Polarization/self-depolarization studies on Ag\textsuperscript{+} ion conducting quenched [0.75AgI:0.25AgCl] mixed system/solid solution

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Temperature dependent dc polarization/self-depolarization studies, on a Ag\textsuperscript{+} ion conducting system: a quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution, are reported. This system has recently been investigated in the present laboratory as a new and better alternate material in place of conventional host salt AgI. Sample pellets of different thicknesses were sandwiched between graphite (blocking) electrodes and polarized under a constant dc potential (\(-0.5\) V) for different intervals of time. A potential gradient develops across the sample pellet due to accumulation/polarization of mobile Ag\textsuperscript{+} ions at one end. At the state of complete polarization, the potential measured instantly after the removal of the external dc field has been referred to as peak potential $V_p$. $V_p$-values directly indicate the availability of number of mobile Ag\textsuperscript{+} ions in the system at a particular temperature. $V_p$-measurements have been carried out as a function of polarization time and temperature in both $\beta$ and $\alpha$-like phases of the system. The study revealed that the material attains the state of complete polarization in time $t > 5$ min. irrespective of the sample thickness. It is also observed that log $V_p$ versus $1/T$ variation, in both $\beta$ and $\alpha$-like phases of the material, is almost analogous to log $n$ versus $1/T$ variation, reported earlier for the present system. This, in turn, has confirmed one of our assertion made earlier in regards to superionic conduction of $\alpha$-like phase of the material which is predominantly due to an abrupt increase in $n$ in this phase.

1 Introduction

'Superionic solids' or 'solid electrolytes' are a new class of solid state ionic materials which exhibit high ionic conductivity comparable to those of liquid/aqueous electrolytes. These solids show tremendous technological promises to develop various kinds of solid state electrochemical devices such as solid state batteries, fuel cells, sensors, electrochromic display devices etc\textsuperscript{1-3}. Amongst known superionic systems, Ag\textsuperscript{+} ion conducting materials exhibit highest room temperature conductivity ($\sim 10^{-1} - 10^{-2}$ S.cm\textsuperscript{-1}) and are available in various phases viz. crystalline/poly crystalline, glassy/amorphous, composite electrolyte etc. These systems are prepared, in general, by stabilizing the characteristic superionic $\alpha$-phase of AgI at room temperature by way of solid solution with other ionic systems\textsuperscript{4} or in a glass former/modifier network\textsuperscript{4} or dispersion of submicron particles of an insulating 'second phase' dispersoids\textsuperscript{5}. AgI is well-known for its characteristic structural transition after \(-147\) °C at which it undergoes from a low conducting $\beta$-phase to superionic $\alpha$-phase\textsuperscript{5}. Recently, a new compound\textsuperscript{6}: a quenched/annealed [0.75AgI: 0.25AgCl] mixed-system/solid-solution\textsuperscript{7} has been investigated by us, which exhibits exactly identical transport characteristics as AgI including $\beta \rightarrow \alpha$-like phase transition at a substantially low temperature i.e. \(-135\)°C. Detail investigations on various ionic transport parameters of the new host salt viz. conductivity ($\sigma$), ionic mobility ($\mu$), mobile ion concentration ($n$), ionic transference number ($t_\text{ion}$), ionic drift velocity ($V_d$) etc. revealed that the new host has several ionic transport properties superior to AgI. Hence, the new system can very well be used as an alternate host salt in place of conventional host AgI in the preparation of fast Ag\textsuperscript{+} ion conducting systems in various phases, as mentioned above. In fact, number of superionic systems in glassy/composite phases have already been prepared by us using the new host\textsuperscript{8,9}. These systems exhibit superior electrolyte properties as compared to those prepared by conventional host AgI.

The electrical conductivity ($\sigma$) measurements, on the new host: "a quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution" were carried out using impedance spectroscopy\textsuperscript{10}, while ionic mobility ($\mu$) and ionic transference number ($t_\text{ion}$) and hence, mobile ion concentration ($n$) and ionic drift velocity ($V_d$) were determined by transient ionic current\textsuperscript{11} (TIC) and Wagner's dc polarization\textsuperscript{12} techniques respectively. TIC and Wagner methods are essentially a dc polarization technique in which
The sample pellet is subjected to an external dc field. This results in the polarization/accumulation of mobile Ag⁺ ions at one end of the sample pellet. The details of the experimental procedures have already been discussed elsewhere in the number of papers [8-13]. In the present paper we report another novel method, based on dc polarization technique, to study polarization/self-depolarization phenomenon in the new host salt. This technique has recently been employed on the conventional host-salt AgI to study similar phenomenon. The results reported here for the present system are merely an extension of exactly identical studies.

2 Experimental Procedure

The details related to the preparation of new host compound: "a quenched/annealed [0.75AgI:0.25AgCl] mixed-system/solid-solution" and its material and ionic transport characterizations have already been reported elsewhere [9]. A homogeneous mixture of extra pure chemicals, procured from M/s Reidel (India) Chem., AgI and AgCl (purity > 98 %) in 75:25 mol. Wt. (%) was uniformly melted at ~ 650°C and quenched rapidly in a laboratory-built roller quencher (speed ~ 3000 rpm). The final product was finely ground and then pressed ~ 2 tons/cm² to form cylindrical pellet of dimensions: diameter ~ 1.185 cm and thickness ~ 1-2 mm.

To study polarization/self-depolarization phenomenon, a constant dc potential (~ 0.5 V, well below the decomposition potential of AgI) was applied across the thickness of the sample pellet sandwiched between two blocking (graphite) electrodes in the following cell configuration:

C (+) / [0.75AgI:0.25AgCl] / C (-).

The potential gradient developed across the sample pellet due to polarization/accumulation of mobile Ag⁺ ions, was measured instantly after the removal of the external dc field. This is referred to as the instant peak potential, \( V_p \). \( V_p \)-measurements were carried out using an x-y-t recorder (Graphtec, model 2300-1L, Japan).

3 Results and Discussion

As mentioned in Section 2, \( V_p \)-values were measured instantly after the removal of the applied external dc field. A self-depolarization phenomenon starts immediately after removal of the field, as the polarized/accumulated mobile Ag⁺ ions begin to diffuse/redistribute throughout the bulk. In order to explore the time required by the material to attain the state of complete polarization, \( V_p \)-measurements were carried out as a function of temperature on the sample pellets of varying thicknesses polarized for different intervals of time. Fig. 1 shows \( V_p \)-versus polarizing time plots obtained in both \( \beta \) and \( \alpha \)-like phases of the system: quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution for the three pellets of thicknesses: 0.135, 0.167 and 0.2 cm. The polarizing time refers to the time interval for which the external dc field is applied across the sample. The plots in Fig. 1 exhibit following important features:

(1) \( V_p \)-value in all the pellets increases initially with increasing polarizing time, then attains a saturation level after \( t > 5 \) min. The saturation state is indicative of the state of complete polarization. Hence, the state of complete polarization is attained by the material in time \( t = 5 \) min, irrespective of the thickness.

![Fig. 1 - \( V_p \) versus time plots for [0.75AgI:0.25AgCl]](image-url)
(2) The magnitude of $V_p$ increases with increasing thickness of the sample pellet. This seems logical, since the $V_p$ directly gives the information about the number of mobile Ag$^+$ ions available in the system at a particular temperature. Thicker is the sample, larger would be the number of mobile Ag$^+$ ions in the materials, which get polarized and hence, result into higher $V_p$-value.

(3) The magnitude of $V_p$ for all the sample pellets of different thicknesses in $\alpha$-like phase is large and comparable to the applied dc potential. While, a much lower $V_p$-value is obtained in the $\beta$-like phase of the material.

As reported earlier from an independent study that in $\beta$-like phase, the number of mobile Ag$^+$ ions per unit volume is much lower ($\sim 10^{17}$ cm$^{-3}$) than that in the $\alpha$-like phase ($n \sim 10^{22}$ cm$^{-3}$). The above result once again indicates a direct correlation between $V_p$ and the number ($n$) of mobile Ag$^+$ ions in the system. An exactly similar results$^{17}$ were obtained earlier for AgI$^{17}$ also. Hence, it can be positively concluded that the magnitude of instant peak potential $V_p$ at the state of complete polarization gives a direct information (although qualitatively) about the availability of mobile Ag$^+$ ions in the system at a particular temperature. This conclusion is well espoused once again in our temperature dependence of $V_p$ studies, as discussed below.

Fig. 2 shows log $V_p$ versus $1/T$ plot for the system : ‘quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution’ of pellet thickness $\sim$ 0.2 cm. log $n$ versus $1/T$ Arrhenius plot, reported earlier by us for the present system$^8$, is redrawn in Fig. 2 for direct comparison. One can obviously note that both the variations are almost analogous. We observe that an abrupt change in $V_p$ as well as in $n$ has initiated well ahead of the $\beta \rightarrow \alpha$-like phase transition temperature $\sim 135^\circ$C. The reason for this may be attributed as a pre-transition effect. An exactly similar results were reported earlier$^{17}$ for AgI. Hence, this study reconfirmed again that the abrupt increase in $V_p$ after $\beta \rightarrow \alpha$-like phase transition is a direct indication of a large increase in $n$ of mobile Ag$^+$ ions in the $\alpha$-like phase. This, in turn, reaffirmed one of our assertion made earlier in regards to superionic conductivity of $\alpha$-like phase of the system which is predominantly due to the abrupt increase in $n$ in this phase$^8$.

4 Conclusion

Polarization/self-depolarization studies, on a Ag$^+$ ion conducting system : “a quenched [0.75AgI:0.25AgCl] mixed-system/solid-solution”, were performed by a novel method based on dc polarization technique. Sample pellets of varying thicknesses, placed in between graphite (blocking) electrodes, were subjected to a constant external polarizing dc field for different intervals of time. Potential gradient developed across the sample, due to polarization/accumulation of the mobile Ag$^+$ ions, was measured instantly after the external dc field was switched off. This potential was referred to as instant peak potential $V_p$. The magnitude of $V_p$ directly relates, although qualitatively, the number of mobile Ag$^+$ ions present in the system at a particular temperature. $V_p$-measurements were carried out at various temperatures in both $\beta$ and $\alpha$-like phases of the material. These studies revealed the facts : (a) the material at-
tained the state of complete polarization in time to \( t > 5 \) min, irrespective of the thickness and (b) \( \nu_p \) increased abruptly after \( \beta \rightarrow \alpha \)-like phase transition of the material, hence, reaffirmed that an abrupt increase of conductivity in \( \alpha \)-like phase is predominantly due to the abrupt increase in \( n \).

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