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# Transport properties and battery performance studies of $AgI–Ag_2O–Se_2O–P_2O_5$ glass

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**Abstract**

Various compositions of silver-based quaternary superionic conducting (SIC) [$AgI–Ag_2O–(SeO_2 + P_2O_5)$(SSP)] glasses were prepared by melt quenching technique. The X-ray diffraction (XRD) and conductivity studies were carried out to identify the amorphous nature and to select high ionic conducting composition of the SSP system for the fabrication of batteries. Solid-state primary batteries were fabricated using the $66.67\%AgI–23.07\%Ag_2O–10.26\%(0.3SeO_2 + 0.7P_2O_5)$ (66SSP37) glass with different cathode materials [I:C, (I + C):SE and {(I + C) + SE}:T*A*AI, where I is Iodine, C is graphite, SE is solid electrolyte (SSP glass) and T*A*AI is tetraalkyl (methyl and butyl) ammoniumiodide]. The open circuit voltage (OCV), polarization and discharge characteristics were measured to estimate the lifetime of the batteries made up of SSP glass. 

*Keywords:* Silver selenophosphate (SSP) glass; XRD; Conductivities; Batteries; OCV; Polarization and discharge characteristics

## 1. Introduction

Batteries made up of solid electrolytes (SEs) can eliminate the problems faced by the liquid electrolyte batteries (LEBs) such as leakage due to corrosion, short shelf life, limited temperature range of operation, less thermal stability, less ruggedness, heavy weight, no possibility of miniaturization, etc. [1,2]. The stability, ruggedness and miniaturization of solid-state batteries (SSBs) opened the wide range of applications, from low- to high-power devices, like watches, calculators, cameras, toys, computers, measuring meters, biomedical devices, space, defense, and electric vehicles, etc., [3–6]. Since the batteries made up of SEs have wide range of applications, there have been increasing interest in developing the new solid electrolyte materials. Variety of lithium, silver, copper, proton, etc., based solid electrolyte materials were synthesized and it is found that the silver based SEs show better stability and transport properties over the others [2,7–13]. We have investigated the synthesis, nature and transport properties of the $AgI–Ag_2O–(SeO_2 + P_2O_5)$ (SSP) system. Also, we have fabricated the set of solid state primary batteries using the high ionic conducting SSP glass with different cathode materials synthesized in this work and measured their open circuit voltage (OCV), polarization and discharge characteristics.

## 2. Preparation

The $X\%AgI–(1 - X)\%[M\% Ag_2O–F\%(0.3SeO_2 + 0.7P_2O_5)]$ ($X = 20$ to 80% in steps of 10 and $M/F = 2.25$) system was prepared for various dopant salt (AgI) compositions by melt quenching technique. Analar grade chemicals of AgI, $Ag_2O$, $SeO_2$ and $P_2O_5$ were weighed and mixed thoroughly, according to their molecular weight percentages. The mixture was taken into a quartz crucible and melted at 500°C for about 30 min. The bulk compounds were obtained by quenching the molten liquid into liquid nitrogen and they were made into fine powders using mortar and pestle.

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## 3. Characterization

All the compositions of the SSP system were characterized by recording the X-ray diffractogram, for 2 values from 10 to 70° at a rate of 2°/min, using the Rikagu make minuflux X-ray diffractometer with CuK$\alpha$ monochromatic radiation of wavelength $\lambda = 1.5418$ Å. The absences of the peaks in the observed diffractogram spectra confirm the glassy nature and the existence of partial peaks in the diffractogram spectra were attributed to the mixture of polycrystalline and amorphous. The glass forming region for various dopant salt (AgI) compositions of the SSP system is shown in Fig. 1, and it confirms that the $X = 20$, 70 and 80% of dopant salt (AgI) compositions of the SSP system are mixed in nature (open circles) and all other compositions ($X = 30$ to 66.66%) are glassy in nature (solid circles).

## 4. Electrical conductivity

The electrode/electrolyte(SSP glass)/electrode type pellets were made by applying an optimum pressure of 5000 kg/cm$^2$. The electrode material is a mixture of 85% silver metal powder and 15% SSP glass powder. The electrical conductivity measurements were made on the pellets at 1 kHz using two-probe a.c. conductivity bridge (Elico make, model CM82T). The conductivity measured at room temperature (303 K) for various dopant salt (AgI) compositions of the SSP system is shown in Fig. 2. It is found that the conductivity increases up to 66.67% of AgI content in the SSP system and thereafter decreases, where, the high content of AgI (70 and 80%) in the SSP system is a mixture (Table 1). Hence, the 66.67% of AgI in the SSP system is fixed as the highest conducting ($\sigma = 2.93 \times 10^{-2}$ S/cm) composition.

## 5. Electronic conductivity

The electronic conductivity was measured for the highest conducting composition 66.67%AgI–23.07%$Ag_2O$–10.26%($0.3SeO_2 + 0.7P_2O_5$) of the SSP system using the Wagner's d.c. polarization method [14]. The SSP glass was sandwiched between the ion blocking electrode (graphite) and non-ion blocking electrode (silver) and it was polarized by applying the d.c. potential. Under this condition, the ionic conduction was suppressed and the non-ionic conduction (current) was measured as a function of applied voltage shown in Fig. 3. The type of non-ionic current ($I_e$) is due to electrons that exist in the SSP glass was obtained from the shape of $I$ vs. voltage graph (Fig. 3). Hence, the following expression is used to obtain the electronic conductivity of the SSP system [14].

$$I_e = (RTA/LF)\,\sigma_e\{1 - \exp(EF/kT)\}$$

where $A$ is area of cross-section, $L$ is thickness of the sample, $E$ is applied potential, $R$ is gas constant, $F$ is faraday constant, $T$ is absolute temperature and $\sigma_e$ is electronic conductivity. The current, $I$ vs. $\{1 - \exp(-EF/kT)\}$ is plotted in Fig. 4 and the electronic conductivity is obtained from the slope of the plot (Fig. 4), which ($\sigma_e = 4.29 \times 10^{-8}$ S/cm) is less by six orders of magnitude, when compared to the total conductivity ($2.93 \times 10^{-2}$ S/cm) of the SSP glass. Hence, our SSP glass is almost a pure ionic conductor and it can be used for any electrochemical devices, especially solid-state batteries.

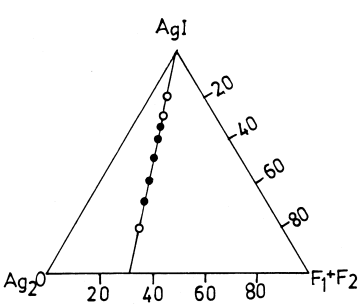


Fig. 1. Glass-forming region for various compositions of dopant salt (AgI) in SSP system. ● represents glassy compounds and ○ represents mixture of glass and polycrystalline.

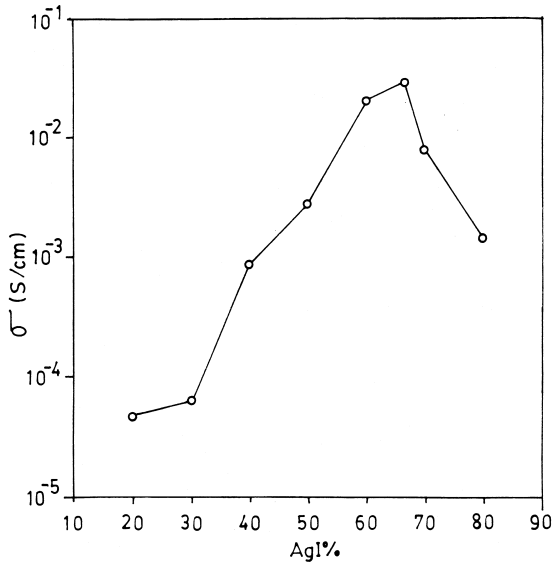


Fig. 2. Conductivity obtained at room temperature as a function of dopant salt (AgI) in SSP system.

## 6. Solid-state batteries (SSBs)

The high ionic conducting 66.67%AgI–23.07%$Ag_2O$–10.26%($0.3SeO_2 + 0.7P_2O_5$) (66SSP37) glass was used as solid electrolyte and fabricated the following type of primary batteries with different cathode materials.anode/solid electrolyte/cathode

$$(Ag + SE)/(SSP\,glass)/\{[(I + C) + SE] + TAAI\}$$

Table 1
Cell parameters measured at room temperature (303 K) for the batteries made up of SSP[a] glass
P1 = Ag + SE(1:1)/66SSP37/I:C = 7:3.
P2 = Ag + SE(1:1)/66SSP37/(I + C):SE = 7:3.
P3 = Ag + SE(1:1)/66SSP37/(I + C + SE): TMAI = 9:1.
P4 = Ag + SE(1:1)/66SSP37/(I + C + SE): TBAI = 9:1.

| Sl. no. | Cell type | Open circuit voltage (mV) | [for 0.4 V of its OCV] | | Discharge capacity at 100 $\mu A/cm^2$ (mAh) | Energy density (Wh/kg) |
|---|---|---|---|---|---|---|
| | | | Current drain (mA) | Discharge time (h) | | |
| Eq. (1) | P1 | 686 | 1.26 | 56 | 4.4 | 1.95 |
| Eq. (2) | P2 | 686 | 3.50 | 66 | 5.18 | 2.30 |
| Eq. (3) | P3 | 672 | 8.50 | 90 | 7.0 | 3.14 |
| Eq. (4) | P4 | 636 | 16.0 | 118 | 9.2 | 4.12 |

[a] 66.67%SSP–23.07%$Ag_2O$–10.26% ($0.3SeO_2 + 0.7P_2O_5$).

where Ag is silver powder, SE is solid electrolyte of SSP glass, I is iodine, C is graphite and T*A*AI is tetra alkyl (methyl, and butyl) ammoniumiodide.

### 6.1. Preparation of anode / solid electrolyte (66SSP37) pellet

The fine powders of SSP glass and analar grade silver powder were mixed (1:1) by weight ratio to form the anode material. The addition of SSP glass to the silver powder to improve the interfacial properties [15,16]. The fine powders of SSP glass is used as solid electrolyte (SE). The anode mixture, as one layer, and SE, as another layer, were pressed at an optimum pressure 5000 kg/$cm^2$ to form a single pellet.

### 6.2. Preparation of cathode pellet

The {[(I + C) + SE] + T*A*AI} cathode materials were prepared in different compositions, by varying the weights ratio of iodide, graphite, SSP glass and T*A*AI, and pressed at an optimum pressure of 2000 kg/$cm^2$ to form pellets. The graphite is used as a current collector and the SE and T*A*AI are added to the cathode to improve the interfacial properties [15–19].

### 6.3. Cell fabrication

The anode/solid electrolyte and cathode pellets were sandwiched between graphite discs and the copper foils used over the two graphite discs, as leads, to form a solid state primary battery. The outer jacket of the battery assembly was made up of two ebonite discs with nuts and bolts. Immediately after the fabrication, the batteries were sealed with epoxy resin to isolate from the atmosphere. More details about the battery assembly were presented elsewhere [20]. Different types of the solid-state primary batteries were fabricated using the anode/SSP glass and with different cathode materials. The fabricated solid-state primary batteries are as follows:

$$\mathrm{Ag + SE(1{:}1)/66SSP37/I{:}C = 7{:}3\,(P1\,cell)} \quad (1)$$

$$\mathrm{Ag + SE(1{:}1)/66SSP37/(I + C){:}SE = 7{:}3\,(P2\,cell)} \quad (2)$$

$$\mathrm{Ag + SE(1{:}1)/66SSP37/(I + C + SE){:}TMAI = 9{:}1\,(P3\,cell)} \quad (3)$$

$$\mathrm{Ag + SE(1{:}1)/66SSP37/(I + C + SE){:}TBAI = 9{:}1\,(P4\,cell)} \quad (4)$$

From our earlier studies, the cathode compositions of I:C = 7:3, (I + C):SE = 7:3 and the addition of 10% of

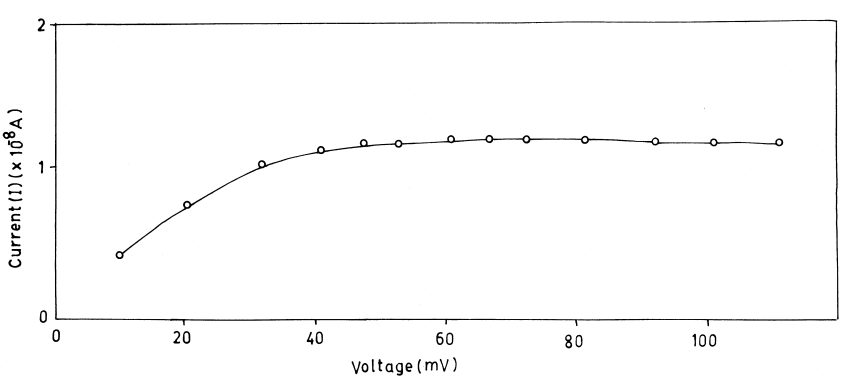


Fig. 3. *I* vs. *V* for the highest conducting composition of SSP system.

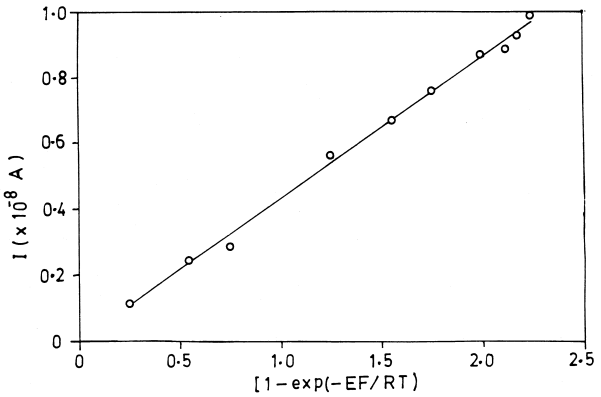


Fig. 4. $I$ vs. $(1-\exp(-EF/kT)$ for the highest conducting composition of SSP system.

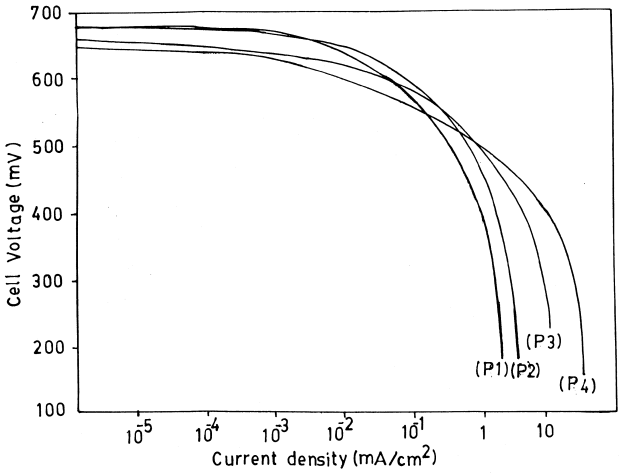


Fig. 5. Polarization characteristics of batteries made up of 66SSP37 glass with different cathode (P1 = I:C = 7:3; P2 = (I + C):SE = 7:3; P3 = [(I + C) + SE}:TMAI = 9:1; P4 = [(I + C) + SE}:TBAI = 9:1.

tetraalkylammoniumiodide to the (I + C):SE = 7:3 are found to exhibit high efficiency [19,20]. Hence, the high-efficiency cathode compositions were used to fabricate the above mentioned P1 to P4 cells with SSP glass. Systematically, the OCV, polarization and discharge characteristic measurements were made on the above mentioned cells to estimate the performance of each battery.

### 6.4. Open circuit voltage (OCV)

The first parameter to be measured to test the fabricated cell is its OCV. The cell voltage was measured under no load condition, which is the OCV of the cell, for the batteries made up of 66SSP37 glass with different cathode materials. The OCV is found to decrease from 686 to 636 mV, respectively, for the various types of cells from P1 to P4. The highest OCV of 686 mV is found for the P1 and P2 type of cells, which is very close to the theoretical OCV (687 mV) of the silver based cells with iodine as cathode [16]. The decrease in the OCV from P1 to P4 cells is may be due to physical and chemical compatibility of the electrolyte and cathode materials [17–19].

### 6.5. Polarization and discharge characteristics

Fig. 5 shows the voltage vs. current density curves obtained from the polarization measurements for the P1 to P4 cells. From the Fig. 5, the current drain is obtained for the drop of 400 mV of its OCV (686 mV) and it is found to vary from 1.26 to 15.5 mA with the different cathode compositions (P1 to P4). The polarization studies suggest that these cells can be drawn at a current of 100 $\mu A/cm^2$. Hence, discharge characteristics were made to P1 to P4 cells with a particular load of current density of 100 $\mu A/cm^2$. The measured discharge data plotted as voltage vs. time are shown in Fig. 6 and it is found that the cell made up of I:C = 7:3 cathode composition gives the discharge capacity of 4.39 mAh. The addition of SSP glass to the cathode materials improved the discharge capacity and energy density. The improvement of battery parameters with the addition of SSP glass to the I:C may be due to the better interfacial properties at electrode and electrolyte interface [15,17]. The addition 10% of tetramethyl (butyl)ammoniumiodide to the (I + C + SE) cathode results drop in open circuit voltage but the discharge time increases. The reason for the drop in OCV is due to partial tarnishing of molecular iodine with the electrolyte [9,12]. The increase of the discharge time may be due to the formation of high conducting product at the interface [9,12]. Hence, there is an improvement in discharge capacity and energy density parameters compared to the P1 and P2 cells. From Figs. 5 and 6, it is found that the addition of TAAI to the cathode [(I + C):SE] improves the discharge capacity and energy density of P3 and P4 cells. The overall improvement of polarisation and discharge characteristics from P1 to P4 cells are attributed to better physical and chemical compatibility of the electrode and electrolyte materials, which improve the interfacial properties and hence, small internal resistance (IR) drop even at higher current densities [17–20].

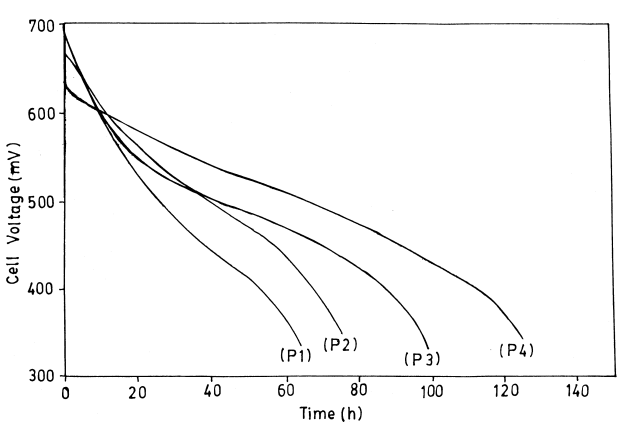


Fig. 6. Discharge characteristics of batteries made up of 66SSP37 glass with different cathode P1 = I:C = 7:3; P2 = (I + C):SE = 7:3; P3 = [(I + C) + SE}:TMAI = 9:1; P4 = [(I + C) + SE}:TBAI = 9:1.

## 7. Conclusions

Various compositions of the SSP glasses were prepared and the glass forming region was established from the X-ray diffraction spectra, where the 30 to 66.67% of AgI compositions form glass and the other compositions of SSP system show the mixed nature (polycrystalline and glass). From the electrical conductivity studies, the highest conducting ($\sigma = 2.93 \times 10^{-2}$ S/cm) composition 66.67%SSP–23.07%$Ag_2O$–10.26% ($0.3SeO_2 + 0.7P_2O_5$) of SSP system is fixed It is found to be almost a pure ionic, since the electronic conductivity of the SSP glass is the order of $10^{-8}$ S/cm compared to the total conductivity ($10^{-2}$ S/cm). From the battery studies, the highest OCV is obtained for the P1 and P2 cells, which is close to the theoretically calculated OCV for the silver and iodide electrode cells. From the polarisation and discharge characteristics, it is found that the addition of solid electrolyte and tetramethyl(butyl) ammonium iodide to the (I + C) cathode improved the performance of the batteries made up of the SSP glass. Hence, the present battery measurements are helpful to choose proper cathode composition. Also, from the observed battery parameters, it is found that these batteries made up of 66SSP37 glass are suitable for low electrical power device applications.

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