Ionic Mobility, Drift Velocity, and Dielectric Studies on Ag⁺ Ion Conducting Glassy Electrolytes

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(Received February 4, 2013; Revised April 30, 2013)

Ionic mobility ($\mu$), ionic drift velocity ($v_d$), and dielectric measurements of new Ag⁺ ion conducting glassy systems: $x[0.75\text{AgI}: 0.25\text{AgCl}]$: $(1-x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5]$, where $0.1 < x < 1$ in molar weight fraction, are reported. The present glassy electrolytes have been synthesized by the melt-quench technique using a high-speed twin roller-quencher. An alternate host salt: ‘quenched [0.75AgI: 0.25AgCl] mixed system/solid solution’ has been used in place of the traditional host AgI. The compositional dependence conductivity studies on the glassy systems indicated that the composition $0.8[0.75\text{AgI}: 0.25\text{AgCl}]$: $0.2[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5]$ shows the highest conductivity ($\sigma \sim 9 \times 10^{-3}$ S/cm) at room temperature. Some other basic ion transport parameters, viz. the mobile ion concentration ($n$) and ion transference number ($t_\text{ion}$), have also been characterized using different experimental techniques.

DOI: 10.6122/CJP.52.864 PACS numbers: 66.30.hh, 51.10.+y, 78.20.Ci

I. INTRODUCTION

Ion conducting superionic solids or solid electrolytes show tremendous technological promise for developing a variety of solid state electrochemical devices, viz. batteries, fuel cells, sensors, supercapacitors, electrochromic displays, etc. On the basis of the physical properties, microstructures, and preparation routes, solid electrolytes have been broadly grouped into different phases, viz. crystalline/polycrystalline, glassy/amorphous, composite, polymeric, etc. Amongst the variety of superionic glasses, Ag⁺ ion conducting glassy electrolytes attracted relatively wider attention, due to the reasons that they exhibit relatively higher room temperature conductivity and the materials handling and synthesizing of the glass are easier. The first Ag⁺ ion conducting glassy electrolyte system, AgI: Ag₂SeO₄, exhibiting very high room temperature conductivity, $\sigma \sim 10^{-2}$ S/cm⁻¹, was synthesized by Kunze in 1973 [1]. Since then, large numbers of fast ion conducting glasses involving a variety of mobile ion species, viz. Ag⁺, Cu⁺, Li⁺, Na⁺, F⁻ etc., have been discovered [2–9]. Fast ion conducting glasses possess several advantageous material properties as compared to their crystalline/polycrystalline counterparts. Some definite advantages include: high

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isotropic ionic conduction, ease of synthesis in a wide variety of shapes/sizes including thin films, wider compositional variations possible, higher structural/chemical/mechanical stability, etc. The majority of the fast Ag\(^{+}\) ion conducting glasses reported in the past are AgI based systems. They are prepared in general by melt-quenching a mixture of AgI as the host salt with glass modifier Ag\(_2\)O and glass former such as B\(_2\)O\(_3\), MoO\(_3\), CrO\(_3\), P\(_2\)O\(_5\) etc. in appropriate molar compositions.

To understand the ion conduction phenomenon and ionic behavior of superionic Ag\(^{+}\) ion conducting glassy systems, the present paper reports on the ionic mobility (\(\mu\)), ionic drift velocity (\(v_d\)), and dielectric measurements of a new Ag\(^{+}\) ion conducting glassy system: \(x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5]\), where \(0.1 < x < 1\) in molar weight fraction, with the help of different experimental techniques.

II. EXPERIMENTAL

The AR grade precursor chemicals: AgI (purity > 98%), AgCl (> 99%), Ag\(_2\)O (> 98%), and V\(_2\)O\(_5\) (> 99%) as supplied by Reidel India Chemicals Pvt. Ltd. have been used for synthesis of the silver vanadate glassy systems: \(x[0.75\text{AgI}: 0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5]\). The details about the synthesis route has been given in our previous communications [10, 11].

The conductivity (\(\sigma\)) measurements were carried out by the following equation:

\[
\sigma = \frac{l}{R_b \cdot A} \text{[S.cm}^{-1}] \tag{1}
\]

where \(R_b\) is the bulk resistance, \(l\) is the thickness and \(A\) is the cross sectional area of the sample material. The bulk resistance \(R_b\) was determined on different samples using an LCR- bridge (model: HIOKI 3520-01, Japan).

The ionic mobility was determined with the help of the following equation:

\[
\mu = \frac{d^2}{V \cdot \tau} \text{[cm}^2\text{V}^{-1}\text{s}^{-1}] \tag{2}
\]

where \(d\) is the thickness of the samples, \(V\) is the applied external d.c. potential (\(\sim 0.5\) V) and \(\tau\) is the time of flight. The time of flight (\(\tau\)) was determined directly employing the dc polarization transient ionic current (TIC) technique by using an x-y-t recorder (model: Graphtec WX 2300-1L, Japan) [12]. The mobile ion concentration (\(n\)) was evaluated from the \(\sigma\) and \(\mu\) data by using the well-known relation:

\[
\sigma = n \cdot q \cdot \mu \text{[cm}^{-3}] \tag{3}
\]

where \(q\) is the charge. The ionic transference number (\(t_{\text{ion}}\)) has also been evaluated using dc polarization technique with the help of the following equation: [12]

\[
t_{\text{ion}} = 1 - \frac{I_e}{I_T} \tag{4}
\]
where \( I_e \) is the electronic current and \( I_T \) is the total current of the solid state cell.

The ionic drift velocity \( (v_d) \) of the mobile ion has been evaluated using the following well-known equation:

\[
v_d = \frac{I_T}{A.n.q},
\]

where \( A \) is the cross-sectional area of the sample pallet and \( q \) is the charge on the mobile ion.

The dielectric constant \( (\varepsilon^*) \) has also been determined with the help of the following well-known equation:

\[
\varepsilon^* = \frac{Z_i}{\omega C_0 (Z_i^2 + Z_r^2)},
\]

where \( \omega \) is the angular frequency \( \equiv 2\pi \nu \), \( C_0 \) is the parallel plate (empty) capacitance, \( Z_i \) is the complex impedance of the imaginary part and \( Z_r \) is the complex impedance of the real part.

III. RESULTS AND DISCUSSION

Figure 1 shows the room temperature conductivity \( (\sigma) \) variations with composition \( (x) \) for the newly synthesized silver-vanadate glassy systems: \( x[0.75 \text{ AgI}: 0.25 \text{AgCl}]: (1 - x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \) as well as the glass electrolyte systems: \( x\text{AgI}: (1 - x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \) prepared in the identical manner using the traditional host salt AgI [10]. The conductivity maxima for both the glass electrolytes was found at \( x = 0.8 \). The newly synthesized glassy electrolyte system: \( 0.8[0.75 \text{AgI}: 0.25 \text{AgCl}]: 0.2[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \) exhibited relatively higher room temperature conductivity as compared to the glass system: \( 0.8[\text{AgI}]: 0.2[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \). This has been referred to as ‘Optimum Conducting Composition (OCC)’ with conductivity \( \sigma \sim 9 \times 10^{-3} \text{ Scm}^{-1} \) at room temperature. A conductivity increase of more than an order of magnitude has been achieved in OCC, from that of the pure quenched host: \( [0.75 \text{Ag}_2\text{O}: 0.25 \text{AgCl}] \), having \( \sigma \sim 3.14 \times 10^{-4} \text{ Scm}^{-1} \) at room temperature [13]. This is indicative of the fact that the superionic \( \alpha \)-like phase of the host has been partially stabilized and/or locked-in in the glass network. The ionic conductivity of the present glassy electrolytes for both the host salts: \( [0.75 \text{AgI}: 0.25 \text{AgCl}] \) and pure AgI are very close to each other, but the ionic conductivity of the present glassy OCC: \( 0.8 [0.75 \text{AgI}: 0.25 \text{AgCl}]: 0.2[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \) is more stable, as compared to traditional glassy electrolytes: \( x\text{AgI}: (1 - x)[\text{Ag}_2\text{O}: \text{V}_2\text{O}_5] \). Hence the present host salt: \( [0.75 \text{AgI}: 0.25 \text{AgCl}] \) is superior as compared to the traditional host salt pure AgI, and a large number of ion conducting glasses as well as other ion conducting electrolytes have been discovered using this alternate host which exhibits electrolyte properties superior to those prepared by the traditional host [10, 13, 14]. The conductivity enhancement in OCC may be due to the increase in the ionic mobility \( (\mu) \) and/or mobile ion concentration \( (n) \). The temperature dependent ionic mobility \( (\mu) \) and mobile ion concentration \( (n) \) measurements were carried on a glass electrolyte OCC with
the help of the dc polarization TIC technique, as mentioned in the Experimental Section. Plots of \( \log \mu - 1/T \) and \( \log n - 1/T \) are shown in Figure 2, which can be expressed by the following Arrhenius equations:

\[
\mu = 4.49 \times 10^{-5} \exp(+0.2/kT) \quad \text{[cm}^2\text{V}^{-1}\text{s}^{-1}] ,
\]

\[
n = 2.76 \times 10^{28} \exp(-0.48/kT) \quad \text{[cm}^{-3}] ,
\]

where the numerals 0.2 and 0.48 are the energies in eV, and, as mentioned, can be designated as the energy of migration (\( E_m \)) and energy of formation (\( E_f \)), involved in the two thermally activated processes, respectively. The positive and negative signs in the arguments of the exponentials indicate the decrease and increase, respectively, of the factors on the left hand side of the above equations with increasing temperature. It can be observed from the figure that \( n(\mu) \) increased (decreased) with increasing temperature, and this can be explained with the help of various theoretical as well as experimental models [15–18]. As the temperature increases the silver salt: Ag\(_2\)O may get dissociated, which in turn, provided additional Ag\(^+\) ions for conduction. The dissociated Ag\(^+\) ions from Ag\(_2\)O are also likely to get attached with the non-bridging oxygen bonds of the different functional groups of the vanadate glass network and become immobile. However, as the temperature increased, some of these immobile Ag\(^+\) ions may get detached from the non-bridging oxygen bonds and become mobile, resulting in an increase in \( n \) with increasing temperature. Nevertheless, Ag\(^+\) ions from silver halides (AgI and/or AgCl) remain always free for transport. The decrease in \( \mu \) with increasing temperature can be understood in terms of the ‘cluster by-pass model’ [17]. According to this model, a glass consists of short range ordered clusters embedded in a highly conductive disordered medium, referred to as connecting tissue, for ion migration. As the temperature increases, some of the non-bridging oxygen functional groups get converted into bridging oxygen functional groups, resulting in the formation of partial/blocked pathways for ion migration by inter-connecting some of the conductive tissues. This, consequently, results in a decrease in the mobility as temperature increases.

The ionic transference number (\( t_{\text{ion}} \)) gives the quantitative information regarding the extent of the ionic contribution to the total charge transport in an ionic/superionic system. \( t_{\text{ion}} \) measurements on the Ag\(^+\) ion conducting glass electrolyte OCC: 0.8\[0.75\text{AgI}: 0.25\text{AgCl}: 0.2\text{Ag}_2\text{O}: \text{V}_2\text{O}_5\] were carried out at room temperature using the TIC technique. Figure 3 shows the current vs. time TIC plots, obtained at different temperatures. It can be clearly noted that the initial total peak current \( (I_T) \) of all the TIC plots eventually approaches zero with the lapse of time. This is indicative of the fact that the Ag\(^+\) ion conducting glass electrolyte OCC remained purely ionic at all temperatures of measurement. Hence, \( t_{\text{ion}} \sim 1 \) which, in turn, revealed the fact that Ag\(^+\) ions are the sole charge carriers in the glass electrolyte. One can further note that the magnitude of \( I_T \) increased as the temperature increased. This is due to the increase in \( n \) with increasing temperature, as clearly observed in the \( \log n - 1/T \) variation (Fig. 2). It can also be noticed that the time required for the peak current to approach zero got longer and longer as the sample temperature increased. Since at higher temperatures the ions are thermally more agitated,
FIG. 1: ‘Plots of log $\sigma - x'$ for glass electrolyte systems: $x[0.75 \text{AgI} : 0.25 \text{AgCl}]$; $(1 - x)[\text{Ag}_2\text{O} : \text{V}_2\text{O}_5]$ (●) and $x\text{AgI} ; (1 - x)[\text{Ag}_2\text{O} : \text{V}_2\text{O}_5]$ (■) [10].

FIG. 2: Plots of ‘log $\mu - 1/T'$ and ‘log $n - 1/T'$ for the glass electrolyte OCC: 0.8[0.75 AgI: 0.25 AgCl]: 0.2[Ag$_2$O: V$_2$O$_5$].

hence they would require more time to get polarized under a fixed value of the applied d.c. voltage. Using the $I_T$ - data of Fig. 3 and $n$ data from Fig. 2, $v_d$ values were calculated at different temperatures. Figure 4 shows the ‘log $v_d - 1/T'$ plot for the Ag$^+$ ion conducting
glass electrolyte OCC: 0.8[0.75AgI: 0.25AgCl]: 0.2[Ag2O: V2O5]. This measurement was also done below T_g. It can be noted that v_d decreased with increasing temperature, obeying the following Arrhenius type equation:

\[ v_d = 3.08 \times 10^{-8} \exp(+0.198/kT) \, [\text{cm. s}^{-1}], \] (9)

where the numeral 0.198 is the drift energy (E_d) in eV involved in this thermally activated process, and the positive sign in the argument of the exponential has the same meaning as explained above. Since, at a fixed value of the applied field across the sample pellet, v_d would always be directly proportional to \( \mu \), hence the temperature variation of v_d must be analogous to that of \( \mu \), and the energies involved in the two separate thermally activated processes should be the same. On comparing ‘log \( \mu \) - 1/T’ (Fig. 2) and ‘log v_d - 1/T’ (Fig. 4), one can clearly note that the two variations are almost similar, and the E_m and E_d values are in very good agreement with each other.

FIG. 3: ‘Current vs time’ plots of glassy electrolyte OCC: 0.8[0.75AgI: 0.25AgCl]: 0.2[Ag2O: V2O5]; I_T – Initial total peak current values at different temperatures.

The frequency dependence dielectric constant (\( \varepsilon^* \)) of the glass electrolyte OCC: 0.8[0.75 AgI: 0.25AgCl]: 0.2[Ag2O: V2O5] has also been evaluated at different temperatures, as mentioned in the Experimental Section. Figure 5 shows the frequency dependent dielectric constant (\( \varepsilon^* \)) of glassy OCC at different temperatures. It can be clearly shown from the figure that the dielectric constant increases as the temperature increases, and this is due to the availability of a larger number of mobile ions in the glass network. It is also clearly observed from the figure that the dielectric constant (\( \varepsilon^* \)) increases with increasing temperature in the low frequency region and decreases with higher frequency. The increase
FIG. 4: Plot of \( \log v_d \cdot 1/T \) for the Ag\(^+\) ion conducting glass electrolyte OCC: 0.8[0.75 AgI: 0.25AgCl]: 0.2[Ag\(_2\)O: V\(_2\)O\(_5\)].

FIG. 5: Frequency dependence of the dielectric constant (\( \varepsilon^* \)) of the glass electrolyte OCC: 0.8[0.75 AgI: 0.25AgCl]: 0.2[Ag\(_2\)O: V\(_2\)O\(_5\)] at different temperatures: 27 (■), 40 (△), 50 (◇), 60 (×), 70 (●), 80 (▲) in °C.

in the dielectric constant in the low frequency region is due to the contribution of charge (Ag\(^+\) ions) accumulation at the interface leading to a net polarization, which results in the formation of a space-charge region [17, 18]. At the higher frequency region, the dielectric constant approaches a constant value, which is due to the result of much more rapid polarization processes occurring in the glasses, and such a type of mechanism can also be
understood with the help of various models, as reported in our recent review article [18].

IV. CONCLUSION

A new fast Ag\(^+\) ion conducting silver vanadate glass solid electrolyte: 0.8[0.75AgI: 0.25AgCl]: 0.2[Ag\(_2\)O: V\(_2\)O\(_5\)] has been synthesized. The drift velocity is directly proportional to the ionic mobility, and hence the energies \(E_d\) and \(E_m\) involved in the two thermally activated processes would be identical. The measurements on the ionic transference number (\(t_{ion}\)) indicated that the system remained purely ionic, with Ag\(^+\) ions as the sole charge carriers even above room temperature.

References