Ion Transport and Solid State Battery Studies on a New Silver Molybdate Superionic Glass System: x[0.75AgI: 0.25AgCl]: (1-x)[Ag$_2$O: MoO$_3$]


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Abstract. Preparation, material characterization, ion transport and battery discharge characteristic studies are reported for a new silver molybdate glass system: x[0.75AgI: 0.25AgCl]: (1-x)[Ag$_2$O: MoO$_3$], where 0 < x < 1 in molar weight fraction. The traditional host AgI has been replaced by an alternate compound: "a quenched [0.75AgI: 0.25AgCl] mixed system/solid solution". Electrical conductivity ($\sigma$), ionic mobility ($\mu$) and mobile ion concentration ($n$) measurements were carried out as a function of 'x'. The composition: 0.8[0.75AgI: 0.25AgCl]: 0.2[Ag$_2$O: MoO$_3$] exhibited the highest conductivity (~6x10$^{-3}$ S.cm$^{-1}$) at room temperature and has been referred to as 'optimum conducting composition (OCC)'. The compositional variation of 'n' revealed that the enhancement in the room temperature conductivity of OCC is predominantly due to the increase in mobile ion concentration. The XRD and DSC analysis on OCC indicated the formation of glassy phase with partial presence of unreacted polycrystalline phase of the host salt. The temperature dependence of various ionic transport parameters viz. $\sigma$, $\mu$, 'n' and ionic transference number ($t_{\text{io}}$) were carried out on the OCC and the results have been discussed on the basis of theoretical models suggested for superionic glasses. In addition to this, solid state batteries were fabricated using OCC as electrolyte and discharge characteristics were studied under varying load conditions.

1. Introduction

In view to develop solid state electrochemical devices viz. batteries, sensors, fuel cells, supercapacitors, electrochromic display devices etc., silver ion conducting superionic glasses attracted widespread attention in the recent years. These glasses exhibit several distinct advantages over their crystalline/polymer/organic counterparts [1-5]. They show isotropic ionic conductivity as high as ~10$^{-3}$ 10$^{-2}$ S.cm$^{-1}$ at room temperature. Traditionally, Ag$^+$ ion conducting superionic glasses have been prepared by melt-quenching technique. AgI and Ag$_2$O have been used in common as host salt and glass modifier respectively, while B$_2$O$_3$/CrO$_3$/P$_2$O$_5$/MoO$_3$ etc. as glass former. Attempts have also been made to improve the conductivity and stability of the system by mixing two or more glass formers. This has been referred as 'mixed former effect (MFE)' [6,7]. The present paper reports the preparation of a new silver molybdate glass system: x[0.75AgI: 0.25AgCl]: (1-x)[Ag$_2$O: MoO$_3$], where 0 < x < 1 in molar wt. fraction, in which an alternate host compound: "a quenched [0.75AgI: 0.25AgCl] mixed system/solid solution" has been used in place of the traditional host AgI. The new host, investigated in the present laboratory, exhibits transport characteristics identical to AgI [8,9]. However, it has been observed that the new host yielded
glass/composite electrolytes exhibiting ionic parameters superior to those prepared using AgI [10-18]. The present system is another addition to the series. For direct comparison of room temperature conductivity values of various compositions of the new system, silver molybdate glass systems: xAgI: (1-x)[Ag2O: MoO3], using traditional host AgI have also been prepared in the identical manner. To identify the optimum conducting composition (OCC) in the new glass system and to address the reason of enhancement in the room temperature conductivity of OCC, the compositional variation studies on conductivity (σ), ionic mobility (μ) and mobile ion concentration (n) were carried out. X-ray diffraction (XRD) and differential scanning calorimetric (DSC) analysis were done on OCC for the purpose of phase identification and thermal characterization respectively. The temperature dependence of some important ionic transport parameters viz. 'σ', 'μ', 'n' and ionic transference number (t_ion) were carried out on OCC and the mechanism of ion transport has been discussed in the light of theoretical models proposed for the superionic glasses. Finally, solid state batteries were fabricated using the OCC as electrolyte and the discharge characteristics were studied under varying load conditions.

2. Experimental Details

The starting chemicals: AgI (purity > 98 %), AgCl (> 99 %), Ag2O (98 %) and MoO3 (99 %), [Reidel (India) Chem.], were used, as procured. Silver molybdate glass systems: x[0.75AgI: 0.25AgCl]: (1-x)[Ag2O: MoO3] were prepared by rapidly cooling the molten mixtures of different molar compositions (x) in a twin-roller quencher. The rate of quenching was ~ 10^2 - 10^3 Ks^-1. These samples are hereafter named as “roller-quenched samples”. After identifying the optimum conducting composition, two additional samples of this composition were prepared at slower rates of cooling: (i) the melt was left outside the furnace to cool by itself in air, and (ii) the melt was left in the furnace to cool by itself after switching the furnace off. These samples are hereafter named as “air cooled” and “furnace cooled” samples respectively. The finished products were finely ground and pressed at ~ 2 tons-cm^-2 to form pellets of diameter 1.185 cm and thickness 1-3 mm. The phase identification and thermal characterization studies on OCC were done using Philips X-ray diffractometer (model PW1710) and Mettler differential scanning calorimeter respectively.

The conductivity (σ) measurements were carried out by impedance spectroscopy (IS). A computer-controlled HIOKI LCR bridge (model 3520-01, Japan) in the frequency range 40 Hz-100 kHz was used. Colloidal silver paint was applied on both sides of pellet as reversible electrode. The bulk conductance was calculated from the complex impedance (Z'-Z") plot. The ionic mobility (μ) was measured by transient ionic current (TIC) technique [19, 20]. Subsequently, mobile ion concentration (n) was determined with the help of σ & μ data. The ionic transference number (t_ion), which measures the extent of ionic contribution to the total conductivity, was determined by Wagner's dc polarization method [21]. A Graphtec x-y-t recorder (model WX 2300-1L, Japan) was employed in all these measurements. Solid state batteries, in the cell configuration: Ag (anode) | Electrolyte | C + I_2 (cathode), were fabricated using OCC as electrolyte. Battery discharge behaviors under varying load conditions and the cell parameter measurements were carried out in a vacuum desiccator to avoid humidity. To prevent the surface diffusion of iodine, all the batteries were sealed with epoxy resin. A digital multimeter (Philips, model PM2518) was used for cell potential measurements. The details related to above experimental studies have been discussed extensively by us elsewhere in the literature [8-18].

3. Results and Discussion

3.1. Compositional Dependence of σ, μ and n. Figure 1 shows 'log σ - x' plots for the 'roller-quenched' silver molybdate glass systems: x[0.75AgI: 0.25AgCl]: (1-x)[Ag2O: MoO3] as well as xAgI: (1-x)[Ag2O: MoO3]. A conductivity maxima was obtained at 'x' = 0.8 for both the systems. However, the new host yielded an electrolyte composition: 0.8[0.75AgI: 0.25AgCl]: 0.2[Ag2O: MoO3] exhibiting highest room temperature conductivity (σ_0 ~ 6x10^{-3} S-cm^{-1}). This has been referred to as ‘optimum conducting composition (OCC)’. The effect of quenching on the room temperature conductivity was also studied for the OCC samples prepared at slower rates of cooling, as mentioned in Section 2. The conductivity values for both ‘air-cooled’ and ‘furnace-cooled’ samples are 2.60 x 10^{-3} S-cm^{-1} and 1.15 x 10^{-3} S-cm^{-1}, respectively. One can