of Ag⁺ ion conducting GPE systems, the present paper reports, the measurement of ionic drift velocity (v_d) and some other important ionic parameters of hot-press synthesized GPEs: $(1-x)$ PEO : x [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)], where $0 < x < 50$ wt%.

2. Experimental

The AR grade precursor chemicals: poly(ethylene oxide) PEO (10⁵ Mw, Aldrich, USA), AgI (purity > 98%), AgCl (> 99%), Ag₂O (> 98%) and V₂O₅ (> 99%) as supplied by Reidel India Ltd. have been used for synthesis of Ag⁺ ion conducting GPEs : $(1-x)$ PEO : x [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)], where $0 < x < 50$ wt%. The details about the synthesis of the present GPEs have been given in previous communication.¹⁸ The ionic conductivity (σ)-measurements were carried out by using the well-known equation: $\sigma = [l/(R_b \cdot A)]$, where R_b is the bulk resistance, l the thickness and A the cross-sectional area of the sample pallet. The bulk resistance R_b was determined from the impedance analysis by using an LCR-bridge (model: HIOKI 3520-01, Japan). The ionic mobility was determined with the help of following equation: $\mu = [d^2/V \cdot \tau]$, where d is the thickness of NCPE films, V the applied external d.c. potential, and τ the time of flight. The time of flight (τ) was determined directly employing the d.c. polarization Transient ionic current (TIC) technique using an x - y - t recorder (model: Graphtec WX 2300-1L, Japan).^{14,19} The mobile ion concentration (n) was evaluated from σ and μ data by using the well-known relation: $\sigma = [n \cdot q \cdot \mu]$, where q is the charge. To ascertain the extent of the ionic and electronic

(chandrassi@gmail.com)

contributions to the total conductivity, a measurement of ionic transference number (t_{ion}) was made using the d.c. polarization technique with the help of the following equation: $t_{ion} = [1 - (I_e/I_T)]$, where I_e is the electronic current and I_T the total current. Finally, the ionic drift velocity (v_d) of GPE OCC has been evaluated using the following well-known equation: $v_d = [I_T/A \cdot n \cdot q]$, where A is the cross-sectional area of the sample pallet and q the charge on the mobile ion.

3. Results and discussion

Figure 1 shows the room-temperature conductivity (σ) variation as a function of salt (glass electrolyte) concentration for the hot-pressed GPEs: $(1-x)$ PEO : x [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)], where $0 < x < 50$ wt%. The GPE films beyond 50% salt concentration were unstable and brittle. One can clearly note from the figure that the conductivity increased rapidly as the salt concentration increased upto 30 wt%, then decreased on further addition of the salt. A conductivity enhancement of approximately two and half orders of magnitude was achieved at room temperature complexes with 30 wt% of glassy salt: [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)] as compared with the conductivity of pure PEO. This GPE composition: 70PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)] with conductivity (σ) $\sim 7.7 \times 10^{-7}$ S cm⁻¹ has been referred to as optimum conducting composition (OCC).¹⁸ The increase in conductivity upto 30 wt% of addition of salts is due to the increase in the degree of amorphicity or decrease in the degree of crystallinity and

the decrease in ionic conductivity at higher salt concentration is due to the usual blocking effect which can also be explained by the various models.^{14,20,21}

The ion transport in superionic solids including the present GPE or polymeric phase is generally governed by hopping/jumping mechanism. The ionic conductivity in such solids can be expressed by the following equation:¹⁴

$$\sigma(T) = n_i(T) q_i \mu_i(T), \quad (1)$$

where n_i , μ_i and q_i are the mobile ion concentration, ionic mobility and charge, respectively, of the i th type of transporting ion. These ionic parameters (σ , μ , n) are the temperature dependent and usually follow the Arrhenius variation. In case of normal ionic solids (e.g., alkali/silver halides), the extent of ionic conductivity predominantly depends on concentration of the point defects (viz., Schottky and Frenkel). However, in superionic solids, the number of mobile ions available for conduction at the initial stage is usually very large due to their microscopic/macrosopic disordered structures and the ions are continuously jumping/hopping to various equienergetic sites akin to the ionic movement in liquid phase. Hence, the factor involving energy of defect formation is negligibly small for superionic systems and the equation for conductivity can simply be generalized to the following Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/kT), \quad (2)$$

where σ_0 is the pre-exponential factor and E_a the activation energy for ion transport, k the Boltzmann constant, and T the temperature in Kelvin. To evaluate the activation energy (E_a) and ionic drift velocity (v_d) of the present GPE OCC, the temperature-dependent conductivity measurements were carried out. Figure 2 shows 'log $\sigma - 1/T$ ' plot for the GPE OCC: 70 PEO : 30 [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].

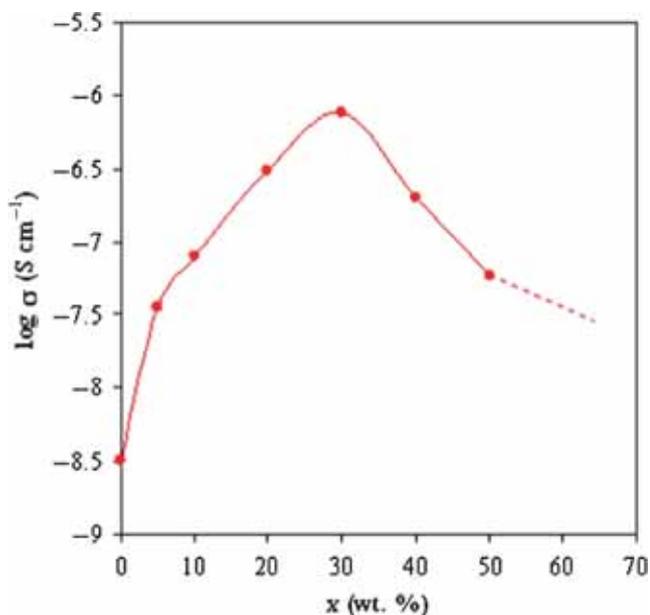


Figure 1. 'log $\sigma - x$ ' plot for GPEs: $(1-x)$ PEO : x [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].^{17,18}

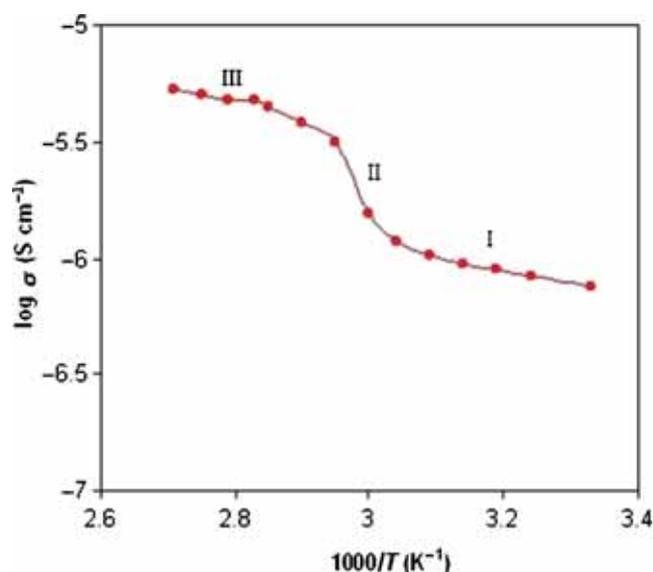


Figure 2. 'log $\sigma - 1/T$ ' plot for GPE OCC: 70PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].

The conductivity increased with temperature followed by the three important regions I, II and III, as indicated in figure 2. The regions I and III might be due to intra-chain and inter-chain segmental motions of Ag⁺ ions and region II may be due to the phase transition of the polymer from the crystalline to amorphous. The increase in conductivity with temperature can also be related to the increase in the number of mobile charge carriers and available of more number of conduction paths/free volumes to the transport of ions. The higher the number of charge carriers, higher the mobility and hence higher the conductivity. This can be explained on the basis of the free volume model and hopping of charge carriers.^{14,17,21,22} The straight line portion of ‘log $\sigma - 1/T$ ’ plot (below the transition temperature, i.e., region I) gives the following Arrhenius-type equation:

$$\sigma(T) = 9.63 \times 10^{-5} \exp(-0.126/kT) \text{ [S cm}^{-1}\text{]}, \quad (3)$$

where 9.63×10^{-5} is the pre-exponential factor (σ_0), 0.126 the activation energy (E_a) in eV. The low ‘ E_a ’ is indicative of relatively easier ion migration in the present GPE system and this can be potentially used for solid-state electrochemical device applications.

The ionic mobility (μ) and mobile ion concentration (n) also vary with the temperature akin to conductivity, as mentioned in equation (1). Therefore, the ionic mobility (μ) and mobile ion concentration (n) of GPE OCC: 70 PEO : 30 [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)] have also been measured as a function of temperature by the d.c. polarization technique, as mentioned in Section 2. ‘log $\mu - 1/T$ ’ and ‘log $n - 1/T$ ’ variations for the GPE OCC are shown in figure 3, which can be expressed by the following Arrhenius equations:

$$\mu(T) = 1.79 \times 10^2 \exp(-0.256/kT) \text{ [cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{]}, \quad (4)$$

$$n(T) = 3.37 \times 10^{20} \exp(-0.326/kT) \text{ [cm}^{-3}\text{]} \quad (5)$$

where the numerals 0.256 and 0.326 in the arguments of exponentials are the energies in eV, involved in the thermally activated process, designated as the energy of migration (E_m) and energy of formation (E_f), respectively. It is obvious from the figure that n increased with the increase in temperature in GPE OCC which may be attributed to the fact that many of Ag⁺ ions, loosely entangled with the polymeric chain, got themselves detached as the temperature increased and became available for conduction. μ also increased with temperature for GPE OCC. Increase in μ may be a consequence of structural expansion of the polymeric host as well as increase in the kinetic energy of mobile ions with the increase in temperature.

To understand the ionic nature of the present GPE system, ionic transference number (t_{ion}) measurement have been carried out with the help of total current (I_T) with time plots at different temperatures, as shown in figure 4. The t_{ion} has

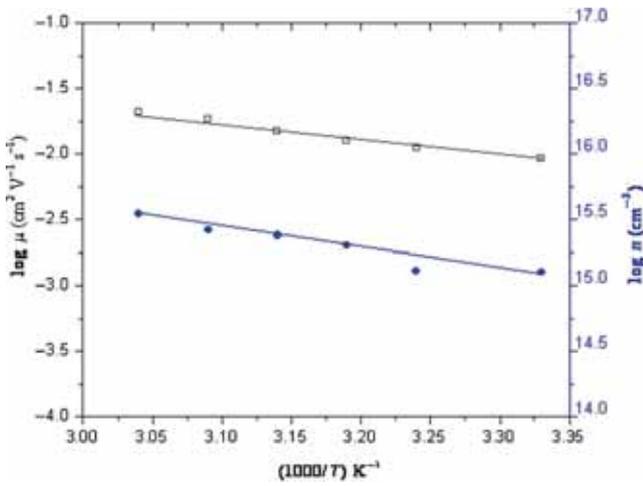


Figure 3. ‘log $\mu - 1/T$ ’ (\square) and ‘log $n - 1/T$ ’ (\bullet) plots for GPE OCC: 70 PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].

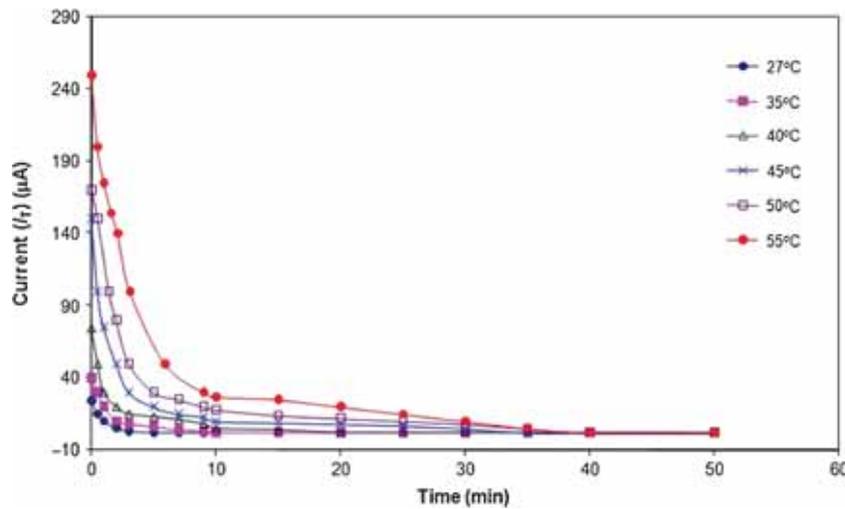


Figure 4. ‘Current vs. time’ plots for GPE OCC: 70PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)] at different temperatures.

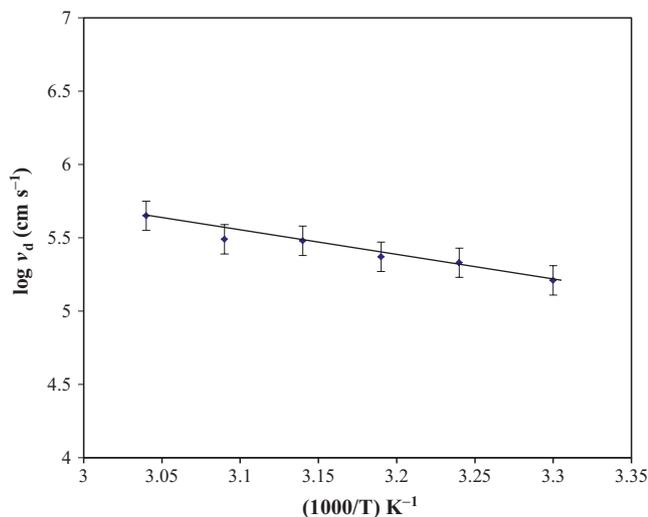


Figure 5. ‘log $v_d - 1/T$ ’ plot for GPE OCC: 70 PEO : 30[0.8(0.75 AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].

been evaluated using the d.c. polarization technique, as mentioned in Section 2. In the present GPE system, $t_{ion} = 0.98$ obtained, i.e., ~98% of Ag⁺ ions are mobile in the system and only 2% of Ag⁺ ions are blocked by the nonconducting pure polymer PEO. It is also indicated that a very small contribution (~2%) of anion (I⁻) in the total conductivity of the present GPE system.

The time elapsed for I_T to approach a minimum value of the current got prolonged as the sample temperature increased. The mobile ions would be more agitated thermally at higher temperatures, would require relatively longer time to get polarized with a fixed value of d.c. potential applied across the sample. Also, the magnitude of peak current (I_T) increased as the sample got hot, as also observed in our earlier communications.^{14,23,24} This may be attributed to the increase in n and/or ionic drift velocity (v_d).

This experimental result on t_{ion} was used to evaluate v_d at different temperatures. Figure 5 shows ‘log $v_d - 1/T$ ’ plot for GPE OCC: 70 PEO : 30 [0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)], which can be expressed by the following Arrhenius-type equation:

$$v_d = 1.78 \times 10^3 \exp(-0.243/kT) \quad [\text{cm s}^{-1}], \quad (6)$$

where the numeral 0.243 is the drift energy (E_d) in eV, involved in this thermally activated process for GPE OCC. v_d is directly proportional to μ at a fixed external d.c. electric field, ‘log $v_d - 1/T$ ’ and ‘log $\mu - 1/T$ ’ variations and the energies: E_d and E_m , involved in the two separate thermally activated processes (figures 4 and 6), are almost identical.

To check again that during the d.c. polarization measurements the externally applied potential should not cause any polarization build-up effect in the sample, the applied voltages (below 0.5 V) applied across the sample were plotted against instant current values obtained. Figure 6 shows ‘ I_T vs. V ’ plot for GPE OCC and it is clearly illustrated that the current varied linearly with applied voltage following Ohm’s

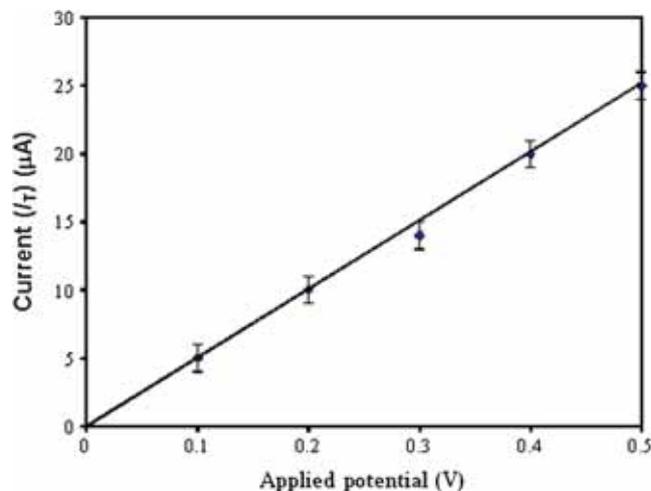


Figure 6. ‘ I_T vs. V ’ plot for GPE OCC: 70 PEO : 30[0.8(0.75AgI : 0.25AgCl) : 0.2(Ag₂O : V₂O₅)].

law very well and hence, indicative of no-polarization-charge build-up effects in the present GPE system.

4. Conclusion

The ionic drift velocity (v_d) of hot-pressed GPE has been determined at different temperatures. Drift velocity is directly proportional to ionic mobility and hence the energies E_d and E_m involved in the two thermally activated processes would be identical. The measurements on ionic transference number (t_{ion}) indicated that the system remained purely ionic with Ag⁺ ions as the sole charge carriers even above the room temperature and hence this can be potentially used for solid-state device application.

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